

ENVIRONMENTAL HAZARDS OF THE BACTERIAL LEACHING OF ORE MINERALS FROM WASTE AT THE PEZINOK DEPOSIT (MALÉ KARPATY MTS., SLOVAKIA)

Peter ANDRÁŠ^{1,2}, Marcel ADAM³, Martin CHOVAN⁴,
Andrea ŠLESÁROVÁ⁵

¹ Geological Institute, Slovak Academy of Sciences, Severná 5, 974 01 Banská Bystrica,
Slovakia, andras@savbb.sk

² Department of Ecology and Environmental Education, Matej Bel University, Tajovského 40,
974 01 Banská Bystrica, Slovakia

³ Department of geology, Faculty of Natural Sciences, Comenius University, Mlynská dolina G,
842 15 Bratislava, Slovakia, adam@fns.uniba.sk

⁴ Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University,
Mlynská dolin G, 842 15 Bratislava, Slovakia, chovan@fns.uniba.sk

⁵ Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 043 53 Košice,
Slovakia, aslesar@saske.sk

Abstract: The article reports the chemical characteristic of acid mining drainage waters as well as the results of leaching experiments conducted with and *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* at the same conditions in solution. The experiments were realized using tailing impoundment sediments and ore minerals from the Sb-(Au-) base metal deposit Pezinok (Malé Karpaty Mts., Western Carpathians, Slovakia). The research study shows the oxidation sequence and the leaching progression on surface of the following ore minerals: löllingite, arsenopyrite, stibnite, native Sb, gudmundite, berthierite, pyrite, sphalerite and chalcopyrite. The differences between chemical and biological-chemical leaching activity of various ore minerals on the polished sections surface is discussed. The extent and the kinetics of the biological-chemical leaching of ore minerals is significantly higher than the chemical leaching of ore minerals without bacteria.

Keywords: acid mine drainage water, ore minerals, biological-chemical oxidation, chemical oxidation, *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, etching-patterns.

1. INTRODUCTION

The supergene oxidation of sulphide minerals is the main source of acidity and increased content of heavy metals and sulphates both in drainage or surface waters as

well as in groundwaters. Acid mine drainage (AMD) is usually the most important source of contamination in mining regions. The process can be substantially accelerated by influence of the bacterial oxidation. These bacteria, mainly of the *Acidithiobacillus* genus, are always involved in natural supergene weathering of sulphide ores.

The mining activity at the Pezinok deposit caused changes of the land relief. The ore material was displaced from the original environment of the mountain massive, in which it was in the relatively equilibrium state to the environment exposed to the combined action of atmosphere and water saturated with atmospheric gases and to the biological effects. The fine grinding of ores and application of chemical reagents in the technological process of sulphide concentrates production increased the reactive surface of the relict ore minerals in the deposited waste.

The sludge lagoons and setting-pits contain a lot of waste ore minerals which represent the main substrates necessary for the metabolic activity of autochthonous, acidophilous and thionic bacteria *Acidithiobacillus ferrooxidans* (ATF), *Acidithiobacillus thiooxidans* (ATT) and *Leptospirillum ferrooxidans* (LF) catalysing the ore minerals oxidation processes. The high residual concentrations of metals Sb, Fe, As in the deposited solid wastes and contaminated soils are currently the permanent source of in-situ pollution and due to the activity of autochthonous microflora the source of acid mine drainage generation. Surface and underground waters are also polluted with elements from the floatation agents used in the ore processing. The released metals and other chemical agents may enter to the food chain of animals and humans through plants and water.

1.1. The Pezinok deposit

The Pezinok deposit (fig. 1) is situated in a 1200 m long tectonic fault of NW-SE direction. The mineralized structure is 25-70 m thick at the surface and about 430 m long (Chovan et al., 1992).

At the Pezinok deposit two types of ore mineralisation were described: 1 – metamorphosed, primarily exhalation-sedimentary pyrite mineralisation genetically related to Devonian basic volcano-sedimentary cycle which was subsequently metamorphosed and 2 – hydrothermal Sb-Au-As mineralisation of epigenetic character which is most frequently localized in beds of tectonically deformed black schists (Chovan et al., 1992).

About 20 000 tons of antimony was exploited from this deposit. The reported content of Sb ranges from 1% to 4%, of As from 0.5% to 1.5% and the average content of Au is 3.60 ppm (Uher et al. 2000). The exploitation of Sb-Au ores at the Pezinok deposit was terminated in 1991. The mine was closed in 1992.

1.2. The deposited waste

The mining-waste is deposited in several tailing impoundments and two sludge lagoons (fig. 1) containing 380 000 m³ of material (Trtíková, 1999). As- and Fe-minerals (predominantly arsenopyrite and pyrite) were during the ore dressing process

suppressed and moved to the waste. The content of these minerals in the sludge lagoons is considerably higher than that of Sb-minerals. The most frequent sulphide minerals in the sludge lagoons are arsenopyrite and pyrite. Gudmundite and stibnite occurs rarely, pyrotine sporadically. In some samples were determined Sb- and Fe-oxides, tetrahedrite, löllingite and chalcopyrite (Chovan et al., 1994).

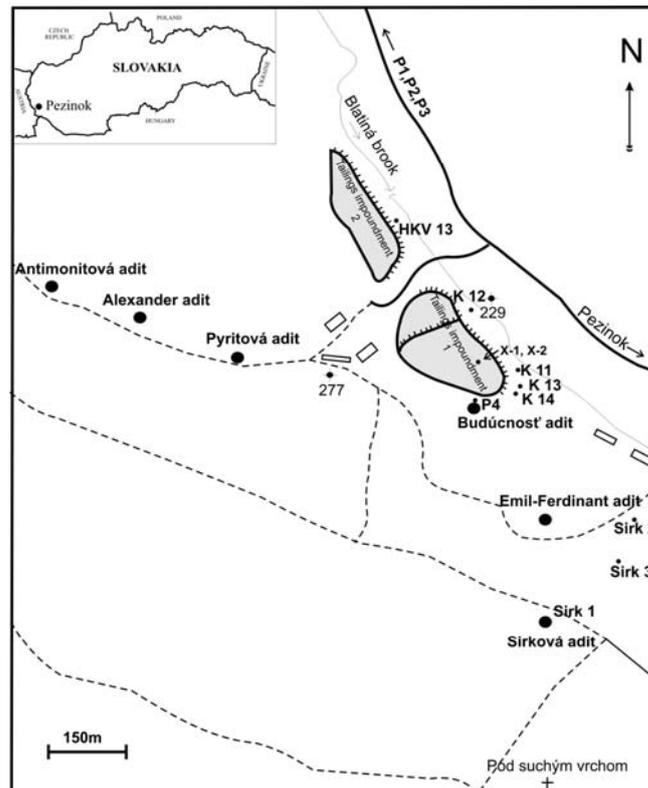


Fig. 1 Sketch of the studied area at the Pezinok deposit and the sampling localities

The gangue minerals are represented mainly by carbonates and quartz. The schist fragments occur only rarely. The dominant clay mineral is illite. Chlorite is abundant but caolinite is very rare (Chovan et al., 1994). Also Fe-oxyhydroxides and Sb-oxides are formed in the oxidation zone of the sludge lagoons (Trtíková et al. 1999).

1.3. Biological – chemical oxidation

The principle of biogenic catalysis of sulphide oxidation consists in the activity of acidophilous, thionic, sulphur and iron oxidising bacteria having a transporting function in the oxidation process, i.e. in the transfer of released electrons from donor - sulphide to acceptor – oxygen (Mustin et al. 1992). Such activity of specific species of

acidophilous bacteria results in the $2 \cdot 10^5$ multiple acceleration of Fe^{2+} oxidation (Bennett and Tributsch 1978; Dopson and Borje 1999 and others).

As for sulphide minerals the autochthonous, acidophilous, chemolithotrophic bacteria of *Pseudomonales* family and *Thiobacillus* genus represent one of the basic components of the biogenic catalysis. A large number of species of these bacteria was discovered and at least 14 species fall into the *Acidithiobacillus* genus. Mesophilic *ATF* species are of the highest value, sometimes *ATT*, but also the *Spirillaceae* tribe *LF* bacteria oxidising Fe^{2+} in ultra acidic environment. *ATF* species are gramnegative nonsporeforming rods, 0.5 – 0.8 μm in diameter and 0.9 – 1.5 μm in length with one spiral flagellum (Spirito et al. 1982). Bacteria obtain the energy by oxidising of Fe^{2+} -ore minerals. All bacteria of *Acidithiobacillus* genus also oxidise the elementary sulphur formed during the sulphides decomposition.

Sulphide minerals can be oxidised by indirect biological-chemical process (metabolic catalysis), i. e. by products of *ATF* bacteria metabolism formed in the presence of sulphides. In most cases both processes occur simultaneously. In addition to the oxidation of sulphides, there are reactions with CO_2 observed in the system.

Activity of *ATF* is usually associated with the aerobic environment. In the anaerobic conditions *ATF* bacteria oxidise sulphur indirectly by the biological-chemical oxidised Fe^{3+} cations (Pronk et al., 1994).

The direct effect of biological-chemical oxidation processes is the marked alternation of surface morphology and consequently the structure uniformity of oxidised minerals. The changes are of individual character and related to the energetic state of individual parts and the whole crystalline structure of attacked sulphide mineral (Kušnierová and Štyriaková, 1994; Gueremont et al. 1998).

Morion et al. (1991) reported that there is a galvanic interaction between sulphides and occurs the transport of electrons from the sulphide mineral forming anode to the electrochemically less electro-active mineral. According to Crundwell (1989) Silva (2003) it is possible to interpret this effect as the modification of the semiconductive properties of sulphides accompanied with the tiny changes in the structure and physical properties such as reflection, microhardness, conductivity, etc.

2. MATERIAL AND METHODS

The AMD waters were analysed by atom absorption analyse for Fe, Mn, As, Cu, Ni, Pb, Sb and Zn. Two types of leaching experiments were realized to study the mobility of previously mentioned metals from the tailing impoundment sediments as well as the oxidation of ore minerals.

1. During the first experiment the tailing impoundment sediment and the polished sections of ore minerals were introduced to solution containing *ATF* bacteria isolated from the mine waters from Pezinok deposit (biological-chemical process) at pH 1.57. Biogenic catalysis of the selected sulphides oxidation was studied using the leaching nutrient medium 9K, part A according to Silverman and Lundgren (1959) with the content of nutrients for *ATF* cells growth.
2. The second experiment was the abiotic control carried out with the chemically identical leaching agent without bacteria *ATF* (chemical process)

The selected sample of the sediment X-1, the ochre sample X-2 from the tailings impoundments and the AMD of various pH and origin were analysed by atom absorption analyse (AAS).

Polished sections of natural arsenopyrite, löllingite, native Sb, stibnite, gudmundite, berthierite, sphalerite, pyrite and chalcopyrite were studied under conditions of two parallel experiments (biological-chemical and chemical processes):

The polished sections of the ore samples were within the both experiments leached in Petri's dishes. Experiments took place at the room temperature. The changes on the ore minerals surface were evaluated optically at set time intervals using electron microprobe JEOL JXA – 840 in CLEOM laboratories at the Faculty of Natural Sciences of the Comenius University in Bratislava. Analytical conditions were as follows: accelerating voltage 10 – 20 kV, distance of sample from the secondary electrons detector 39 mm.

3. RESULTS

3.1. Characterisation of AMD water

The investigated sample of sediment from tailing impoundments X-1 used for the next experiments was analyzed by atom absorption analysis (tab. 1). This sediment sample was employed in experimental works for the investigation of the leaching process by using of both types of drainage waters: acidic and neutral.

Table 1. AAS analysis of the chemical composition of sediment sample from tailing impoundments

Sample	pH	ppm							
		Fe	Mn	As	Cu	Ni	Pb	Sb	Zn
X – 1	1,67	1 071	3,45	0,104	0,69	1,34	0,05	220,7	0,76
X – 1	1,67	1 014	2,57	0,090	0,48	0,02	0,05	196,1	0,52

The AMD waters contain relatively high contents of Sb, As, Fe, Cu, Cd, Ni, Zn and other metals. The set of the drainage waters from Pezinok was completed with one sample of water from the wider mining ore field (P 1) (tab. 2).

Table 2 Characteristic of acid mine waters from Pezinok mining area. Including pH, content of investigated elements and presence of acidophilous bacteria.

Sample	pH	g/l						mg/l		Bacteria	
		As	Cu	Fe	Pb	Sb	Zn	Ag	Au	ATF	ATT
P 1	5.54	<5	<0.02	24.50	<2	<2	0.16	1.3	<2	+	+
P 2	4.50	<5	0.03	0.12	3.1	<2	0.11	0.9	<2	+	+
P 3	6.63	<5	<0.02	8.36	<2	3.4	0.12	0.8	<2	-	+
P 4	6.64	5.1	<0.02	31.20	<2	6.6	0.12	0.9	<2	-	-

Explanatory notes: P 1 – drainage water from the Pernek, P 2 – drainage water from measuring-point 8, P 3 – drainage water from the creek near adit Michal, P 4 – Pezinok, drainage water from adit Budúcnosť.

The leaching activity in dependence to the leaching medium is presented in tab. 3. For this experiment was used drainage water P 2 from Pezinok with autochthonous *ATF* and *ATT* bacteria. The pH of the water was 4.5. The second sample of drainage water used for experiments was drainage water from Pezinok P 4 without bacteria (pH = 6.45). During the study of catalytic influences were realized parallel experiments with rainwater for comparison.

Tab. 3 AAS analysis of various liquid media of different pH and rainwater used for leaching of the sediments from the tailing impoundments.

Medium	Time of Leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
Drainage water P 2 <i>ATF+ATT</i> pH = 4.5	I	17.8	<0.06	0	213.7	2.7	8.0
	II	16.5	<0.06	0	253.4	5.3	8.8
	III	<2.0	0	6.3	195.7	5.2	<0.4
	IV	<2.0	0	5.2	126.5	4.4	<0.4
Drainage water P 4 pH = 6.45 no bacteria	I	16.8	<0.06	0	225.2	3.0	9.4
	II	12.1	<0.06	0	157.0	3.9	7.0
	III	<2.0	0	5.9	156.0	5.4	<0.04
	IV	<2.0	0	5.2	84.2	4.4	<0.04
Rainwater pH = 5.6 no bacteria	I	13.3	<0.06	0	188.9	2.9	8.8
	II	9.6	<0.06	0	142.1	3.5	7.4
	III	<2.0	0	4.1	115.3	3.2	<0.4
	IV	<2.0	0	5.1	95.6	4.1	<0.4

The results show negligible differences of leaching activity between the medium containing bacteria species and those without bacteria but there was a great difference between two AMD samples and rainwater. We suppose that when pH of drainage water containing bacteria was >4, the activity of bacteria was very low (the highest activity of bacteria is in medium with pH <3) and caused the comparable results with the results of drainage water without bacteria.

The next experiment was realized using nutrient medium 9KA according to Silverman and Lundgren (1959) with bacteria and without bacteria (abiotic control). For the study of the biogenic catalytic influence in oxidation processes of weathering at the tailings impoundments was used pure culture of autochthonous *ATF* and *ATT* bacteria isolated from the drainage water P 1 at the deposit Pernek. Bacteria were dispersed into nutrient medium WHH pH 1.57 at following conditions: P : K=1 : 3, temperature 30° C, agitation at laboratory shaker during 4 weeks (tab. 4).

The leaching of the X-1 sediment sample and heavy fraction of this sample by nutrient medium containing bacteria was compared with the results of X-1 sample leaching by nutrient medium without bacteria. The leaching continuance was studied by monitoring of selected elements (As, Cu, Co, Fe, Ni and Sb) and the experiment was interrupted after 4 weeks to segregate the product of precipitation: secondary salts and Fe ochres created by biological-chemical transformation.

Tab. 4. Leaching of the sediment sample (A) and of its heavy fraction (B) from the tailing impoundments by *Acidithiobacillus ferrooxidans* (ATF). a) nutrient medium (pH = 1.57); b) abiotic control without bacteria (pH = 1.57)

Medium	Time of leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
(A) 9K-A ATF pH = 1.57	I	23.9	<0.06	0	4259.0	<0.1	9.0
	II	123.2	<0.06	0	2100.0	1.2	12.3
	III	72.0	0	3.3	167.4	1.5	7.5
	IV	58.6	0	3.6	135.6	1.7	9.2
(B) 9K-A ATF pH = 1.57	I	72.1	<0.06	0	4576.0	0	12.6
	II	317.3	<0.06	0	3183.0	0	21.6
	III	288.0	0	8.0	280.2	7.2	19.7
	IV	208.1	0	7.5	249.4	6.5	13.0
(A) 9K-A no bacteria pH = 1.57	I	32.6	<0.06	0	167.0	1.2	1.2
	II	36.8	<0.06	0	578.4	4.5	10.1
	III	22.6	0	8.8	378.0	7.1	<0.04
	IV	<2.0	0	7.4	271.1	5.9	<0.04

From the tab. 4 it follows, that in strongly acidic medium (pH=1.57) *ATF* and *ATT* are active, and vigorously assist the oxidation of ore minerals. Extraction rate of Fe, As and Sb is highest in the first week of leaching. As it could be expected, concentration of metal cations in the leaching product is highest in the run, where the heavy fraction of the sediment sample was employed.

In the second period of leaching we can observe the gradual decrease of Fe concentration in liquid phase in consequence of precipitation of Fe-oxyhydroxides. After leaching, the solid fraction was examined by means of XRD. Besides the detritic minerals (quartz, muscovite, phlogopite, chlorite and clinocllore) secondary minerals, such as jarosite, hydrojarosite and gypsum were detected.

The activity of *ATF* bacteria considerable accelerated predominantly the extraction process of Fe, As and Sb both from the sample of the sediment (X-1) as well as from the sample of the heavy fraction.

3.2. Biological – chemical oxidation of As-Minerals (Löllingite and arsenopyrite)

The experimental study of biogenic catalysis of As-minerals showed that löllingite (mineral with the highest As content) is the first that is intensively attacked by biological-chemical oxidation. Already after 5 days of leaching was its surface markedly etched. After 14 days of leaching the minerals were entirely dissolved to the depth of about 100 µm (fig. 2).

After 2 days of biological-chemical oxidation of arsenopyrite it was possible to observe the creation of dissolving channels at the cracks and at the contact of individual grains. The first pearl-string-like-chains began appear after 10 days of oxidation. The chains followed along the structural macro-defects of grain (fig. 3) are

probably formed due to the accumulation of metals at the surface of *ATF* cells. The heterogenous distribution of As within the arsenopyrite grains is a characteristic feature, along with well developed zonal microstructures, which may be interpreted as growth-banding in the oscillatory hydrothermal fluid system. The creation of caves and preferential dissolution of As-abundant growth zones (fig. 4) suggest the positive impact of galvanic effect of contact zones with the different As content. This galvanic dissolution allows to explain a complete dissolution of arsenopyrite on the contact with pyrite already after 18 days of leaching (fig. 5). Kinetics of chemical corrosion of pyrite was slower. In comparison with the biological-chemical oxidation the less intensive decomposition of the crystal surface was observed after 18 days of chemical leaching.

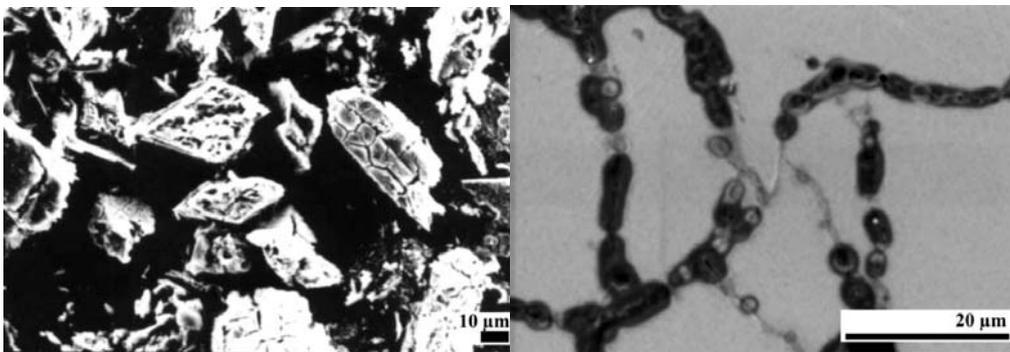


Fig. 2. Aggregate of euhedral löllingite crystals after 14 days of biological-chemical leaching. SEM secondary electron image.

Fig. 3. Pearl-string-like chains at the arsenopyrite surface after 10 days of biological-chemical leaching. SEM secondary electron image.

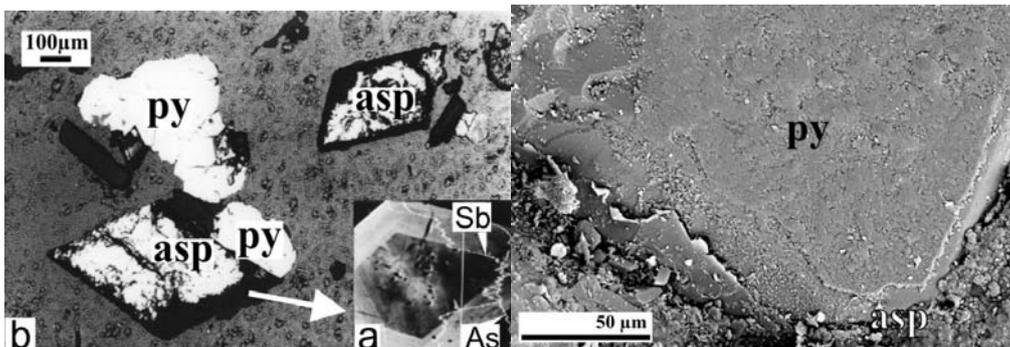


Fig. 4. a) Arsenopyrite crystal with line diagram of As and Sb contents. SEM image. B) Preferential dissolution of arsenopyrite (asp) compared with pyrite during biological-chemical oxidation of sulphide ores (As-abundant arsenopyrite zones show intensive corrosion). After 18 days of biological-chemical leaching the surface of pyrite (py) remains intact.

Fig. 5. Preferential dissolution of arsenopyrite (asp) on the contact with pyrite (py) as a result of galvanic effect after 18 days of leaching.

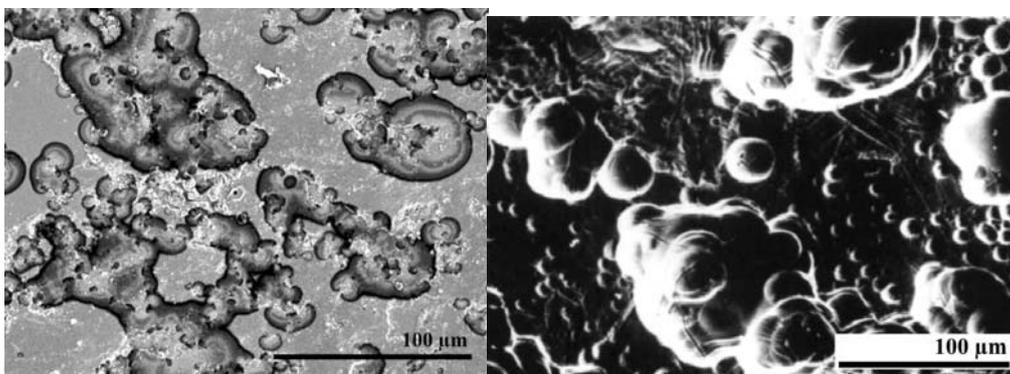


Fig. 6. Colomorphous etching patterns on the surface of native antimony formed after 2 days of biological-chemical leaching.

Fig. 7. Concentrically lined globular shapes at the surface of native Sb after 18 days of biological-chemical leaching. SEM secondary electron image.

3.3. Biological - chemical oxidation of Sb - minerals (Native Sb, stibnite, gudmundite and berthierite)

The first signs of dissolution and subsequent degradation of native antimony surface as a result of *ATF* bacteria activity was possible to observe already after 2 days of oxidation. Etching-patterns reminding the colomorphous structure were formed gradually with the period of leaching (fig. 6), as well as the dissolving cracks at the points of bacteria attachment. The advancing etching gradually denuded the trigonal structure of the mineral. The interesting concentrically lined spherical shapes were created in consequence of surface dissolution after 10 days of biological-chemical oxidation (fig. 7). Chemical oxidation of native antimony is not so intensive. After 18 days of oxidation is its surface only planary etched (fig. 8).

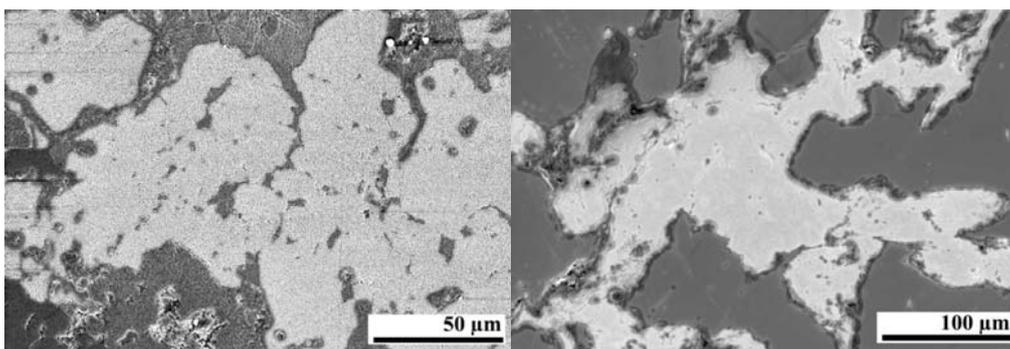


Fig. 8 After 18 days of chemical oxidation is the surface of native antimony planary etched.

Fig. 9 The first indications of dissolution by *ATF* bacteria on the stibnite surface after 7 days of oxidation

The first indications of dissolution by *ATF* bacteria medium were on the

stibnite - Sb_2S_3 surface observed after 7 days of oxidation (fig. 9). The etching-patterns and triangular-shaped caves appeared after 10 days of leaching (fig. 10) arranged along lines parallel with axis c of the stibnite needle. Such progress of leaching reflected the stibnite crystallographic structure. At the contact of stibnite with sphalerite there was observed an intensive dissolution and hollows forming process after 10 days of leaching.

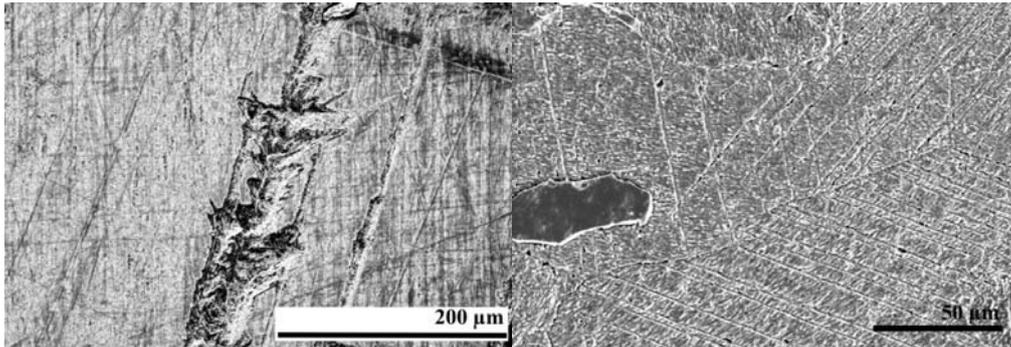


Fig. 10. Triangular-shaped etching-patterns at the stibnite surface after 10 days of biological-chemical oxidation. a) Attachment of *ATF* bacteria on the stibnite surface after 7 days of biological-chemical leaching.

Fig. 11 Etching-patterns on stibnite surface after 15 days of chemical leaching.

Etching-patterns highlighting the crystal structure were observed after 15 days of chemical leaching of stibnite (fig. 11). The gypsum crystals formation along the carbonate veins and the intensive mineral dissolution was observed at the stibnite surface after 18 days (fig. 12).

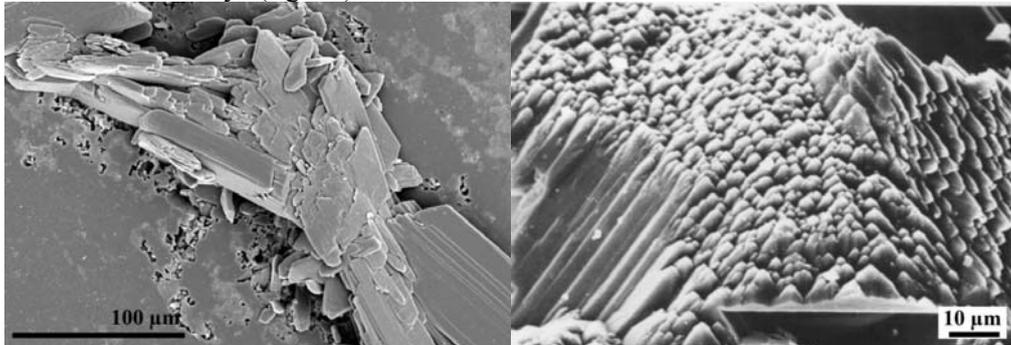


Fig. 12 Gypsum crystals formation along the carbonate veins

Fig. 13 Etched gudmundite crystal structure after 18 days of biological-chemical leaching.

Biological-chemical dissolution of gudmundite is relatively fast. The attachment of bacteria on the surface of crystal and the creation of dissolving rims round the mineral circuit and along the mineral cracks were possible to observe after 7 days of oxidation. The linear depressions following the gudmundite crystal structure were formed after 18 days of leaching (fig.13). The gudmundite surface chemical etching was ascertained only after 15 days (fig.14).

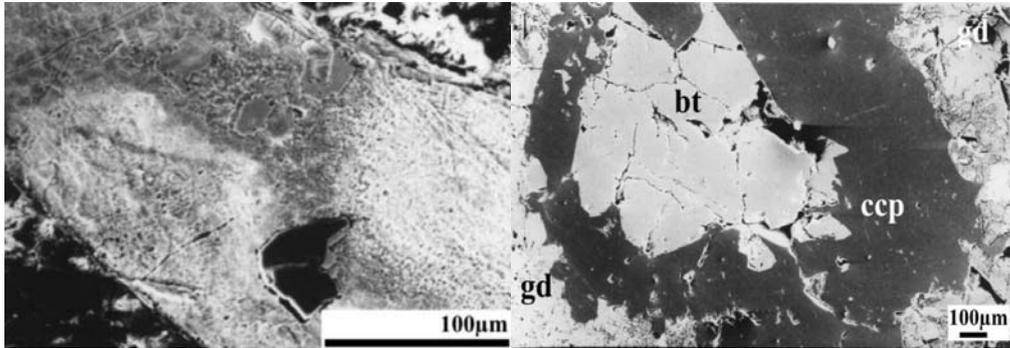


Fig. 14 Etched surface of gudmundite after 15 days of chemical leaching.

Fig. 15 Uninterfered chalcopyrite (ccp) surface, moderately etched berthierite (bt) and intensively oxidized surface of gudmundite (gd) after 18 days of biological-chemical leaching.

Berthierite is more resistant to biological-chemical and chemical oxidation in comparison with gudmundite (fig.15). The first signs of etching appeared at the crystals after 18 days of oxidation process. The intensive biological-chemical degradation started after 21 days. The significant chemical dissolution began markedly after 30 days.

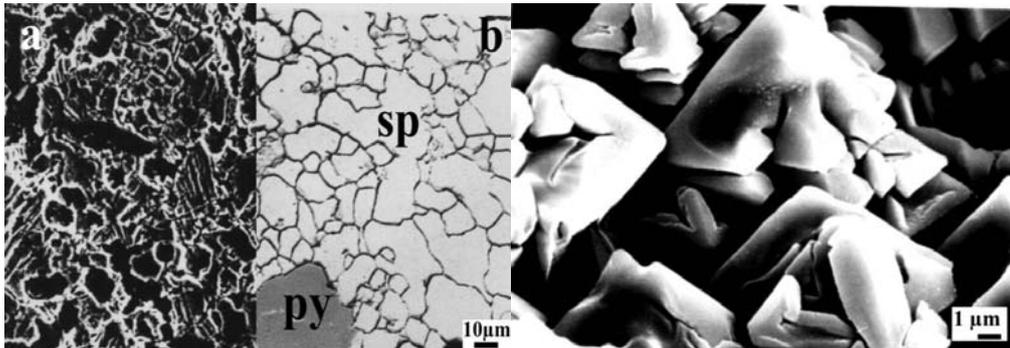


Fig. 16 a) Dissolution of sphalerite (sp) along interstitial lines after 20 days of chemical leaching. Pyrite (py) surface show no dissolution or etching patterns. b) Channelled surface of grains of sphalerite aggregate after 25 days of biological-chemical leaching by ATT and ATF containing medium;

Fig.17 Etched texture of sphalerite crystal after 40 days of biological-chemical leaching using ATT and ATF containing medium.

3.4. Biological – chemical oxidation of sphalerite

The selected sphalerite polished crystal pieces were kept in *ATF* cultures containing solution for a period of 50 days. The first signs of dissolution along the inclusions of individual grains (fig. 16a) of mineral aggregate were observed after 18 days of leaching but the crystal surface was channelled markedly only after 25 days of leaching (fig. 16b). However, no significant signs of biodegradation were observed on

the euhedral inclusions of pyrite crystals (except for the flat etching-patterns). The final phase of biological-chemical oxidation of sphalerite is the intensive crystal etching after 40 days uncovering the tetrahedral structure of lattice (fig. 17).

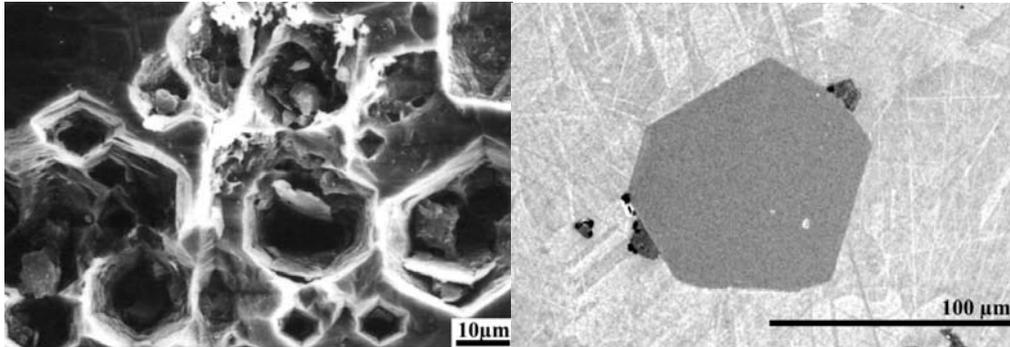


Fig. 18 Hexagonal corrosion pits on pyrite octahedron face after 40 days of biological-chemical leaching, developed on screw dislocations of the cubic lattice.

Fig. 19 After 30 days of chemical oxidation is pyrite still intact.

The chemical leaching had minor kinetics. Only moderate etching patterns and channels were described after 20 days of leaching. The surface of crystals was evenly etched after 25 days. After 10 days of leaching the intensive dissolution of sphalerite was observed only along the contact of sphalerite, pyrite and chalcopyrite, probably as a result of galvanic effect.

3.5. Biological – chemical oxidation of pyrite

After 10 days of biological-chemical leaching the morphological changes at the pyrite surface were possible to find only along the cracks: cells of bacteria formed chains or aggregates. After 25 days of leaching the surface of pyrite grains was covered with the rough crust of secondary minerals. The microprobe examination of pyrites reveals that the dissolution developed preferentially along preexisting cracks and veinlets, as well as along grain contacts. The point dissolution and the creation of caves in the size of several μm were possible to see on the edges and in the centre of grain. The porous parts of the crystal were biodegraded faster than the compact growth zones.

The shape of caves depended on the orientation of individual crystallographic faces. The caves of hexagonal cross-section (fig.18) are developed on screw dislocations of the cubic lattice, the triangular caves on (111) faces while square holes on (001) faces of pyrite cubes.

After 30 days of chemical oxidation of pyrite the grains surface seemed to be intact (fig. 19). Only euhedral gypsum crystals were found along the calcite veins. The linear depressions and oriented tunnels were formed gradually after about 2 months of leaching. They were developed, similarly as in case of arsenopyrite, preferentially in As-rich zones. The pyrite dissolved at first around the inclusions of other sulphide minerals as a result of galvanic effect. Inclusions of euhedral pyrite in carbonates dissolved slower than those in quartz.

3.6. Biological – chemical oxidation of chalcopyrite

The product of the chalcopyrite chemical oxidation is the elementary sulphur inhibiting the surface of chalcopyrite grains and is responsible for the process deceleration. Already Baláž et al (1994) showed that the biological-chemical oxidation with *ATF* bacteria enables this deceleration partly eliminate. Even the leaching in the *ATF* bacteria-containing medium showed that the kinetics of oxidation processes is the slowest for chalcopyrite. After 30 days of chemical and biological-chemical oxidation there was only a weak etching of surface observed.

4. DISCUSSION

Research studies of Trtíková et al. (1999) and Andráš et al. (2004) demonstrated that there are two types of acid mine drainage in the area of the Pezinok deposit:

- First type → extremely acid (pH < 3) mine waters associated with synsedimentary massive pyrite-pyrotine ores,
- Second type → neutral mine waters (pH 5.5 – 7) associated with Sb-carbonate mineralisation.

The activity of *ATT* and *ATF* bacteria in the first type of acid mine drainage is much higher. It is the neutral waters that percolate through the sludge lagoons of Sb-ores in the Kolarsky hill area and that is why the leaching intensity is much lower than in the area of pyrite-mineralised parts (Augustin adit and the like). A considerable amount of Fe precipitates in form of ochres during the neutralisation of solutions. Ochres form the geochemical barrier and their surface serve as a sorbent of a considerable amount of metals. It is impossible to exclude that during torrential rains and under other influences the ochres may overcome the barriers of the tailing dams and reach the water flows. According to Luptáková (2001) concentration of heavy metals in the waters of sludge lagoons may be influenced also by anaerobic sulphate reducing bacteria producing hydrogen sulphide reacting with ions of heavy metals producing the secondary minerals. Luptáková realized the isolation of those bacteria from the solid samples of the reducing zone of the sludge lagoon. The undercritical content of metals in waters, if flowing through the country for a long time, intoxicates river-sediments and gradually increases the metal concentrations as well.

Experimental studies of biogenic catalysis from the point of view of changes in the ore mineral surfaces in the sludge lagoons confirmed considerable differences in the kinetics and decomposition of studied minerals. The reaction ability of minerals reflects the distribution of the reactive planes and points at the crystal surfaces and the relation of these points to the energy of mineral crystalline lattice. During the biological-chemical oxidation processes it was possible to observe various signs of dissolution at the mineral surfaces that related to the metabolic processes of bacteria. For instance, the biological-chemical oxidation of pyrite is marked by the formation of characteristic etching-holes described by Morion et al. (1991). Morion described the galvanic interaction between different sulphide minerals during which the electrons are transferred from one sulphide mineral (anode) to less electroactive sulphide mineral. According to Crundwell (1989) this effect can be interpreted as the modification of

sulphide semiconductive properties accompanied with the tiny changes in the structure and physical properties (reflection, microhardness, conductivity, etc.) of sulphide minerals. The galvanic effect accelerates the dissolution of minerals. Such an effect was also observed during experiments carried out with the selected sulphide minerals from the Pezinok deposit. The preferential dissolution of contact grains was observed at the interface of different sulphide minerals or around the inclusions of sulphide minerals. On the other hand, a considerable deceleration of chemical and biological-chemical oxidation (with the formation of gypsum as an associate phenomenon) was observed as a result of neutralisation effect of inherent carbonate component for sulphide inclusions in carbonates.

The presented results of native Sb biological – chemical leaching suggest also the possible role of b in metabolism of *ATF* bacteria.

5. CONCLUSIONS

The control of acidity is of utmost importance in leaching, because of acidic environment must be maintained in order to keep ferric iron and other metals in solution. Acidity is controlled by the oxidation of iron, sulphur (and also antimony?), by the dissolution of carbonate ions and by the decomposition of ferric iron through reaction with water.

The process of studied ore minerals degradation during biological-chemical oxidation in the presence of autochthonous, acidophilous, sulphur and iron oxidising *ATF* and *ATT* bacteria and during chemical oxidation is principally similar, but the kinetics of both processes is different. Higher kinetics of biological-chemical oxidation processes of studied minerals confirms the bio-catalytic influence of autochthonous bacteria.

The result of experiments confirmed that the biogenic catalysis is the most intensive at löllingite. The other studied minerals are possible to arrange according to the decreasing oxidation kinetics as follows: arsenopyrite, native Sb, stibnite, gudmundite, berthierite, and sphalerite. Pyrite and chalcopyrite seemed to be the most resistant to the biological-chemical as well as chemical oxidation.

The positive correlation between the oxidation rate and As contents was ascertained for löllingite, arsenopyrite and pyrite. At the contact of two different minerals or two mineral growth zones with the different content of isomorphic components (in arsenopyrite, pyrite and gudmundite) the galvanic effect was ascertained. Pyrite crystals in carbonates are degraded slower than those in quartz. In some minerals (mainly pyrite) the shape of dissolving caves and tunnels depend on the crystallographic orientation of individual crystal faces.

The comparison of biological-chemical oxidation with chemical oxidation enabled to find the differences in the leaching mechanism. The structures formed during the biological-chemical oxidation in *ATF* containing medium are characterised as follows:

- The bacterial leaching causes the creation of caves and point etching-patterns probably formed as a result of direct mechanism of biological-chemical oxidation of the contact dissolution by microorganisms and they relate to the metabolic processes of

applied bacteria;

- The shape of created caves depends on the crystallographic orientation of etched faces;

- The formation of various oriented tunnels, lines and dissolving planes is the implication of the chemical corrosion.

After a certain time the crusts of the secondary minerals coats at the mineral surfaces for both types of oxidation mechanisms.

The researches show that the influence of the bacterial leaching can substantially accelerate the ore minerals degradation. In spite of the present favourable pH stage of the AMD it is necessary monitor the development of the conditions at the sludge lagoons. The neutralizing potentiation of the carbonates could be exhausted and the character of the AMD pH could change to the markedly acid values. Such a change could activate the catastrophic biodegradation process and cause the substantial contamination of the surrounding landscape.

6. ACKNOWLEDGEMENTS

The article is the part of the APVV-51-015605 project as well as of the VTP 25 of the Ministry of Education of the Slovak republic.

REFERENCES

- Andráš, P., Milovská, S., Kušnierová, M., Chovan, M., Adam, M., Šlesarová, A., Hajdučková, E., Lalinská, B.:** *Environmental hazards at the Sb- (Au-) deposit Pezinok (Slovakia) in relation to the chemical and biological-chemical oxidation processes.* 7th International symposium on environmental geotechnology and global sustainable development introduction (International Society of Environmental Technology). 2004.Helsinki, 8-20.
- Baláž, P., Kušnierová, M., Varencova, V.I., Mišura, B.:** *Mineral properties and bacterial leaching of intensively ground sphalerite and sphalerite-pyrite mixture.* Int. J. Mineral Processing. 1994. 40, 273-285.
- Bennett, J. C., Tributsch, H.:** *Bacterial leaching patterns on pyrite crystal surfaces.* Journal of Bacteriology. 1978. 134, 1, 310-316.
- Chovan, M., Rojkovič, I., Andráš, P., Hanas, P.:** *Ore mineralisation of the Malé Karpaty Mts. (Western Carpathians),* Geologica Carpathica. 1992. 43, 5, 275-286.
- Chovan, M., Khun, M., Vilinovič, V., Šucha, V., Trtíková, S.:** *Mineralógia, petrografia a geochemia Au - As - Sb mineralizácie v štôlni Trojárová.* Univerzita Komenského, Bratislava – Geologický prieskum, Spišská Nová Ves, Manuscript. 1994. 83 p.
- Crundwell, F.K.:** *The influence of the electronic structure of solids on the anodic dissolution and leaching of semiconducting sulfide minerals.* Hydrometallurgy. 1989. 22, 141-157.
- Dopson, M., Borje, L. E.:** *Potential role of Thiobacillus caldus in arsenopyrite.* Applied and Environmental Microbiology. 1999. 65, 1, 36-43.
- Guereumont, J. M., Elsetinow, A. R., Strongin, D. R., Bebie, J., Schoonen, M. A. A.:** *Structure sensitivity of pyrite oxidation. Comparison of the (100) and (111) planes.* American Mineralogist. 1998. 83, 1353-1356.
- Kušnierová, M., Štyriaková, I.:** *Biotransformácia sulfidov.* In: Biohydrometalurgia - III., ÚGt SAV. 1994. Košice, 19-25.
- Luptáková, A.:** *Bioakumulácia ťažkých kovov z kyslých banských vôd.* Acta Avionica. 2001. 4,

104-107.

- Morion, P., Monroy, M., Mustin, C., Berthelin, J.:** *Effect of auriferous sulfide minerals structure and composition on their bacterial weathering.* Source, transport and deposition of metals, Balkema, Rotterdam. 1991. 561-564.
- Mustin, C., Berthelin, J., Marion, P., Donato, P.:** *Corrosion and electrochemical oxidation of a pyrite by Thiobacillus ferrooxidans.* Applied and Environmental Microbiology. 1992. 58, 4, 1175-1182.
- Pronk, T.T., de Bruyn, J.C., Bos, P., Kuenen, J.G.:** *Anaerobic growth of Thiobacillus ferrooxidans.* Appl. Environ. Microbiol. 1994. 58., 2227-2230.
- Silva, G., Lastra, M. R., Budden, J. R.:** *Electrochemical passivation of sphalerite during bacterial oxidation in the presence of galena.* Minerals Engineering. 2003. 16, 199-203.
- Silverman, M. P., Lundgren, D. G.:** *Studies on the chemoautotrophic iron bacterium Ferrobacillus Ferrooxidans II.* Manometric Studies, Bacteriol. 1959. 78(3), 326–331.
- Spirito, Di, A.A., Silver, M., Voss, L., Tuovinen, O.H.:** *Flagella and Pili of Iron-Oxidizing Thiobacilli Isolated from a Uranium Mine in Northern Ontario, Canada.* Appl Environ Microbiol. 1982. 43, 5, 1196–1200.
- Trtíková, S., Chovan, M., Kušnierová, M.:** *Oxidation of pyrite and arsenopyrite in the mining wastes (Pezinok – Malé Karpaty Mts).* Folia Fac. Sci. Nat., Univ. Mas. Brun. Geologia. 1999. 39, 225-231.
- Uher, P., Michal, S., Vitáloš, J.:** *The Pezinok antimony mine, Malé Karpaty Mts., Slovakia.* The Mineralogical Record. 2000. 31, 153-162.

Received at 11. 09. 2007

Revised: 05. 11. 2007

Accepted for publication 15. 11. 2007