

## Bacterial leaching of ore minerals from waste at the Pezinok deposit (Western Slovakia)

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**Abstract** The paper reports the chemical characteristic of acid mining drainage waters as well as the results of leaching experiments conducted with *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* at the same conditions in the 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 results show the oxidation sequence and the leaching progression on the 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 are discussed. The extent and the kinetics of the biological-chemical leaching of ore minerals are significantly higher than the chemical leaching of ore minerals without bacteria.

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

### Introduction

More than 100 years of mining activity in the Pezinok deposit caused changes of the land relief. The ore material was displaced from the original environment of the mountain massif, 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.

Sludge lagoons and setting-pits contain a lot of waste ore minerals which represent the main substrate necessary for the metabolic activity of autochthonous, acidophilous and thionic bacteria *Acidithiobacillus ferrooxidans* (ATF), *Acidithiobacillus thiooxidans* (ATT) and *Leptospirillum ferrooxidans* (LF) catalyzing 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 (AMD) generation. Surface and underground waters are also polluted with elements from the flotation 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.

### Characteristic of the Pezinok deposit

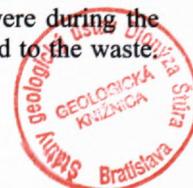
The Pezinok – Kolársky vrch (Fig. 1) deposit is situated in a 1200 m long tectonic fault of NW-SE direction. The mineralized structure is 25-70 m thick at the surface and about 430 m long (Chovan et al., 1992).

In the Pezinok deposit two types of ore mineralization were described: (1) metamorphosed, primarily exhalation-sedimentary pyrite mineralization genetically related to Devonian basic volcano-sedimentary cycle which was subsequently metamorphosed and (2) hydrothermal Sb-Au-As mineralization 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 in the Pezinok deposit terminated in 1991. The mine was closed in 1992.

### Characterization of the deposited waste

The mining-waste is deposited in several tailings impoundments and two sludge lagoons containing 380 000 m<sup>3</sup> of material (Trtiková, 1999). As- and Fe-minerals (predominantly arsenopyrite and pyrite) were during the ore dressing process suppressed and moved to the waste.



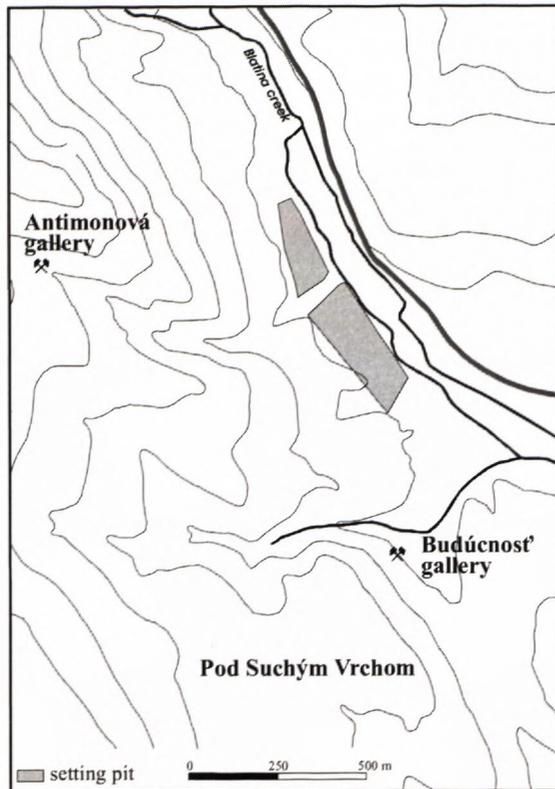


Fig. 1. Sketch of the studied area of the setting pits at the Pezinok deposit.

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 occur rarely, pyrrhotite sporadically. In some samples Sb- and Fe-oxides, tetrahedrite, löllingite and chalcopyrite were determined (Chovan et al., 1994).

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 kaolinite is very rare (Chovan et al., 1994). Also Fe-oxyhydroxides and Sb-oxides are formed in the oxidation zone of the sludge lagoons (Trtíková, 1999; Trtíková et al., 1999).

### Biological–chemical oxidation

The principle of biogenic catalysis of sulphide oxidation consists in the activity of acidophilous, thionic, sulphur and iron oxidizing bacteria having a transporting function in the oxidation process, i.e. in the transfer of released electrons from the 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  $\text{Fe}^{2+}$  oxidation (Bennett and Tributsch, 1978; Martyčák et al., 1994; Dopson and Borje, 1999).

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 ATF, but also the *Spirillaceae* tribe LF bacteria oxidizing  $\text{Fe}^{2+}$  in the ultra acidic environment. *Acidithiobacillus ferrooxidans* species are gram-negative nonsporeforming rods, 0.5–0.8  $\mu\text{m}$  in diameter and 0.9–1.5  $\mu\text{m}$  in length with one spiral flagellum (Spirito et al., 1982). Bacteria obtain the energy by oxidizing of  $\text{Fe}^{2+}$ -ore minerals. All bacteria of *Acidithiobacillus* genus also oxidize the elementary sulphur formed during the sulphides decomposition.

Sulphide minerals can be oxidized 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  $\text{CO}_2$  observed in the system.

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

The marked alternation of surface morphology and consequently the structure uniformity of oxidized minerals represent the direct effect of biological-chemical oxidation processes. 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 sulphide minerals and the transport of electrons from the sulphide mineral forming anode to the electrochemically less electro-active mineral occurs. According to Crundwell (1989) and Silva (2003) this effect can be interpreted as the modification of the semiconductive properties of sulphide minerals accompanied with the tiny changes in the structure and physical properties such as reflection, microhardness, conductivity, etc.

### Materials and methods

The AMD waters were analysed by atomic absorption analysis 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 tailings impoundment sediments as well as the oxidation of ore minerals.

During the first experiment the tailings impoundment sediment and the polished sections of ore minerals were immersed 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.

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 atomic absorption analysis.

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.

## Results

### Characterization of AMD waters

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

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).

The leaching activity in dependence to the leaching medium is presented in Tab. 3. For this experiment the drainage water P 2 from Pezinok with autochthonous *ATF* and *ATT* bacteria was used. 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 the parallel experiments were realized with rainwater for comparison.

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.

From the Tab. 4 there follows, that in strongly acidic medium (pH = 1.57) *ATF* and *ATT* are active, and vigorously assist to 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) the 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.

### 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 which is intensively attacked by biological-chemical oxidation. Already after 5 days of leaching its surface was 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 there 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 heterogeneous 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 origin 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

Tab. 1. AAS analysis of the chemical composition of sediment sample from tailings 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

Tab. 2. Composition of AMD water 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 Pernek locality, 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, ATF, ATT – presence of the bacteria

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

Medium	Time of leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
Drainage water P 2 ATF+ATT 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

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

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

days of leaching (Fig. 5). Kinetics of chemical corrosion of pyrite was slower and was indicated by the formation of linear depressions (Fig. 6). In comparison with the biological-chemical oxidation the less intensive decomposition of the crystal surface was observed after 18 days of chemical leaching.

#### **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. 7), as well as the dissolving cracks at the points of bacteria attachment. The advancing etching gradually denuded the trigonal structure of the mineral (Fig. 8). The interesting concentrically lined spherical shapes were formed as the consequence of surface dissolution after 10 days of biological-chemical oxidation (Fig. 9). Chemical oxidation of native antimony is not so intensive. After 18 days of oxidation its surface is only planary etched (Fig. 10).

The first indications of dissolution by *ATF* bacteria medium were on the stibnite -  $Sb_2S_3$  surface observed after 7 days of oxidation (Fig. 11). The etching-patterns and triangular-shaped caves appeared after 10 days of leaching (Fig. 12) 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.

Etching-patterns highlighting the crystal structure were observed after 15 days of chemical leaching of stibnite (Fig. 13). The gypsum crystals formation along the carbonate veins and the intensive mineral dissolution was observed on the stibnite surface after 18 days.

Biological-chemical dissolution of gudmundite is relatively fast. The attachment of bacteria on the surface of crystal (Fig. 14) and the formation 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. 15). The gudmundite surface chemical etching was ascertained only after 15 days (Fig. 16).

Berthierite is more resistant to biological-chemical and chemical oxidation in comparison with gudmundite (Fig. 17). The first signs of etching appeared on 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. 18).

#### **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 inclu-

sions of individual grains (Fig. 19a) of mineral aggregate were observed after 18 days of leaching but the crystal surface was channelled markedly only after 25 days of leaching (Fig. 19b). 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 the lattice (Figs. 20 and 21).

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 (Fig. 22), probably as a result of galvanic effect.

#### **Biological-chemical oxidation of pyrite**

After 10 days of biological-chemical leaching the morphological changes at the pyrite surface were observable 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 revealed that the dissolution developed preferentially along pre-existing cracks and veinlets, as well as along grain contacts. The point dissolution and the formation of caves in the size of several  $\mu m$  were seen on the edges and in the centre of grain. The porous parts of the crystal were biodegraded faster than the compact growth zones (Fig. 23).

The shape of caves depended on the orientation of individual crystallographic faces. The caves of hexagonal cross-section (Fig. 24) are developed on screw dislocations of the cubic lattice, the triangular caves on (111) faces (Fig. 25a), while the square holes on (001) faces of the pyrite cubes (Fig. 25b).

After 30 days of chemical oxidation of pyrite the grains surface seemed to be intact. Only euhedral gypsum crystals were found along the calcite veins (Fig. 26). The linear depressions and oriented tunnels were formed gradually after about 2 months of leaching. They were developed, similarly as in the case of arsenopyrite, preferentially in As-rich zones. The pyrite firstly dissolved 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.

#### **Biological-chemical leaching 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 Baláz et al. (1994) showed that the biological-chemical oxidation with *ATF* bacteria enables partial eliminating of this deceleration. Even the leaching in the *ATF* bacteria containing medium showed that the kinetics of oxidation processes is the slowest for chalcopyrite.

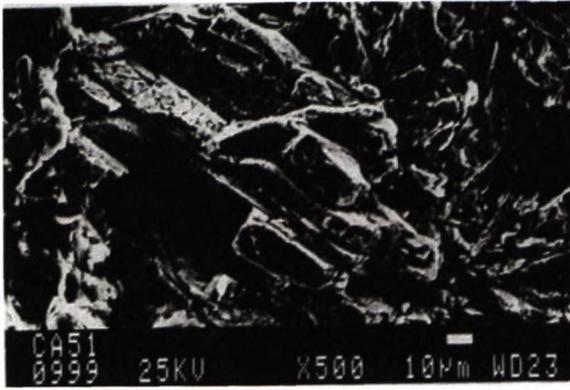


Fig. 2

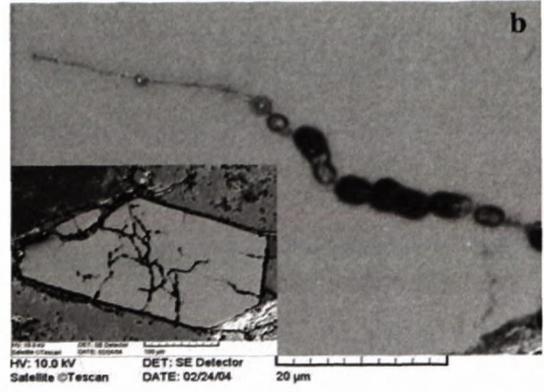


Fig. 3

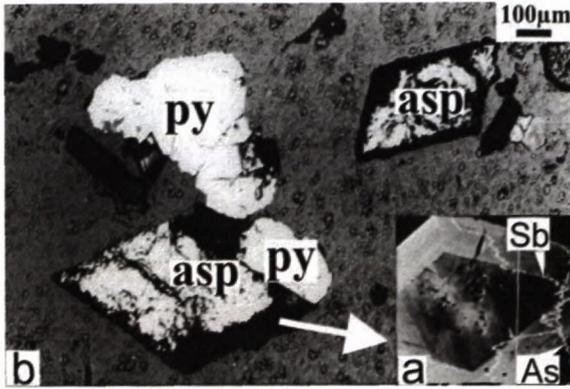


Fig. 4

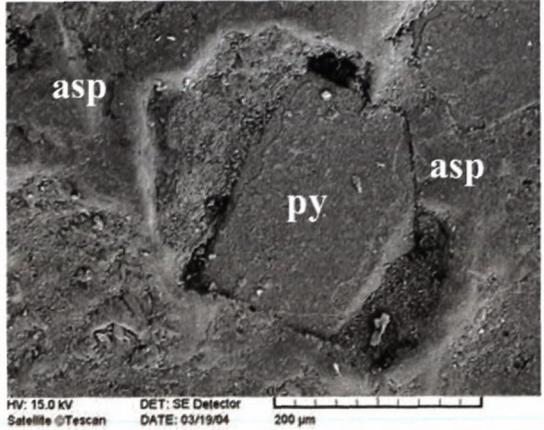


Fig. 5



Fig. 6

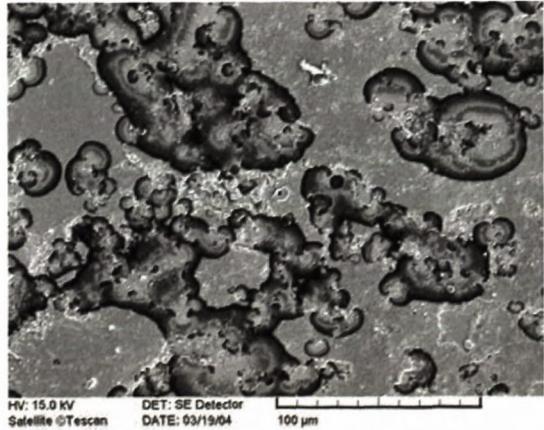


Fig. 7

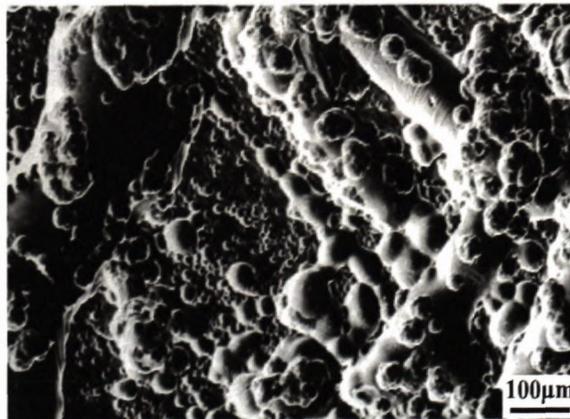


Fig. 8

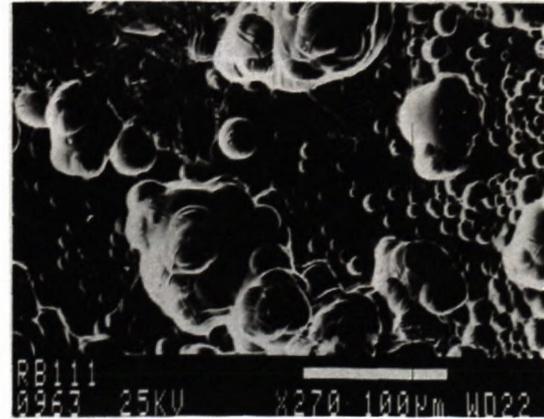


Fig. 9

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

Fig. 3. a – Demonstration of the pearl-string-like chains at the arsenopyrite surface after 10 days of biological-chemical leaching, b – detail of patterns after attachment of ATF bacteria (SEM secondary electron image).

Fig. 4. 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. a) Arsenopyrite crystal with line diagram of As and Sb contents (SEM secondary electron image).

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. Linear depressions on the pyrite surface after chemical leaching (SEM secondary electron image).

Fig. 7. SEM secondary electron image of the colomorphous-like etching patterns at the native Sb surface after 6 days of biological-chemical leaching.

Fig. 8. Etching-patterns reflecting the trigonal mineral structure of native Sb after 10 days of biological-chemical leaching.

Fig. 9. Concentrically lined globular shapes at the surface of native Sb after 18 days of biological-chemical leaching (SEM secondary electron image).

After 30 days of chemical and biological-chemical oxidation there was only a weak etching of the surface observed (Fig. 27).

## Discussion

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

- First type → extremely acid (pH < 3) mine water associated with syndimentary massive pyrite-pyrrhotite ores,

- Second type → neutral mine water (pH 5.5–7) associated with Sb-carbonate mineralization.

The activity of *ATT* and *ATF* bacteria in the first type of acid mine drainage is much higher. It is the neutral water that percolates through the sludge lagoons of Sb-ores in the Kolársky hill area and that is why the leaching intensity is much lower than in the area of pyrite-mineralized parts (Augustin adit and the like). A considerable amount of Fe precipitates in the form of ochres during the neutralization of solutions. Ochres form the geochemical barrier and their surface serves 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 water 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 crystal-line 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 associated phenomenon) was observed as a result of neutralization 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 Sb in metabolism of *ATF* bacteria.

## Conclusion

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 oxidizing *ATF* and *ATT* bacteria and during chemical oxidation is

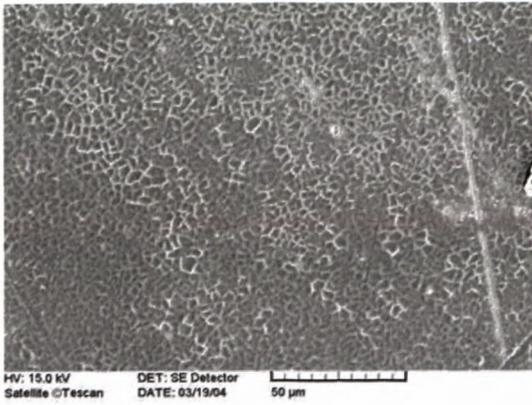


Fig. 10

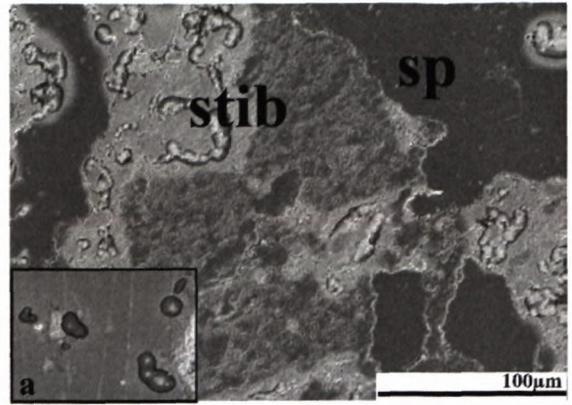


Fig. 11

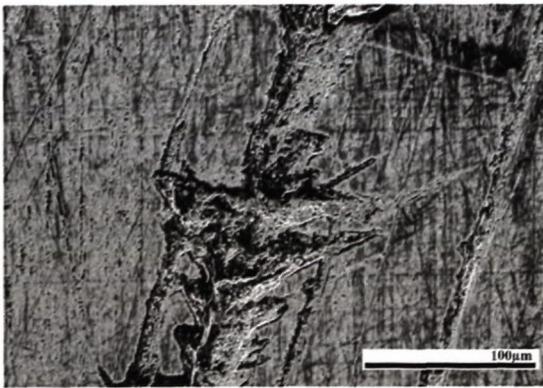


Fig. 12

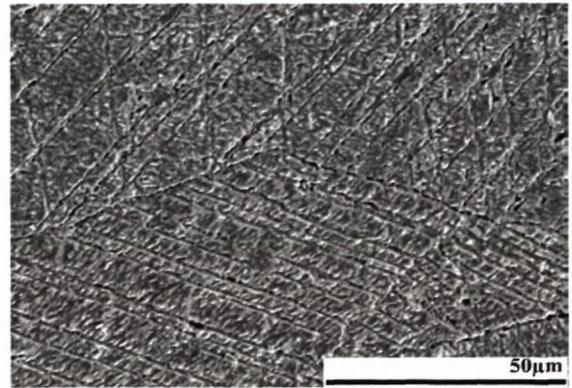


Fig. 13

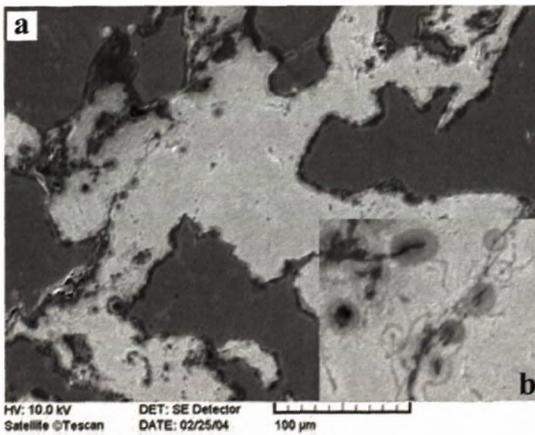


Fig. 14

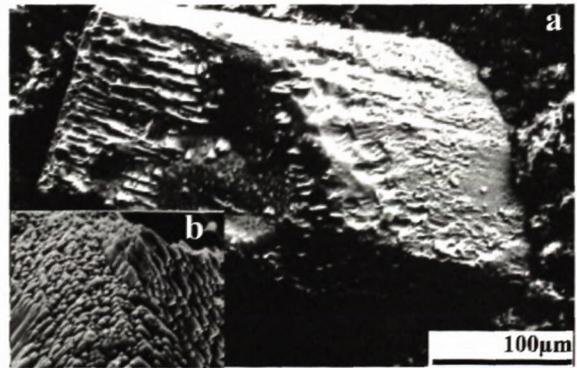


Fig. 15

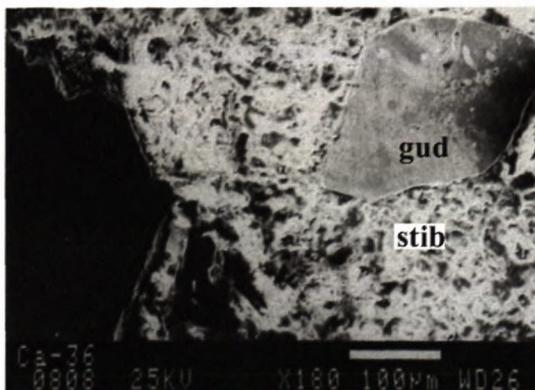


Fig. 16

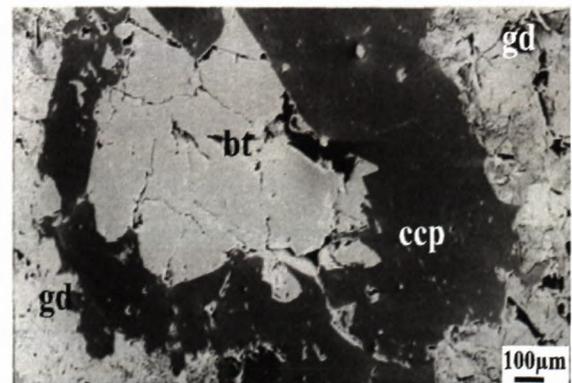


Fig. 17

Fig. 10. Biodegradation of native Sb after 18 days of chemical leaching (SEM secondary electron image).

Fig. 11. First etching patterns (a) on the stibnite (stib) after 7 days of biological-chemical leaching (sp - sphalerite).

Fig. 12. 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. 13. SEM secondary electron image of the etching-patterns (reflecting the lattice structure) on the stibnite surface after 10 days of chemical leaching.

Fig. 14. a - Attachment of ATF bacteria on the gudmundite surface after 10 days of biological-chemical leaching (b - detail).

Fig. 15. a - SEM secondary electron image of the etched gudmundite surface after 18 days of biological-chemical degradation; (b - detail).

Fig. 16. Chemically etched gudmundite (gud) surface after 18 days of chemical leaching (stib - stibnite).

Fig. 17. Non-interfered chalcopyrite surface (ccp), weakly etched berthierite surface (bt) and markedly corroded gudmundite surface (gd) after 18 days of biological-chemical leaching.

principally similar, but the kinetics of both processes is different. Higher kinetics of biological-chemical oxidation processes of studied minerals confirms the biocatalytic influence of autochthonous bacteria.

The result of experiments confirmed that the biogenic catalysis is the most intensive in löllingite. The other studied minerals can be arranged according to the decreasing oxidation kinetics as follows: arsenopyrite, native Sb, stibnite, gudmundite, berthierite, and sphalerite. Pyrite and chalcopyrite seem 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 characterized as follows:

- The bacterial leaching causes the origin of caves and point etching-patterns probably due to the direct mechanism of biological-chemical oxidation of the contact dissolution by microorganisms. They relate to the metabolic processes of applied bacteria.

- The shape of formed 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 appears at the mineral surfaces for both types of oxidation mechanisms.

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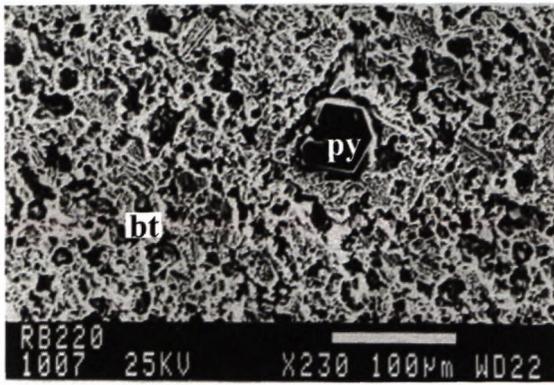


Fig. 18

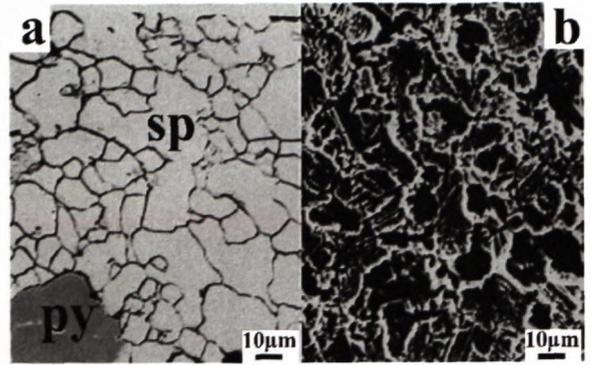


Fig. 19

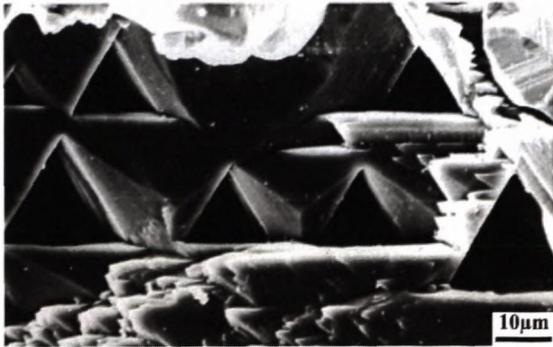


Fig. 20

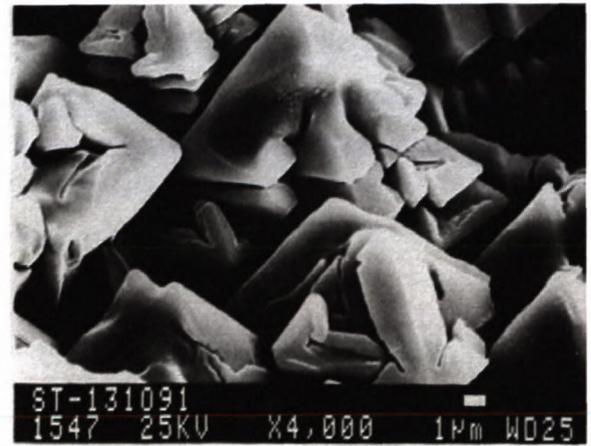


Fig. 21

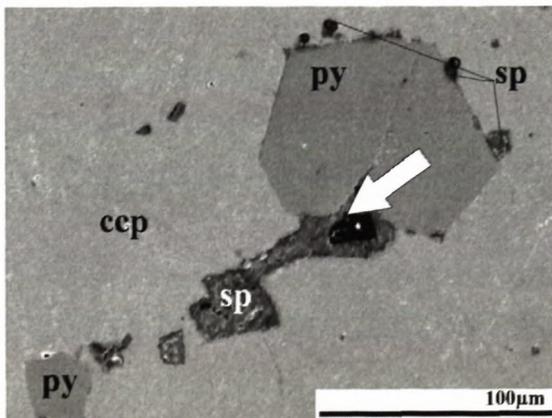


Fig. 22

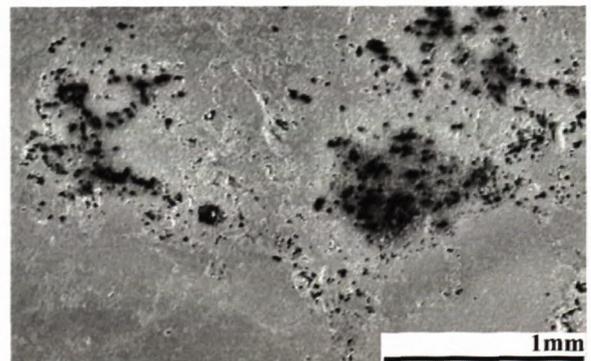


Fig. 23

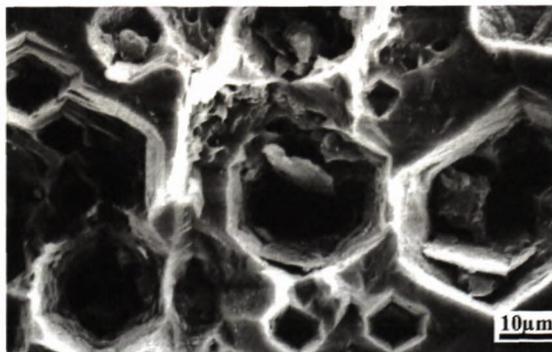


Fig. 24

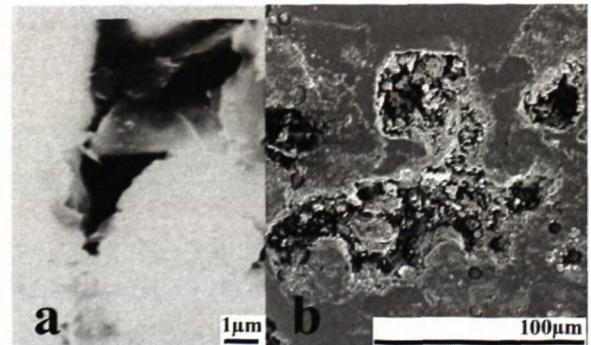


Fig. 25

Fig. 18. Significant chemical dissolution of berthierite (bt) after 30 days (py – pyrite) SEM secondary electron image.

Fig. 19. a - Sphalerite (sp) dissolution along the inclusions after 20 days of chemical leaching. There are no signs of etching or dissolution at the pyrite (py) surface; b - channelled surface of the sphalerite aggregate after 25 days of biological-chemical leaching in ATF containing medium.

Fig. 20. Etched sphalerite crystal structure after 40 days of biological-chemical leaching in ATF containing medium. SEM secondary electron image.

Fig. 21. Etched sphalerite crystal structure after 40 days of biological-chemical leaching in ATF containing medium.

Fig. 22. Preferential sphalerite (sp) dissolution along the contact with pyrite (py) as a result of galvanic effect (ccp – chalcopryite).

Fig. 23. Formation of small caves within the porous parts of pyrite grains after 25 days of biological-chemical leaching.

Fig. 24. Caves of hexagonal cross-section in the points of lattice loop-deformations of pyrite octahedrons after 40 days of biological-chemical leaching.

Fig. 25. SEM secondary electron image of oxidation progress at the surface of pyrite crystals. a) Formation of triangle-shaped caves on (111) faces. b) Formation of square-cross-section holes on (001) faces of pyrite cubes.

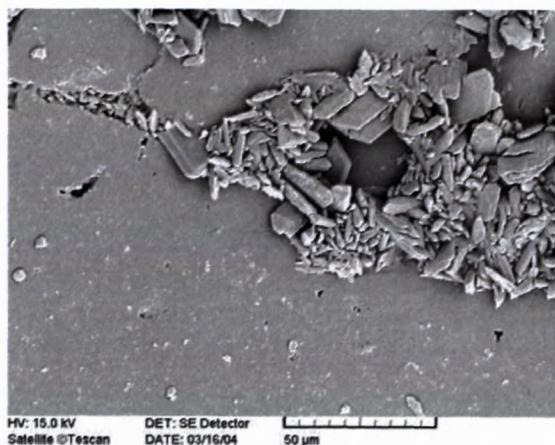


Fig. 26

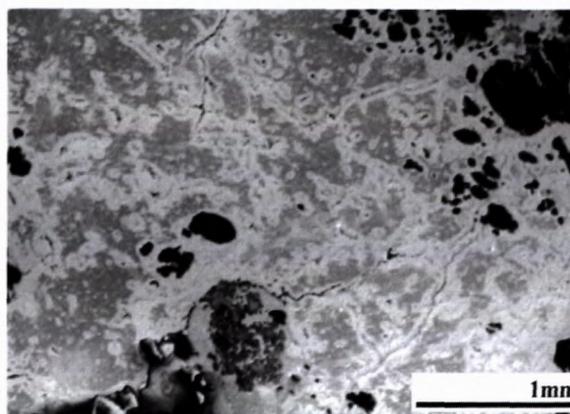


Fig. 27

Fig. 26. Formation of euhedral gypsum crystals (gy) along the carbonate cement within chalcopryite grains (ccp) after 10 days of biological-chemical leaching.

Fig. 27. First etching patterns of chalcopryite surface after 30 days of biological-chemical leaching

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