

**FORMATION OF ACID MINE DRAINAGE WATER
AT Sb (Au) DEPOSIT PEZINOK**

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Abstract

The article presents the results of leaching experiments regarding the comparison of chemical and biological-chemical leaching of ores from the Sb-(Au-) base metal deposit Pezinok (Malé Karpaty., the Western Carpathians) under the same conditions in solution. Discussed are the differences between chemical and biological-chemical leaching activity. The extent and the kinetics of the biological-chemical leaching of the technogenous sediments from the setting-pits are significantly higher than those without bacteria.

Key words

AMD, biological-chemical oxidation, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans

Introduction

More than 100 years of mining at the Pezinok deposit has caused some 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 have increased the reactive surface of the relict sulphides in the deposited waste.

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Sludge lagoons and setting-pits contain a lot of waste sulphide 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 sulphide minerals oxidation processes. The high residual concentrations of metals Sb, Fe and As in the deposited solid wastes and contaminated soils are currently being 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 the elements from the floatation agents used in the ore processing. The released metals and other chemical agents may enter the food chain of animals and humans through plants and water.

Characteristics 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).

At the Pezinok deposit, two types of ore mineralization were described: 1 – metamorphosed, primarily exhalation-sedimentary pyrite mineralization genetically related to the 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 at the Pezinok deposit was terminated in 1991. The mine was closed in 1992.

Characterisation of the deposited waste

The mining-waste is deposited in several tailing impoundments and two sludge lagoons containing 380 000 m³ of material (Trtíková, 1999). During the ore dressing process, As- and Fe- minerals (predominantly arsenopyrite and pyrite) were 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, pyrrhotine sporadically. In some samples, determined were Sb- and Fe- oxides, tetrahedrite, löllingite and chalcopyrite (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 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; 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 *ATT*, but also the *Spirillaceae* tribe *LF* bacteria oxidising Fe^{2+} in ultra acidic environment. *Acidithiobacillus ferrooxidans* species are gram-negative 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+} -sulphides. 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, reactions with CO_2 are 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 complete 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 resulting in the transport of electrons from the sulphide mineral forming anode to the electrochemically less electro-active mineral. According to Crundwell (1989) and Silva (2003), it is possible to interpret this effect as a modification of the semiconductive properties of sulphide minerals accompanied by the tiny changes in the structure and physical properties such as reflection, microhardness, conductivity, etc.

Materials and methods

The AMD waters (samples P-1, P-2, P-3 and P-4; fig. 1) were analysed by atomic absorption analysis for Fe, Mn, As, Cu, Ni, Pb, Sb and Zn. Two types of leaching experiments were carried out to study the mobility of previously mentioned metals from the tailing impoundment sediments:

1. During the first experiment, the samples of tailing impoundment sediment were introduced to the solution containing *ATF* bacteria isolated from the mine waters from the 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.

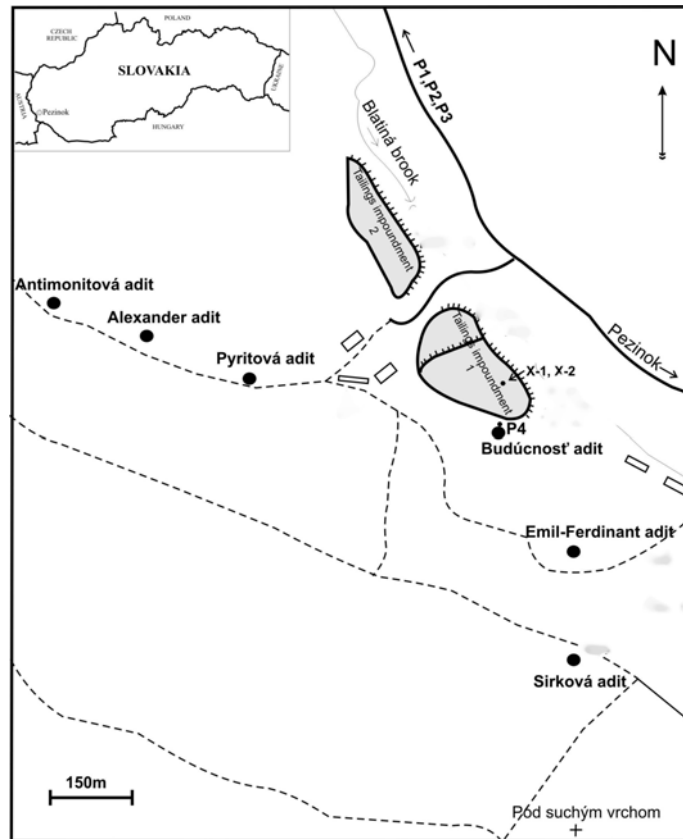


Fig. 1 Sketch of the studied area of the setting pits at the Pezinok deposit with localisation of the samples of water (P1 - P4) and sediments (X-1, X-2)

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 (fig. 1) from the tailings impoundments and the AMD of various pH and origin were analysed by atom absorption analyse.

Results

The selected sample of the sediment X-1, the ochre sample X-2 from the tailings impoundments and the natural drainage waters of various pH and origin were analysed by atom absorption analyse. The research proved that both the sediments of the tailing impoundments and the secondary ochres are very rich in content of selected metal elements: As, Cd, Cu, Co, Fe, Ni, Sb and Zn.

Sulphide minerals (mainly arsenopyrite, pyrite, less Sb-minerals) in the tailings impoundments are oxidized and the toxic elements (As, Sb, Cd etc.) are loosed to water solutions. The chemical composition of groundwater and surface water is influenced by mine water and by sludge water. They leak to the streams without any clearing and dressing. The metal content in the drainage waters depend preferentially on their origin and not on their pH. This part of our present research proved the data published by Kušnierová et al. (1994), Trtíková et al. (1998), Trtíková (1999), Andráš et al. (1994, 2004) and others. The acid drainage waters with pH <5 are rich in bacteria *Acidithiobacillus ferrooxidans* (ATF) and *Acidithiobacillus thiooxidans* (ATT) species. The activity of the bacteria in drainage waters of pH 4.5 to 7 is very low.

For the first experiment, drainage mine water P 1 from Pezinok with autochthonous microorganisms – sulphur and iron oxidizing bacteria *Acidithiobacillus ferrooxidans* (ATF) and *Acidithiobacillus thiooxidans* (ATT) was used. Presence of other species was not verified. The pH of the water was 4.5. The second sample of mine water used for the experiments was a mine drainage water from Pezinok P 3 without bacteria (pH = 6.45). During the study of catalytic influences, parallel experiments with rainwater were carried out for comparison. The results show no important differences of leaching activity between the bacteria species containing liquid phase and those without bacteria, but there was a great difference between the two natural drainage waters and the rainwater. We assume that as the pH of the bacteria containing drainage water was above 4, the activity of the bacteria was very low (the highest activity of bacteria is in media with pH <3), causing the comparable results with the drainage water without bacteria.

The second experiment was conducted using nutrient medium sensu Silverman and Lundgren (1959) 9K with bacteria and without bacteria (abiotic control). To study of the biogenic catalysis influence in oxidation processes of weathering at the tailings impoundments, pure culture of autochthonous bacteria *Acidithiobacillus ferrooxidans* (ATF) isolated from mine drainage water P 4 from the Pernek deposit was used. Bacteria were dispersed in the nutrient medium. The pH was 1.5 at the following conditions: P:K=1:3, temperature 30° C, aeration by mixing in laboratory whisk device during 4 weeks. The leaching of the X-1 sediment sample and of the heavy fraction of this sample by bacteria containing media was compared with the results of the X-1 sample leaching by nutrient medium without media. The leaching continuance was studied by monitoring the selected elements (As, Cu, Co, Fe, Ni and Sb), and the experiment was interrupted after 4 weeks to segregate the product of precipitated secondary salts and Fe ochres created by biological-chemical transformation. Together with the liquid phase, the products were analysed using X-Ray diffraction analysis which proved the origination of the secondary minerals jarosite, hydrojarosite and gypsum, as well as the presence of quartz, muscovite, phlogopite, chlorite and clinocllore.

The investigated sample of the sediment from tailing impoundments X-1 used for the folowing experiments was analyzed by the atom absorption analysis (Tab. 1).

AAS ANALYSIS OF THE CHEMICAL COMPOSITION OF SEDIMENT SAMPLE FROM TAILING IMPOUNDMENTS

Table 1

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-2	1.67	1 014	2.57	0.090	0.48	0.02	0.05	196.1	0.52

The X-1 sediment sample from the tailing impoundments was employed in experimental work for the investigation of the leaching process by using both types of drainage waters: acidic and neutral.

The acidic as well as the neutral drainage 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 a sample of water from the wider mining ore field (P 1) (Tab. 2).

CHARACTERISTIC OF ACID MINE WATERS FROM PEZINOK MINING AREA. INCLUDING pH, CONTENT OF INVESTIGATED ELEMENTS AND PRESENCE OF ACIDOPHILOUS BACTERIA. 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, ATF – *Acidithiobacillus ferrooxidans*, ATT – *A. thiooxidans*

Table 2

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	-	-

The leaching activity in dependence on the leaching medium is presented in Tab. 3. For this experiment, drainage water P 2 from Pezinok with autochthonous bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* was used. Presence of other species was not verified. 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, parallel experiments with rainwater were carried out for comparison.

AAS ANALYSIS OF VARIOUS LIQUID MEDIA OF DIFFERENT pH AND RAINWATER USED FOR LEACHING OF THE SEDIMENTS FROM THE TAILING IMPOUNDMENTS.

ATF - *Acidithiobacillus ferrooxidans*, *ATT* - *Acidithiobacillus thiooxidans*

Table 3

Medium	Time of leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
Drainage water P 2	I	17.8	<0.06	0	213.7	2.7	8.0
	II	16.5	<0.06	0	253.4	5.3	8.8
<i>ATF+ATT</i> pH = 4.5	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 natural drainage waters 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), causing the comparable results with the results of drainage water without bacteria.

The next experiment was conducted 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, pure culture of autochthonous bacteria *A. ferrooxidans* and *A. thiooxidans* isolated from the drainage water P 1 at the Pernek deposit was used. 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).

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)

Table 4

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

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.

The results presented in the Tab. 4 show, that in strongly acidic medium (pH=1.57) *bacteria A. ferrooxidans* are active, vigorously assisting the oxidation of sulphides. Extraction rate of Fe, As and Sb is the highest in the first week of leaching. As it could be expected, concentration of metal cations in the leaching product is the 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.

Discussion

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

- the first type → extremely acid (pH < 3) mine waters associated with synsedimentary massive pyrite-pyrotine ores,
- the 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 the acid mine drainage is much higher. It is the neutral waters that percolate 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-mineralised parts (Augustín 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 conducted 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.

Conclusion

The control of acidity is of utmost importance in leaching, since the 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 sulphides, 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 comparison of biological-chemical oxidation with chemical oxidation enabled to find the differences in the leaching mechanism. The activity of *ATF* bacteria considerably 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.

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