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# Mineralia Slovaca

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**Institute of Geotechnics of Slovak Academy of Sciences, Košice, Slovakia**

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  - physical, used for mineral processing of secondary raw materials
  - mechanochemical, used namely for modifying the reactivity and synthesis of solid materials
- working environment, which investigates the aerosols produced by mining and metallurgy industries

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  - biotechnologické metódy, so zameraním na likvidáciu odpadov
  - fyzikálne metódy zamerané na úpravu druhotných nerastných surovín
  - mechanochemické metódy so zameraním na modifikáciu reaktivity a fyzikálnych vlastností tuhých látok
- životného prostredia, ktorá skúma aerosoly produkované banským a metalurgickým priemyslom

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**The Faculty of Metallurgy of the Technical University in Košice** offers education in nine main disciplines:

- Metallurgy of Iron and Steel
- Foundry
- Material Engineering
- Technology of Ceramic Materials
- Gas manufacture and Transport
- Metallurgy of Non-Ferrous Metals
- Thermal Energetic
- Metals Forming
- Economy and Management in Industry

In these disciplines the students study over a period of five years the main features of development of science and technology.
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- Physical Metallurgy, materials and their Limit States
- Therma Energetics
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- Tepelná energetika
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This extraordinary issue presents the proceedings of the International Conference

# BIOHYDROMETALLURGY
## IV.

held in Košice, Slovakia, on October 23-24, 1996, organized by
Institute of Geotechnics of the Slovak Academy of Sciences in Košice
Faculty of Metallurgy, Technical University in Košice
and Slovak Mining and Metallurgy Society

Toto mimoriadne vydanie je venované medzinárodnej konferencii

# BIOHYDROMETALURGIA
## IV.

konanej v dňoch 23. - 24. októbra 1996 v Košiciach, organizovanej
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## GeOvestník

COVER: Collage photo of polysulphidic ore. Upper left in the electron microphotograph - surface of galena before bacterial leaching, in the middle down - the same after bacterial leaching.

OBÁLKA: Koláž snímky polysulfidickej rudy s mikrosnímkami povrchu galenitu: Vľavo hore - pred bakteriálnym lúhovaním, v strede dole - po bakteriálnom lúhovaní.

*Mineralia Slovaca, 28 (1996), 313 - 317*

# Bio-recycle metallurgy by utilization of algae

AKIRA YAZAWA[1] and TAKAO KUWABARA[2]

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## Abstract

To conserve global environment, bio-recycle metallurgy is proposed for absorption of $CO_2$, regeneration of energy and recovery of metal from lean resources. Recycling of $CO_2$ as fuel is not feasible economically, but it would be reasonable if some biomass can serve as media of metallurgical separation as well as fuel. By use of algae, a part of traditional metallurgy may be replaced by bio-recycle metallurgy. The biosorption of metals by algae is discussed and based on the experimental results. Various applicabilities are suggested for metal extraction and waste water treatment.

**Key words:** algae, biosorption, bio-recycling, metal, ion exchange

## Využitie chalúh v biorecyklačnej metalurgii

Na uchovanie globálneho životného prostredia sú navrhnuté biorecyklačné metalurgické procesy na absorpciu $CO_2$, regeneráciu energie a získanie kovov z chudobných zdrojov. Recyklovanie $CO_2$ na palivo nie je ekonomicky výhodné, ale je možné použiť biomasu ako prostriedok na metalurgickú separáciu aj ako palivo. Použitím chalúh môže byť časť tradičnej metalurgie nahradená biorecyklačnou metalurgiou. Na základe experimentálnych výsledkov je diskutovaná biosorpcia kovov chaluhami a sú navrhnuté rôzne aplikácie na extrakciu kovov a spracovanie odpadových vôd.

## Introduction

In conventional extractive metallurgy, the main route has been the reduction of metal from high grade ore or concentrate spending much fossil fuel, and producting a large amount of wastes. As the results, both resources of mineral and fuel tend to be exhausting, and we are troubled by serious environmental problems. Accordingly, today, prospecting next century, it may be necessary to reconstruct the conventional smelting into a new process more tender for the earth by reviewing the process widely from the point of bio-cycling which has the possibilities of absorbing the wastes and regenerating resources of energy and metal values.

The decrease in atmospheric $CO_2$ content is considered to be the most urgent but difficult problem for today's global environment. The world total $CO_2$ emission accompanied by human activities amounts to 23 billion tons a year (Yazawa, 1994), and around 10 % of this $CO_2$ may be attributed to the industry of primary metal production. As shown in Fig. 1, bio-recycling of $CO_2$ into biomass is the most desirable route, and there are many proposals to accelerate the process. Although this step itself is not the purpose for discussion in the presented paper, $CO_2$ will immediately return again into atmosphere if the produced biomass is used as fuel directly. Accordingly, it is desirable that the produced biomass is supplied first to some useful purpose before combustion, and the utilization of alcohol or algae for separation and concentration of metals has been investigated by the authors.

As a typical example of bio-metallurgy, bacteria leaching has been well known since more than thirty years ago, and recently applied widely not only in the extraction of copper, uranium, gold and silver, but also in various waste water treatment. However, because so many excellent reports are available (Brierley, 1990; Torma et al., 1993), the bacteria metallurgy will not be discussed in this paper.

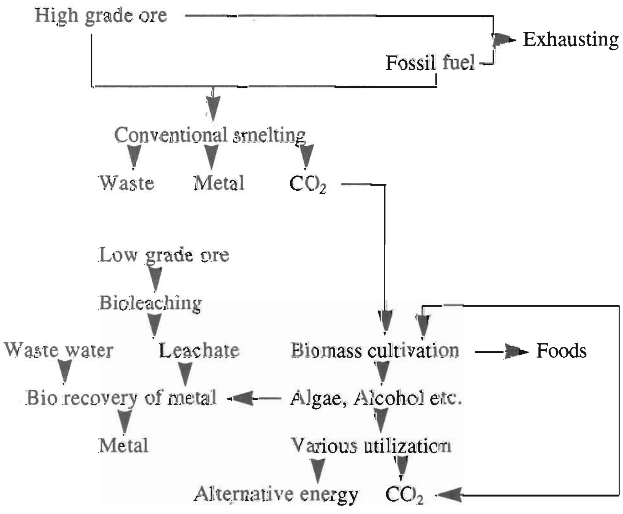

Fig. 1. Conventional smelting and bio-recycle metallurgy.

## Utilization of Algae

### *Adsorption of metal with biomass*

It has been known that living bodies adsorb and accumulate certain kind of metal, such as the examples of zinc in shell fish and copper in crustacea. Among many research data concerning the environmental problems in 1970's, after 1980, specific species of fungi and algae were found to adsorb unexpectedly large amount of metal as shown examples in Tab. 1 (Crist et al., 1981; Strandverg et al., 1981; Tsezos and Volesky, 1982; Darnall et al., 1987; Kuyucak and Volesky, 1988; Majidi and Holcombe, 1989; Kuwabara et al., 1989; Fujita et al., 1992), and especially during recent several years, the application of this adsorption technique has attracted attention in the fields of metal extraction and water treatment. This phenomenon is called biosorption, the biomass bodies biosorbents, and the relating research reports about adsorption with biomass are more and more increasing recently (Volesky, 1990; Smith and Misra, 1991; Torma et al., 1993). This subject is also very interesting from the viewpoint of biomass environment related $CO_2$ problems, therefore, the authors are also accumulating the data on biosorption of various metals with algae (Kuwabara et al., 1989; Kuwabara and Yazawa, 1993; Kuwabara and Yazawa, 1993; Kuwabara et al., 1994).

It is surprising from Tab. 1 that the adsorption of metals amounts from 10 to 70 percent of the weight of dried biomass itself. Moreover, as suggested in Fig. 2 (Kuwabara et al., 1989), it is revealed that the adsorption reaction is quite rapid and complete if the combination between metal and biomass is agreeable. Adsorption of gold by chlorella may be realized in a few minutes, and even from dilute solution of 0.1 ppm Au.

Living biomass was used in the research of earlier stages, but the maintenance of the living biosorbent was not so easy, and mechanical handling of biosorbent such as fixation in the reactor or solid-liquid separation was inconvenient for industrial application. However, it has been found that adsorption capacity of dead cells is sufficiently great, and various techniques such as pulverizing, mixing, fluidizing, encapsulating, etc. are found to be applicable for non-living sorbent preparation. The authors (Kuwabara et al., 1994) confirmed high efficient adsorption and solid-liquid separation by high temperature autoclave treatment of algae, and many researchers (Torma et al., 1993) have recognized that immobilizing non-living biosorbent into a granular or porous polymeric matrix would be hopeful to be used in practice.

Tab. 1
Examples of experimental results of adsorption of metals by algae and fungi

| Adsorbent | Metal | Uptake (mg/g) | Year | Ref. |
|---|---|---|---|---|
| Vaucheria | Cu | 33 | 1981 | 1 |
| Yeast, Pseudomonas aeruginosa | U | 100 - 150 | 1981 | 2 |
| Rhizopus arrhizus | U, Th | 180, 170 | 81, 82 | 3 |
| Chlorella, Green algae | Au | 100 | 1986 | 4 |
| Green, Red, Brown algae | Au, Co | 420, 30 - 180 | 86, 88 | 5 |
| Diatom | Cd | 720 | 1989 | 6 |
| Chlorella, Marine algae | Au, Ag, Co | ca.100 | 1989 | 7 |
| Blue-green algae | Au | 300 | 1992 | 8 |

1 - Crist et al., 2 - Strandverg et al., 3 - Tsezos and Volesky, 4 - Darnall et al., 5 - Kuyucak and Volesky, 6 - Majidi and Holcombe, 7 - Kuwabara et al., 8 - Fujita et al.

### *Metal adsorption with algae by ion exchange reactions*

The mechanism of biosorption is not necessarily simple, but anion or cation exchange reaction must be the most fundamental. Many experimental results of biosorption are conveniently explained by ion exchange reactions as illustrated in Fig. 3 and 4 measured by the authors. Anions such as $AuCl_4^-$, $PtCl_4^{2-}$, $PdCl_4^{2-}$ and $AsO_4^{3-}$ are adsorbed according to anion exchange reaction, and the

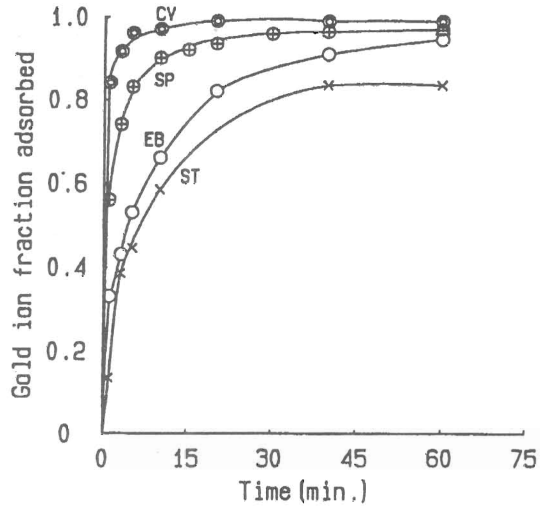

Fig. 2. Adsorption of gold using different algae as a function of contact time. Initial Au concentration, $C_i$: 12 mg/l, pH: 2, sorbent: 3 g/l, CV: *chlorella* sp., SP: *spirulina* sp., EB: *eisenia byciclis*, ST: *sargassum thumbergii.*

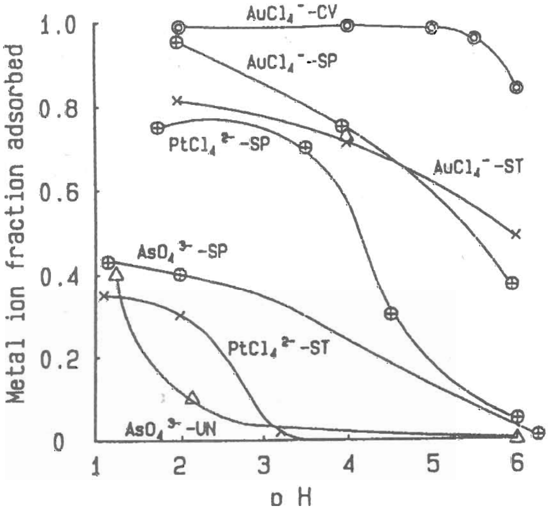

Fig. 3. Adsorption of metal anions by various algae as a function of pH. $C_i$: 12 mg/l, sorbent: 3 g/l, contact time: 1 h. UN: *undaria pinnatifida,* Other algae: see Fig. 2.

metal fraction adsorbed becomes larger when pH becomes low. It is quite attractive that chlorella and spirulina seems to be good adsorbents for the anions of precious metals. In a photomicrograph of chlorella or spirulina after adsorption experiment of gold, a lot of lustrous gold particles were observed. Accordingly, it is estimated that at least a part of gold adsorbed from chloroauric acid aqueous solution is reduced in the form of metal within the body of spirulina.

The adsorption behaviour of almost all cations such as $Cu^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Ni^{2+}$ are attributed to cation exchange reaction, and as shown in Fig. 4, the metal fraction adsorbed becomes small when pH becomes low. Spirulina or chlorella is not necessarily good cation adsorbent, while brown algae such as ST or UN represent much higher adsorption for cations. Each alga seems to have both functions of anion and cation exchanges, but the ability of adsorption is different greatly depending on the kinds of alga and metal, therefore, it is very important to find the optimum combination and conditions.

Elution process is usually based on the reverse reaction of adsorption process, and elution of cations such as cobalt is basically realized by lowering the pH. However, gold ion adsorbed by algae could not return to the aqueous solution by simple pH control, and it was necessary to add sulphur-containing elution agent such as 2-mercaptoethanol or thiourea, probably because the gold adsorbed by algae is converted in the form of metal. It was demonstrated (Darnall et al., 1987) that after adsorbing several kinds of metals from a mixed solution, selective elution process is conveniently applied to obtain each metal solution separately.

Tab. 2
Degree of concentration of metal in algae from marine water
(ppm in living algae/ppm in marine water)

| Ca | K | Mg | Na | Si | P | Al | Fe | Zn | Mn | Cu | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 8 | 2 | 0.2 | 580 | 3800 | 18 000 | 15 000 | 3800 | 12 000 | 1200 | 350 |

Marine algae are known as healthy foods because of high contents of mineral, and the authors estimate that the reason is ascribable to biosorption. In Tab. 2 (Nishizawa, 1993), the degrees of concentration of metals in algae are summarized against metal contents in marine water. Taking into account the pH value of marine water, it is natural that biosorption of heavy metal cations must be easy. Fortunately for us, the degrees of concentration are not so high for Na, K, Mg and Ca, but unfortunately, pH of marine water is not convenient for biosorption of gold or uranium.

### *Metal adsorption with algae by other reactions*

Fig. 5 shows the adsorption behaviour of samarium with various species of algae (Kuwabara and Yazawa, 1993). The adsorption of samarium with chlorella or spirulina is quite different from the other species of algae, represents the maximum peak at pH between 3 and 4.5, and thus, the adsorption mechanism seems to be different from plain ion exchange reaction. The adsorption curves shown in Fig. 6 were obtained by use of the blue pigment which was prepared from spirulina through water leaching and lyophylizing, while, the curves in Fig. 7 suggesting the cation exchange reaction were obtained by leaching residue of this spirulina. The main component of this blue pigment is phycocycyanin representing strong trends to combine with rare earth elements.

As suggested by this example, biosorption is consisting of duplicating reactions such as ion exchange, complex formation, oxidation-reduction, etc. This may be the reason why algae sometimes represent superior adsorption ability to ion exchange resin, and suggesting that the establishment of much excellent separation process is hopeful through the elucidation of the process of biosorption.

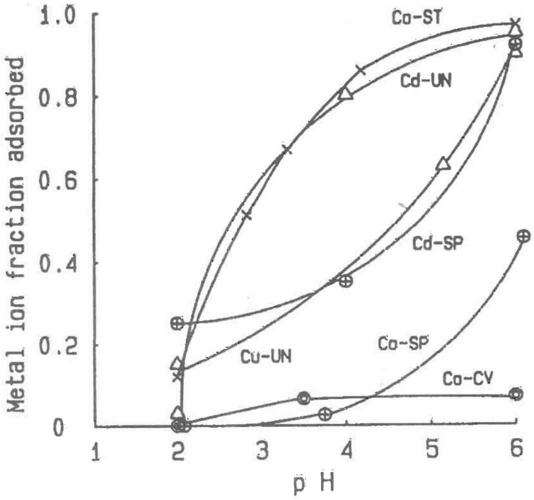

Fig. 4. Adsorption of metal cations by various algae as a function of pH. Conditions: see Fig. 3.

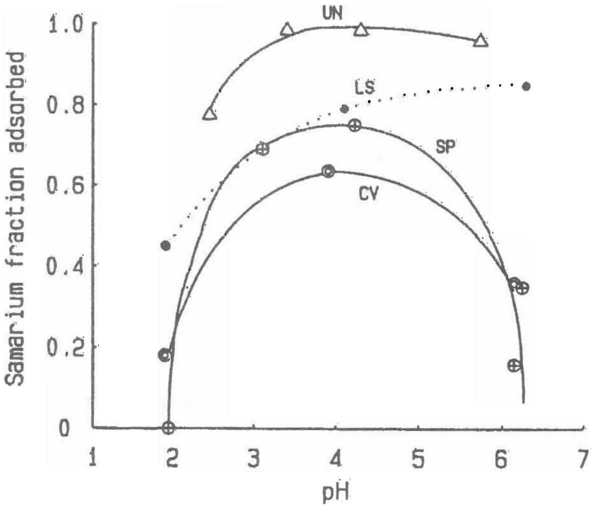

Fig. 5. Effect of pH on adsorption of samarium with different sorbent. $C_i$: 12 mg/l, pH: 2, sorbent: 3 g/l. LS: Laminaria species, Other algae: see Fig. 2 and 3.

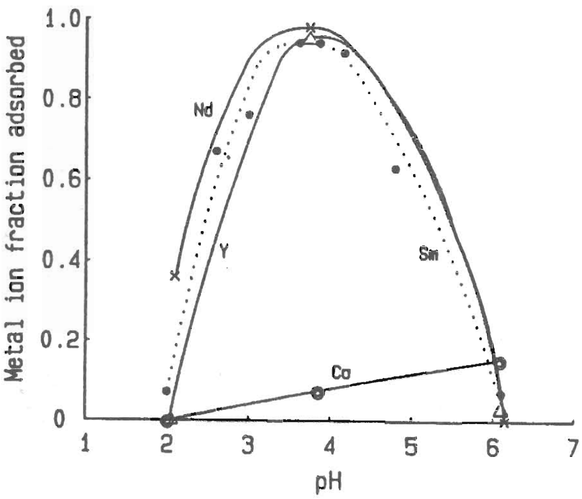

Fig. 6. Adsorption of Sm, Nd, Y and Co by SP-blue (spirulina pigment) as a function of pH. $C_i$: 12 mg/l, sorbent: 3 g/l, contact time: 1 h.

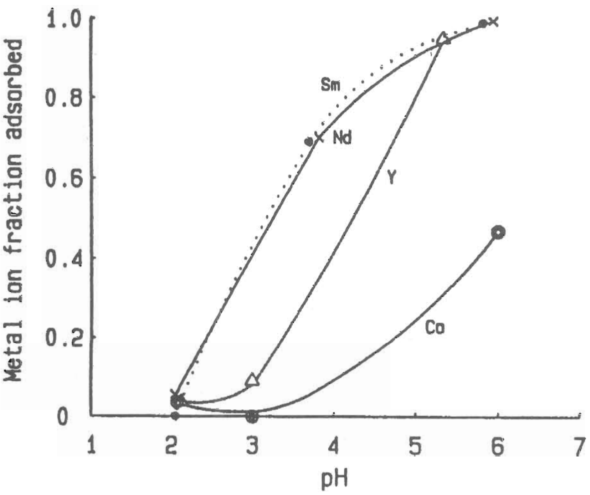

Fig. 7. Adsorption of Sm, Nd, Y and Co by SP-residue as a function of pH. Conditions: see Fig. 6.

Tab. 3
Examples of mineral contents in algae (ppm in wet algae)

| Algae | K | Ca | Ti | Mn | Fe | Cu | Zn | Pb | Hg | As | Br | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Ulva* sp. | 5815 | 557 | 8.7 | 1.6 | 156 | 1.6 | 17 | 0.58 | 0.29 | 1.9 | 68 | - |
| *Hijika fusihorme* | 2276 | 591 | 3.4 | 3.8 | 7 | 0.2 | 4 | 0.64 | 0.08 | 20.9 | 29 | 33 |
| *Eisenia bicyclis* | 889 | 641 | 0.1 | 0.4 | 7 | 2.8 | 7 | 0.03 | 0.06 | 1.6 | 42 | 105 |
| *Chondrus ocellatus* | 2483 | 1745 | 23.9 | 16.6 | 36 | 1.6 | 28 | 1.58 | 0.16 | 97.3 | 72 | 43 |

Biosorption is interesting not only in the metal recovery but also in the waste water treatment. Through inspection of the analytical data of marine algae of which examples are shown in Tab. 3 (Nishizawa, 1993), the author have great interest in the possibility of removal of arsenic by biosorption in non-toxic state. *Hijika* and *Chondrus* are well known as healthy foods disregarding the high contents of arsenic, but it is said that arsenic is mostly in organic form in algae and not toxic. It must be great help for global environment if arsenic is fixed in non-toxic discardable form, and it is suggested (Mann, 1990) that biomethylation seems to be a mechanism of arsenic detoxification.

### *Improvements of bioadsorbents by preliminary treatments*

As descrived above, algae are quite interesting adsorbents for metal ion recovery, but have some deficiencies for practical usage such as difficulty in solid-liquid separation and bulky body of the adsorbent. There are some proposals for improving the immobilization and handling of the biosorbents (Torma et al., 1993), and the similar trials have been carried out also by the present authors.

Adsorbing capacity of algae for gold ion is largely improved by pretreating the algae by hot water leaching in an autoclave (Kuwabara et al., 1994) as illustrated in Tab. 4. This pretreatment is especially efficient for brown algae such as UN or LS than chlorella CV or spirulina SP. Through this pretreatment, soluble substances are removed by hot water, and the obtained algae decrease their apparent density and represent high filterability. The increased adsorbing capacity of gold on algae is convenient because the adsorbed gold may be treated directly by pyrometallurgical way to charge in the smelting furnace.

As shown in Fig. 4, brown algae such as Undaria (UN) or Laminaria (LS) are convenient to recover cation metals such as Cu, Ni, Co or Cd from neutral pH aqueous solution. However, these algae have a deficiency as the industrial adsorbents because the surface of their bodies become very viscous in the neutral aqueous solution. Thus, liquid-solid separation is difficult, and when they are packed in the column, aqueous solution hardly flow through the column. Use of some additions for coagulation, or encapsulating by polymer has been proposed (Torma et al., 1993), but careful considerations must be paid to the environmental influence and the cost performance.

Tab. 4
Improvements of gold ion adsorbing capacity by autoclave pretreatment (mg Au/g)

| Algae | Untreated | Treatment temperature (°C) | | | |
|---|---|---|---|---|---|
| | | 100 | 125 | 150 | 200 |
| *Undaria pinnatifida* UN | 57 | 132 | 134 | 150 | 150 |
| *Laminaria* sp. LS | 40 | - | - | 90 | 90 |
| *Eisenia byciclis* EB | 37 | - | - | 145 | 145 |
| *Entermorpha linza* EL | 38 | - | - | 100 | 100 |

Alginate is originally contained in most algae especially in brown algae. Alginate easily coagulates when it is contacted to bivalent metal salt aqueous solution such as sulphate or chloride. The authors chose $CaCl_2$ aqueous solution because it has good coagulation effect, little interference against other substances, and is cheap and harmless. To UN or LS dried powder, sodium alginate powder is added at amount of 5 to 20 %, and by adding small amount of water, the mixture is brought into pasty state. This algae-alginate paste is extruded into the 5 to 10 % $CaCl_2$ aqueous solution through syringe, and coagulates in the form of noodles. The column packed by the obtained noodle form adsorbents has little resistance for flowing aqueous solution because the adsorbents do not have viscous layer on their surfaces.

## Concluding Remarks

Bio-recycle metallurgy is aiming at absorption of $CO_2$, regeneration of energy, and recovery of metal from low grade resources, and intending to conserve global environment, mineral and fuel resources. Utilizations of algae is hopeful route, but there remain many problems to be investigated. In early 2000, we will be troubled much more seriously by various environmental destructions and scarcity of resources, and restructuring of extractive metallurgy is urgent during this ten years under suitable combination with biological techniques.

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# Biological treatment of acid drainage waters from a copper mine

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### Abstract

Acid mine drainage waters containing copper, arsenic and sulphates as contaminants were treated under laboratory conditions by means of alkalinity-producing and sulphate-reducing anaerobic cells. The cells contained organic substrate mixed with ground limestone and consortia of interdependent anaerobic microorganisms. The sulphate-reducing bacteria were the prevalent microorganisms in these consortia. Under conditions of efficient microbial growth and activity, the heavy metal removal from the waters being treated was practically complete and only concentrations of parts per billion remained in the anaerobic cells effluents. The active microbial sludge blanket in the cells remained stable for a long period of operation (months and years), provided the feed composition and cell conditions were maintained relatively constant during the whole period.

**Key words:** acid mine drainage, waste water treatment, passive treatment systems, sulphate- reducing bacteria, heavy metals

### Biologická úprava odpadovej vody z medenej bane

V laboratórnych podmienkach sa použili na úpravu odpadovej vody znečistenej Cu, As a síranmi baktérie produkujúce alkalické zlúčeniny a redukujúce sulfát. Bunky boli rozptýlené v organickom substráte v zmesi s rozotretým vápencom. V substráte boli obsiahnuté aj symbiotické anaerobné mikroorganizmy. Baktérie redukujúce sulfát boli v majoritnom zastúpení. V optimálnych podmienkach pre rast a aktivitu mikroorganizmov došlo takmer k úplnému odstráneniu ťažkých kovov z média. Zostatkové koncentrácie mali hodnoty ppm. Biologický film (na povrchu aktívneho kalu) bol stabilný dlhú dobu (mesiace až roky). Počas pokusu sa udržiavali konštantné podmienky prostredia a konštantný bol aj prísun živín.

## Introduction

The acid mine drainage is considered to be the major environmental problem associated with mining activities. This phenomenon is connected with the oxidation of pyrite and other sulphide minerals as a result of which acidic waters containing sulphuric acid, dissolved heavy metals and solid iron precipitates are released to the environment. The mine drainage quality depends on a number of factors such as the rate of acid generation and heavy metals leaching from the sulphide minerals during their oxidation, solubility and accumulation of relevant oxidation products, precipitation and/or neutralization reactions along water flowpath, etc.

Several methods for treatment of acid mine waters exist, depending upon the volume of the effluents, the type and concentration of contaminants present. The most largely used method is connected with the chemical neutralization of waters followed by the precipitation of metals. Such active treatment requires the installation of a plant with agitated reactors, precipitators, clarifiers and thickeners with high costs for reagents, operation, maintenance and disposal of resulting metals laden sludge. The only alternative of such high-cost schemes are the passive treatment systems. These systems have been developed on the basis of naturally occurring biological and geochemical processes in order to improve the quality of the influent waters with minimal operation and maintenance costs. Initially the passive treatment was connected with the constructed wetlands (Hammer, 1990) which are very similar to the natural marshes and wetlands. However, it has been shown that they are only able to polish relatively innocuous waters and are unable to cope with high acidity and high metal content.

Recently a different approach to the passive treatment systems has been undertaken. This approach consists in the engineering of different low-maintenance biological systems which can be used in various combinations (Wildeman, Brodie and Gusek, 1993; Hedin, Nairn and Kleinmann, 1994; Cambridge, 1995; Gusek and Wildeman, 1995; Garea, Adam and Kontopoulos, 1995). As a result of this approach, a wide range of passive treatment systems is available currently. The main advantage of these systems over chemical neutralization is that large volumes of sludge are not generated, the metals being precipitated as oxides or sulphides in the different components of the systems.

Very efficient for the treatment of net acidic mine waters (with pH lower than 4.5) containing high levels of dissolved oxygen, $Fe^{3+}$ and/or Al as well as different toxic metals are the anaerobic organic substrate systems. In these systems the heavy metals are removed as a result of the activity sulphate reducing bacteria. These bacteria require a rich organic substrate as a source of carbon and energy for their growth. The electrons removed from the organic substrate are transferred to the sulphate ions which are reduced to free hydrogen sulphide. Alkalinity is also produced as a result of this process (reaction 1) :

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad (1)$$

The in situ generation of hydrogen sulphide is connected with concomitant precipitation of heavy metals as highly insoluble sulphides ( reaction 2):

$$M^{2+} + S^{2-} \rightarrow MS \qquad (2)$$

where M represents a divalent metal ion such as $Cu^{2+}$, $Zn^{2+}$, etc.

The overall reaction can be represented in the following way (reaction 3):

$$\text{Metal sulphate} + \text{Carbon substrate} \rightarrow \text{Metal sulphide} + CO_2 + H_2O + \text{Bacterial biomass} \qquad (3)$$

The microbial sulphate reduction can be arrange in different ways in the varied passive treatment systems. It plays an important role in the constructed wetlands where occurs in the bottom zone. The emergent plants growing in these wetlands produce sufficient organic matter for the sulphate reducing bacteria. However, better results have been achieved by means of the so called anaerobic cells which de facto represent a simplified type of bioreactor containing a rich organic substrate and consortium of sulphate reducing bacteria. In this paper data about the treatment under laboratory conditions of acid drainage waters from an abandoned copper mine in Central Bulgaria by anaerobic cells are shown.

## Experimental procedures

The drainage waters discharged from the mine are highly acidic and their pH is in the range of 2.1-2.7. The waters contain copper and arsenic as main contaminants but sulphates are also present in concentrations much higher than those allowed by the Bulgarian legislation. The flowrate of these waters depends on the rainfall from surface drainage and varies from about 15 $m^3$ per day during dry periods to about 60 $m^3$ per day after heavy rainfall. The detailed geological, mineralogical, hydrogeological and microbiological investigations carried out in the mine and under laboratory conditions using samples of waters and ores from the mine revealed the fact that the discharge of contaminated waters will continue forever and the poor water quality will continue for foreseeable future. For that reason, it was decided to test the possibility for treatment of the discharged waters by means of a low-cost passive system.

The laboratory investigations in this respect were carried out by means of anaerobic cells for sulphate reduction. The cells were of the type of the simultaneous alkalinity-producing systems which combine the microbial sulphate reduction with a chemical production of alkalinity under anoxic conditions. Each cell represented 1000 mm high glass column with internal diameter of 200 mm. The both ends of the column were closed by glass covers possessing pipes with turn-cocks. The column was filled with organic substrate mixed with 10 % high-grade limestone ground to a particle size less than 2 mm. Different organic substrates such as spent mushroom compost, horse and caw manure, straw and sawdust were used for this purpose, either separately or in different combinations. The column was inoculated with sulphate reducing bacteria. Aged cow manure was found to be an excellent source of such bacteria.

Water from a sample collected from the mine was introduced into column through their top end and flowrate was adjusted to desired level by the turn-cock. The water percolated downwards through the mixture of organic substrate and limestone before to leave the columns. The total metal concentration in the waters treated in this way varied in the range from 0.2 to 2 g/l, and their pH varied from 2.1 to 2.7. The experiments were carried out at three different temperatures: 10, 20 and 30 °C.

Tab. 1
Microflora composition of an anaerobic cell with spent mushroom compost at 20 °C

| Microorganisms | CELLS/ML |
|---|---|
| Sulphate-reducing bacteria | $3.10^8$ |
| *Desulfobulbus (D. propionicus, D. elongatus)* | $1.10^8$ |
| *Desulfovibrio (D. vulgaris, D. desulfuricans, D. saprovorans)* | $5.10^7$ |
| *Desulfococcus (D. multivorans )* | $5.10^7$ |
| *Desulfotomaculum (D. nigrificans, D. orientis)* | $3.10^7$ |
| *Desulfobacterium (D. vacuolatum)* | $6.10^5$ |
| *Desulfosarcina (D. variabilis)* | $5.10^3$ |
| Anaerobic bacteria fermenting carbohydrates with gas production | $2.10^8$ |
| *Denitrifying bacteria* | $8.10^4$ |
| *Methane-producing bacteria* | $1.10^2$ |
| Heterotrophic bacteria related to other physiological groups | $6.10^5$ |

It was found that consortia of interdependent anaerobic microorganisms were established in the columns soon after their inoculation. However, usually about three months were needed for these consortia to reach their maximum sulphate-reducing activity and operate under true steady-state conditions. The species composition and the numbers of the different microorganisms in these consortia were different and depended on the type of the inoculum and the organic substrate as well as on some essential environmental factors such as pH, temperature and presence of nutrients during the cultivation. In all cases, however, the sulphate reducing bacteria were the prevalent microorganism in the consortia (Tab. 1). Most of these bacteria were firmly adhered to the sludge blanket where their number exceeded $10^8$ cells/g. The methane-produ-

Tab. 2
Removal of contaminants from acid drainage waters by means of anaerobic cells

| Water parameters | Before treatment | After treatment |
|---|---|---|
| Sample 1 (23.5 h residence time) | | |
| pH | 2.1 | 7.1 |
| Sulphate, mg/l | 3740 | 370 |
| Iron, mg/l | 1081 | 1.2 |
| Copper, mg/l | 74 | <0.05 |
| Arsenic, mg/l | 19 | <0.02 |
| Sample 2 (14.7 h residence time ) | | |
| pH | 2.3 | 7.3 |
| Sulphate, mg/l | 2637 | 284 |
| Iron, mg/l | 721 | 0.7 |
| Copper, mg/l | 55 | <0.05 |
| Arsenic, mg/l | 10 | <0.02 |
| Sample 3 (9.1 h residence time ) | | |
| pH | 2.7 | 7.5 |
| Sulphate, mg/l | 1755 | 212 |
| Iron, mg/l | 452 | 0.5 |
| Copper, mg/l | 23 | <0.05 |
| Arsenic, mg/l | 10 | <0.02 |

Note: All experiments were carried out at 20 °C.

cing bacteria were low in number since the redox potential was still high for these obligately anaerobic microorganisms.

It was found that a very efficient metal removal from the mine waters was achieved by means of the anaerobic cells. The microbial production of hydrogen sulphide and alkalinity was a function of the digestibility of the organic substrate. The spent mushroom compost was the most suitable substrate in this respect. The microbial activity was enhanced by changes of some essential nutrients such as ammonium and phosphate ions. Concentrations of these ions as high as 25 and 10 mg/l, respectively, were sufficient to maintain efficient microbial growth and sulphate reduction. The best results were achieved at a temperature of 30 °C but the process was efficient even at 10 °C. The temperature coefficient $Q_{10}$ in the range from 10 to 30 °C was about 1.7. The optimum pH for growth and activity of the sulphate reducing bacteria was about 7. However, it was not necessary to neutralize the feed before it entered the anaerobic cell since alkalinity was produced there as a result of the limestone solubilization and microbial sulphate reduction. The pH of the effluents from the cell was neutral or slightly alkaline.

The active microbial sludge blanket in the cell remained stable for a long period of operation (months and years), provided the feed composition and cell conditions were maintained relatively constant during the whole period. Under optimum conditions the maximum sulphate reduction rate achieved in this study was 320 mg/l. h. The heavy metals in the feed were not toxic for the microbial populations even at concentrations as high as 2 g/l. Under conditions of efficient microbial growth and activity, the heavy metal removal was practically complete and only concentrations of parts per billion remained in the cell effluents (Tab. 2).

The data from these experiments revealed that anaerobic cells of the type used in this study can be efficiently applied in commercial scale to treat acid mine drainage waters.

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# Biological decontamination of cyanide bearing wastewaters from a gold ore treatment plant

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### Abstract

A mining effluent from a cyanidation plant was biologically treated in fixed-bed reactors at laboratory scale. A mixed population, selected for its ability to degrade SCN, was used. Three materials were tested as supports for bacterial fixation: activated carbon, a combination of pumice-stone/zeolite, and pouzzolana. Thiocyanate was biologically decomposed into $NH_4$, $CO_2$, and $SO_4$ in all reactors. The cyanide forms were also eliminated, probably by the conjunction of physico-chemical and biological mechanisms. The flow-rate and the feeding concentration were progressively increased. Working conditions consistent with industrial data were achieved: feeding solution containing 900 $mg.l^{-1}$ SCN and 100 $mg.l^{-1}$ CN, residence time close to 0.1 day. The best results, in terms of resistance to changes in effluent composition and flow-rate, were obtained with the activated carbon bed. Complete conversion of $NH_4$ to $NO_3$ was only observed with activated carbon and diluted effluent. Accumulation of $NO_2$ was observed in pumice-stone/zeolite and pouzzolana reactors. The bacterial oxidation of $NH_4$ was inhibited by cyanide with all supports, at the highest flow-rates and cyanide concentrations.

**Key words:** fixed-bed reactor, thiocyanate, cyanide, biodegradation, activated carbon, pumice-stone, zeolite, pouzzolana, nitrification

### Biologická dekontaminácia odpadových vôd s obsahom kyanidu z podniku na spracovanie zlatonosnej rudy

Odpadovú vodu z kyanizačnej prevádzky sme podrobili biologickej úprave v laboratórnom reaktore s imobilizovanou vrstvou. Využili sme pritom zmesnú kultúru mikroorganizmov schopnú degradovať SCN. Ako nosiče na imobilizáciu biomasy sme použili tri materiály (každý v samostatnom reaktore), a to: aktivované uhlie, puzolan a zmes pemzy so zeolitom. Vo všetkých reaktoroch bol tiokyanatan degradovaný na $NH_4$, $CO_2$ a $SO_4$. Rovnako došlo (pravdepodobne na princípe kombinácie fyzikálno-chemických a biologických činiteľov) aj k eliminácií kyanidových aniónov. Prietok a koncentrácia zlúčenín v roztoku sa postupne zvyšovali, a to až po dosiahnutie priemyselných parametrov, ktoré mali nasledujúce hodnoty: 900 $mg.l^{-1}$ SCN, 100 $mg.l^{-1}$ CN. Doba zdržania pre jednotlivé reaktory dosahovala hodnotu približne 0,1 dňa. Najlepším nosičom rezistencie voči zmenám koncentrácií a prietoku je aktívne uhlie. Úplná premena alebo konverzia $NH_4$ na $NO_3$ sa pozorovala iba pri zriedení média a použití aktívneho uhlia ako nosiča. V reaktoroch s pemzozeolitovými a pouzzolanovými nosičmi bola pozorovaná akumulácia $NO_2$. Kyanidové ióny inhibovali bakteriálnu oxidáciu $NH_4$ najmä pri maximálnych hodnotách prietokov a koncentrácií.

## Introduction

Cyanide is a toxic compound found naturally in the environment and produced by human activities. It is generated by coal processing and gold and silver extraction. Various methods of chemically degrading and destroying cyanide, such as chemical oxidation by chlorine or hypochlorite, are currently used in wastewater treatment (Hoecker and Muir, 1987). These methods are expensive in reagent consumption, and somehow are inefficient in destroying some cyanide species. Microbiological treatment methods potentially offer the cheapest means of cyanide degradation (Whitlock and Mudder, 1985; Lien and Altringer, 1993). Microorganisms are known to possess various enzymes able to convert cyanide into naturally occurring compounds and sometimes to mineralization products (Ingvorsen et al., 1991; Stratford et al., 1994). Thiocyanate is degraded into sulphate, carbonate and ammonium under aerobic conditions. The ammonium produced as a by-product from cyanide oxidation must be detoxified. This is accomplished in the nitrification stage by means of aerobic autotrophic bacteria, *Nitrosomonas* and *Nitrobacter,* which convert ammonium in nitrate via nitrite (Whitlock and Mudder, 1985).

A research project involving three French institutes (INRA, BRGM, ADEME) started in June 1992 and ended in 1996. The final objective was to set up a biological process to degrade cyanide and thiocyanate from wastewaters. During the first step of this project, a microbial population has been selected and acclimated to degrade up to 200 mg $l^{-1}$ SCN (Boucabeille et al., 1994a, 1994b). The objective of the second step was to select an efficient process to biodegrade the pollutants. A comparison between agitated reactors and fixed bed reactors, which was performed by INRA, showed that the fixed culture was the most efficient. This result is in accordance with previous studies dealing with an higher efficiency of fixed bed reactors used in bioremediation of polluted waters (Zenon, 1985; Babu et al., 1992). From these results, an optimization of cyanide biodegradation using fixed bed columns was carried out by BRGM research team. Three microbial supports, namely Pumice stone - Zeolite (PPZ), Activated Carbon (CA) and Pouzzolana (P) were compared. Cyanide concentration, thiocyanate concentration, and residence time were the main parameters studied during this experimental program.

## Material and methods

Cyanide bearing wastewater composition: Wastewater from the mining site storage (Aude, France) contained 270 - 375 mg $l^{-1}$ of total cyanide and 800 - 1186 mg $l^{-1}$ of thiocyanate. It was previously chemically treated in order to oxidize the major part of free cyanide.

Microbial supports: All supports were sieved to 2.5 - 4 mm, washed and dried before use.

Medium composition: Industrial wastewater was diluted in tap water to give a final concentration in thiocyanate of 180, 400, 600 and 900 mg $l^{-1}$. Phosphorus at a concentration of 5 mg P $l^{-1}$ was added as $K_2HPO_4$ form.

Experimental procedure: Fixed bed reactor consisted of a plastic column of 121 cm, having an inner diameter of 5.7 cm. It is composed of 2 joint parts, a "mixing chamber" of 654 $cm^3$ at the bottom and a "reaction chamber" of 2169 $cm^3$ containing microbial support. The column was filled with the microbial support and loaded with two liters of microbial population taken from a 10 liter agitated bioreactor maintained continuously on the previous medium (180 mg $l^{-1}$ SCN). Immobilization of microorganisms was performed by recirculating the microbial culture in loop during 6 hours at a flow rate of 986 ml $h^{-1}$. Then the reactor was fed with fresh medium by an up-flow mode. The column was aerated with an air flow rate of 720 l $day^{-1}$ injected at the bottom. Experiments were carried out at ambiant room temperature. pH and potential Eh were daily checked, and pH was adjusted to a value comprised between 6.5 and 7.5 by sodium carbonate addition.

Sampling: 25 ml of effluent from the column outflow were sampled, 10 ml were brought to pH above 10 by sodium hydroxide addition for total and WAD cyanide determination, the remaining 15 ml were filtered at 0.45 μm, and analysed for ammonium, nitrate, nitrite and thiocyanate contents.

Analytical techniques: Thiocyanate was determined by colorimetric method (Standard Methods, 1985). Total and WAD (Weak Acid Dissociables) cyanides were analysed using ASTM procedures (ASTM, 1985). Ammonium and Nitrite were analysed by colorimetric methods according to AFNOR (NF T 90-012 and NF T 90-013). Nitrate and sulphate were analysed by ionic chromatography.

## Results and discussion

For an initial thiocyanate concentration of 180 mg $l^{-1}$, the feed flow rate was increased gradually in order to determine the maximum flow rate that can be applied without affecting the biodegradation level. The second objective was to reduce the dilution factor applied to the mining effluent: pollutants concentrations in the feeding were progressively increased.

### *Microbial support CA*

With a decrease in residence time from 6.56 days to 1.95 days, two main phenomena could be observed: no thiocyanate appeared in the effluent, and ammonium accumulated temporarily between 238 and 911 hours of feeding (Fig. 1a, b). The absence of thiocyanate in the outflow may be explained by an adsorption of the compounds on microbial support, or by their biodegradation. Adsorption isotherms of thiocyanate, carried out with activated carbon support, showed that SCN was adsorbed on CA. Then, in early stage of the experiment, the absence of thiocyanate could be related to its adsorption on the support. Nevertheless, biodegradation took place when the support was saturated, as confirmed by $NH_4$ production.

A change in the effluent (F to G), performed after one week of feeding with a synthetic medium, did not produce any effect. The column seemed to react satisfactorily with a residence time down to 0.03 day. After 3600 hours of feeding, thiocyanate concentration was successively increased from 180 mg $l^{-1}$ to 400 mg $l^{-1}$, 600 mg $l^{-1}$, and 900 mg $l^{-1}$. After each change in thiocyanate concentration, SCN was detected in the outflow during the first 24 hours. When the feeding SCN concentration was risen to 900 mg $l^{-1}$, the SCN peak in the outflow reached 750 mg $l^{-1}$. Then, SCN in the outflow disappeared. At this step of the experiment, the support was rinsed with tap water in order to remove the excess of biomass and precipitates. Consequently the feeding flow-rate of the reactor had to be reduced. Biological activity was rapidly restored in the column after this washing operation: free cyanide and thiocyanate were degraded. Nevertheless, some complexed cyanides were released in the outflow: some cyanide-containing precipitates were displaced from the support to the solution.

During the first stage, up to 1500 hours, $NH_4$ produced from SCN degradation was converted into $NO_2$ (750 - 1391 h), then $NO_2$ was transformed in $NO_3$ (1250 - 1500 h). So, nitrification process was efficient with a residence time of 0.5 day. At residence times lower than 0.4 day, the nitrification process was disrupted. An accumulation of

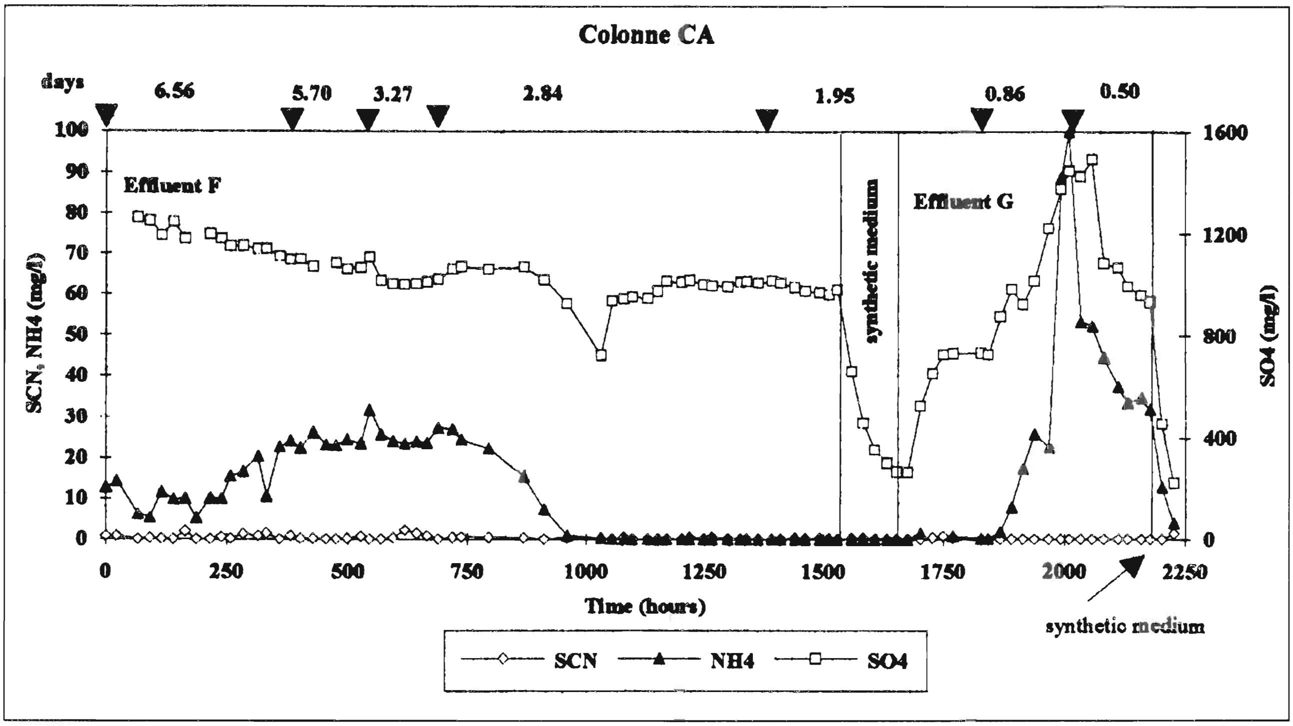

Fig. 1a. Activated carbon support. Evolution of thiocyanate concentration and its degradation by-products at decreasing residence times.

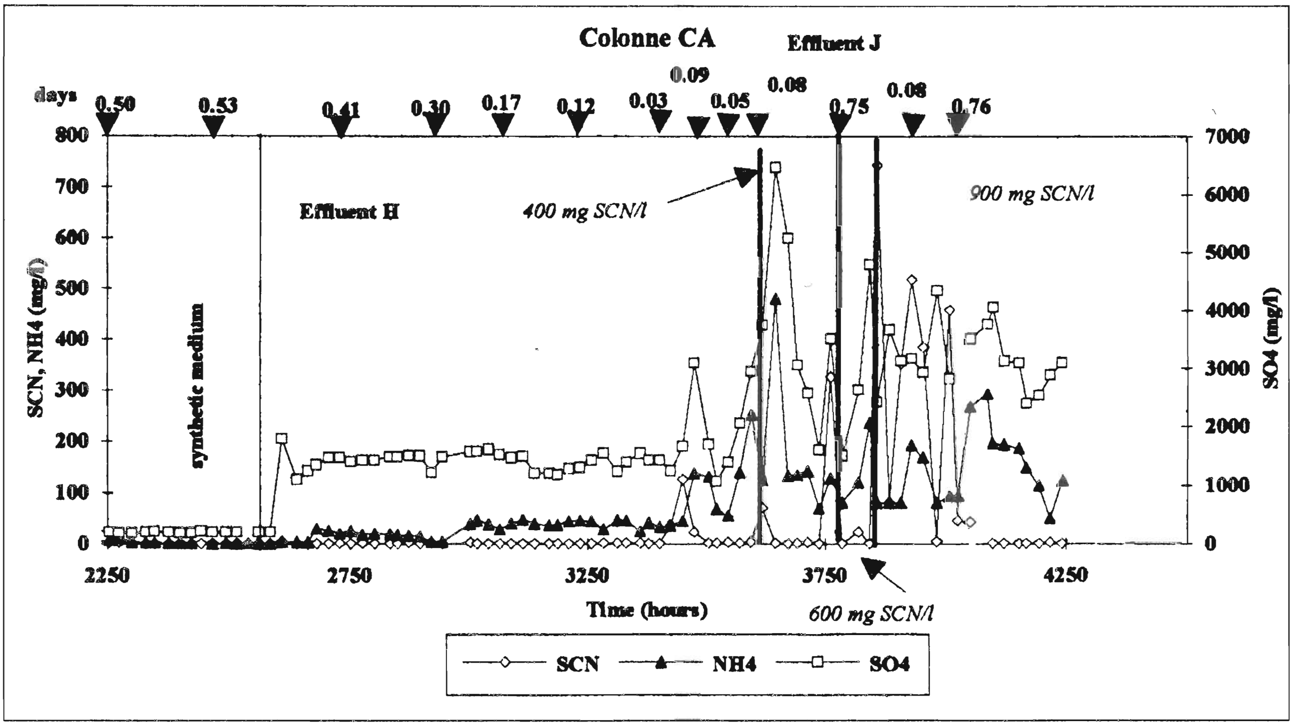

Fig. 1b. Activated carbon support. Evolution of thiocyanate concentration and its degradation by-products at decreasing residence times and increasing SCN feeding concentration.

$NH_4$ and $NO_2$ and nitrate was observed during the decrease in residence time down to 0.09 day, with an initial SCN concentration around 180 mg $l^{-1}$. This phenomenom could be explained by the slower activity of nitrifying bacteria compared to cyanide degrading microorganisms, and was in accordance with previous studies (Whitlock and Mudder, 1985). The increase in SCN concentration up to 900 mg $l^{-1}$ led to accumulation of $NH_4$. Nitrite and

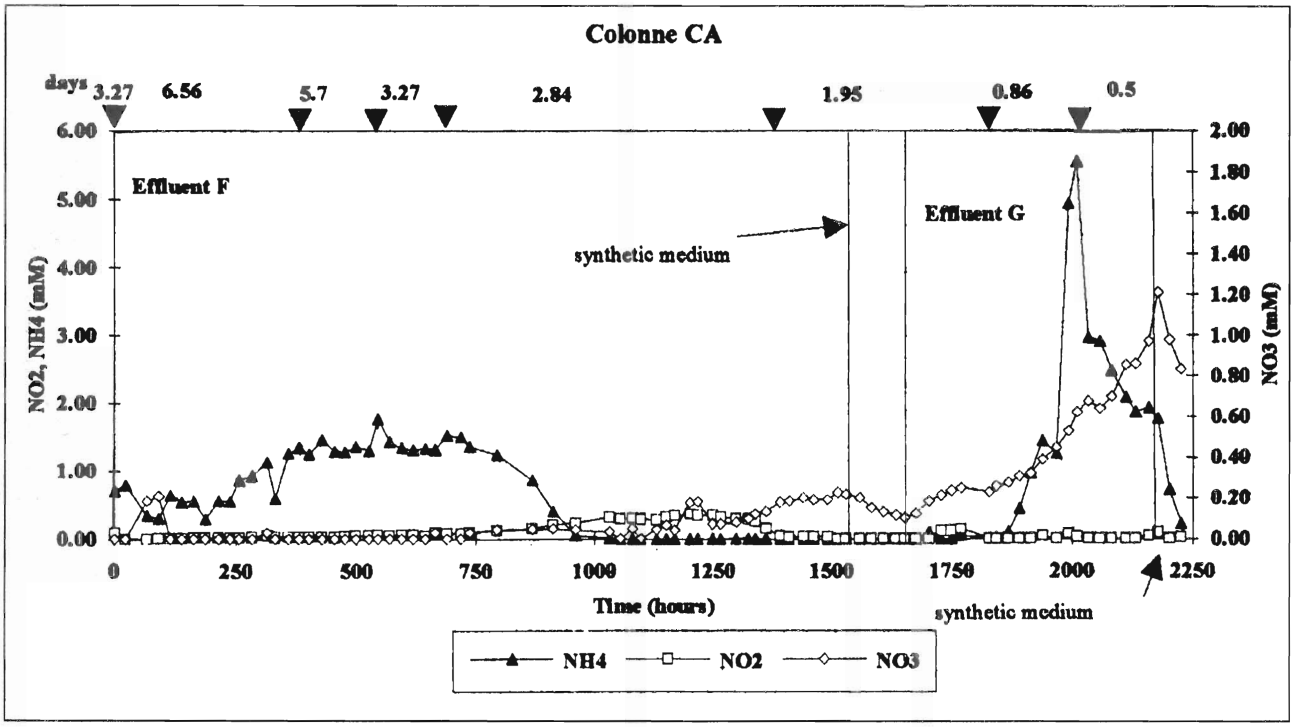

Fig. 2a. Activated carbon support. Evolution of nitrogen forms at decreasing residence times.

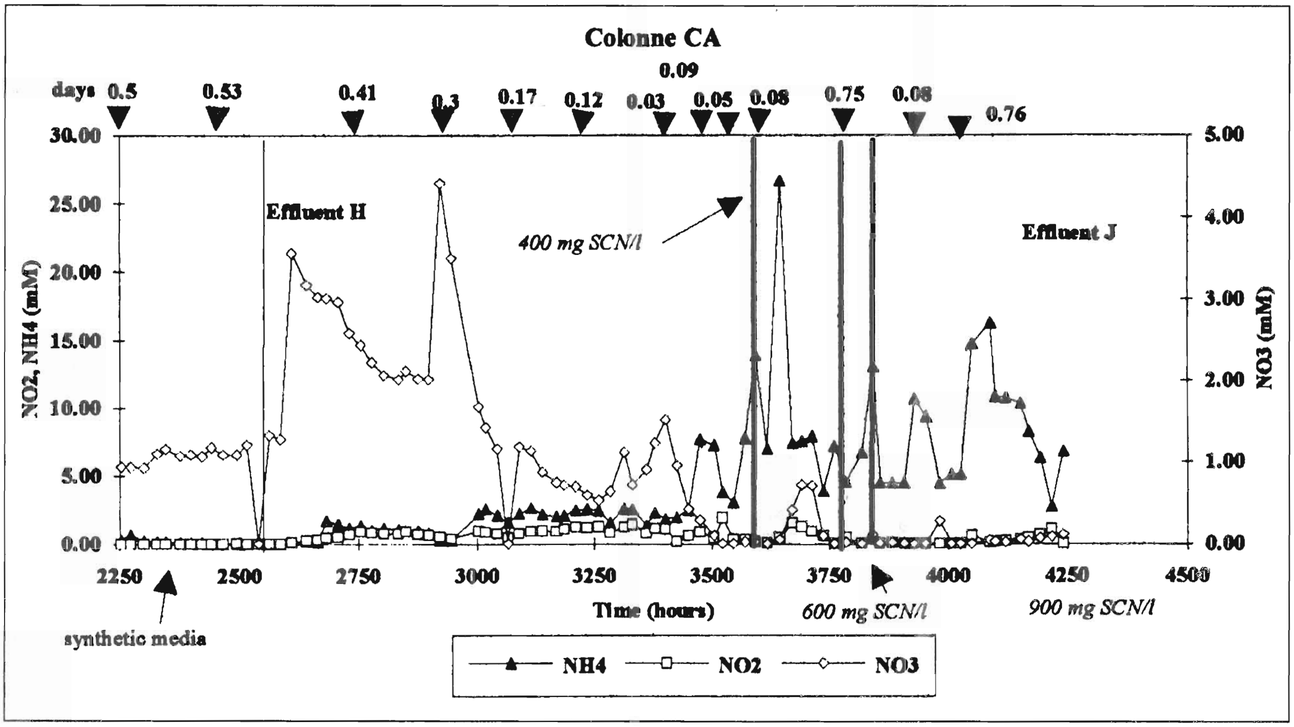

Fig. 2b. Activated carbon support. Evolution of nitrogen forms at decreasing residence time and increasing SCN feeding concentration.

nitrate were not detected, except when the SCN concentration was risen to 400 mg $l^{-1}$. It seemed that nitrifying bacteria were inhibited by high cyanide concentrations, and by a residence time that did not allow their adaptation to these concentrations (Fig. 2a, b).

### *Microbial support PPZ*

With an initial residence time of 14 days, a peak of 18 mg $l^{-1}$ thiocyanate of was detected and followed by a similar one of $NH_4$, showing that SCN was decomposed

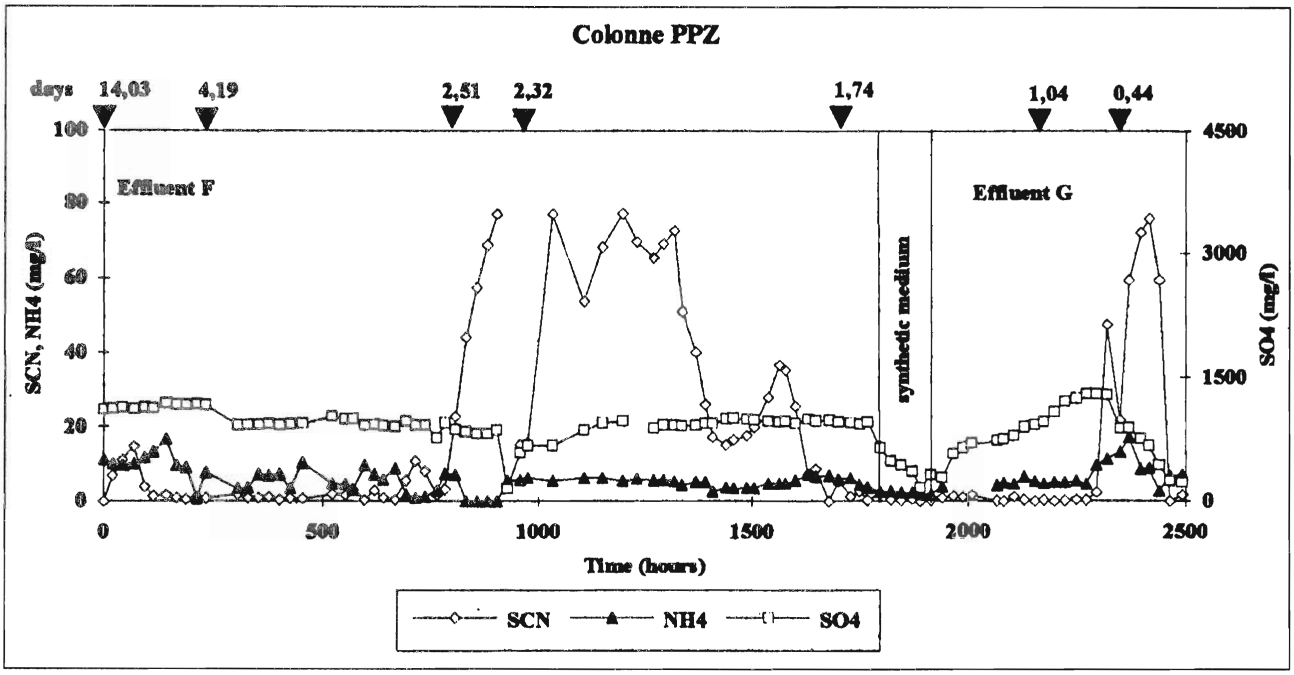

Fig. 3a. Support pumice-stone + zeolite. Evolution of thiocyanate concentration and its degradation by-products at decreasing retention times.

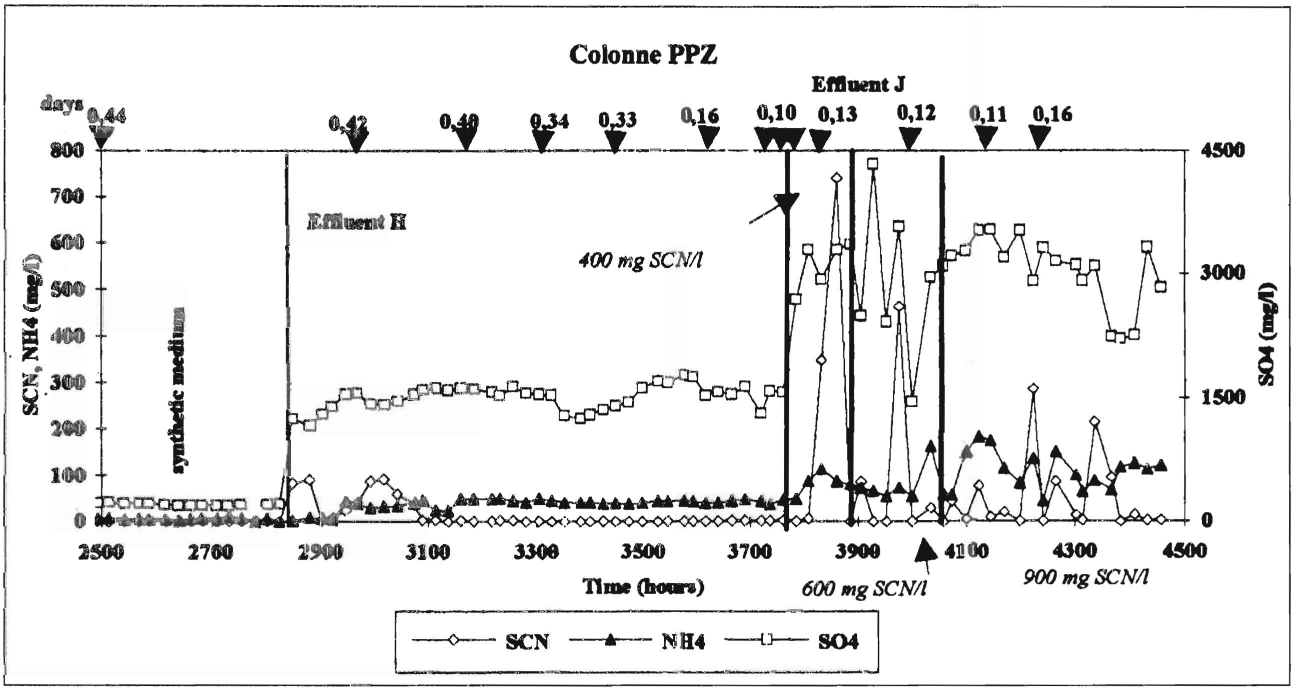

Fig. 3b. Support pumice-ston + zeolite. Evolution of thiocyanate concentration and its degradation by-products at decreasing residence times and increasing thiocyanate feeding concentrations.

(Figs. 3a and 3b). During the first 2500 h of experiment (Fig. 3a), the reactor was strongly affected by each change in residence time. Accumulation of SCN in the outflow was frequent. This lack of stability could be related to the need of adaptation phase when the microorganisms were submitted to a change in feeding flow-rate. During a second phase, from 2900 to 3800 h (Fig. 3b), decreases in residence time down to 0.16 day only induced two peaks of thiocyanate, reaching levels of 100 mg $l^{-1}$. Subsequently to this phase, increasing SCN concentrations were

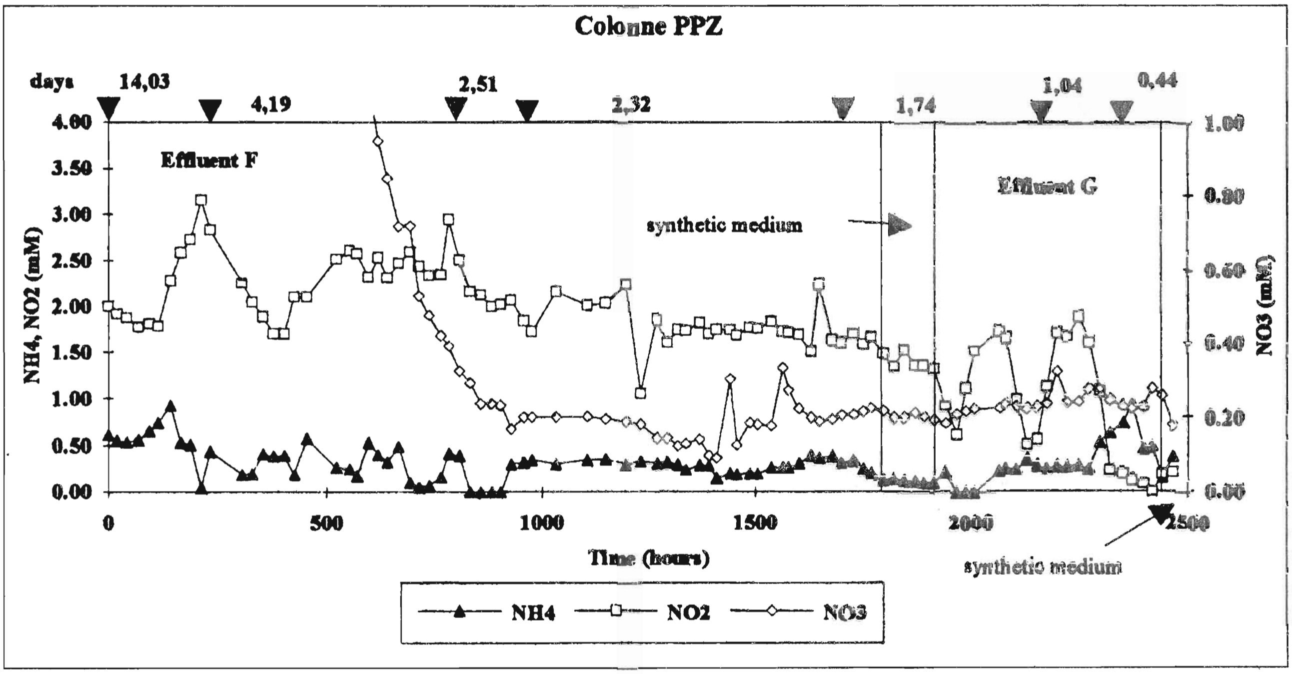

Fig. 4a. Support pumice-stone + zeolite. Evolution of nitrogen forms at decreasing residence times.

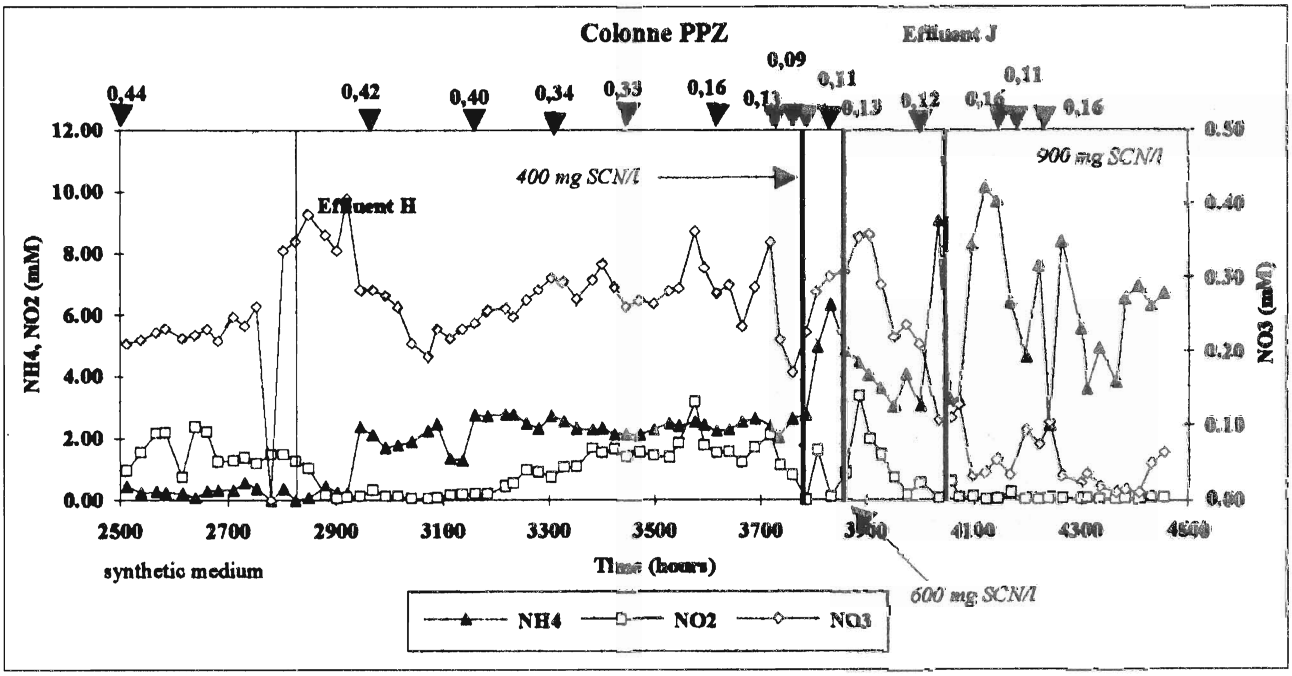

Fig. 4b. Support pumice-stone + zeolite. Evolution of nitrogen forms at decreasing residence time and increasing SCN feeding concentration.

applied. Fluctuations in thiocyanate were recorded, with a maximum reaching 750 mg $l^{-1}$ during continuous supply with 400 mg $l^{-1}$. Then, even with increasing thiocyanate concentrations, the amplitude of the SCN accumulation peaks was lower than it was previously. This stabilization may be explained either by an adaptation of degrading bacteria to high pollutants concentrations, or by an increase in the fixed biomass.

High level of nitrate were released by zeolite support leaching, during the first 1000 hours (Fig. 4a). The major part of $NH_4$ was converted into $NO_2$, whose concentration fluctuated between 90 and 150 mg $l^{-1}$. Nitrite was partially transformed into nitrate, whose concentration rose from 10 to 20 mg $l^{-1}$ till 2400 hours at a residence time of 1.04 days. Changes in effluent quality (synthetic media to real effluent), combined with the reduction of residence

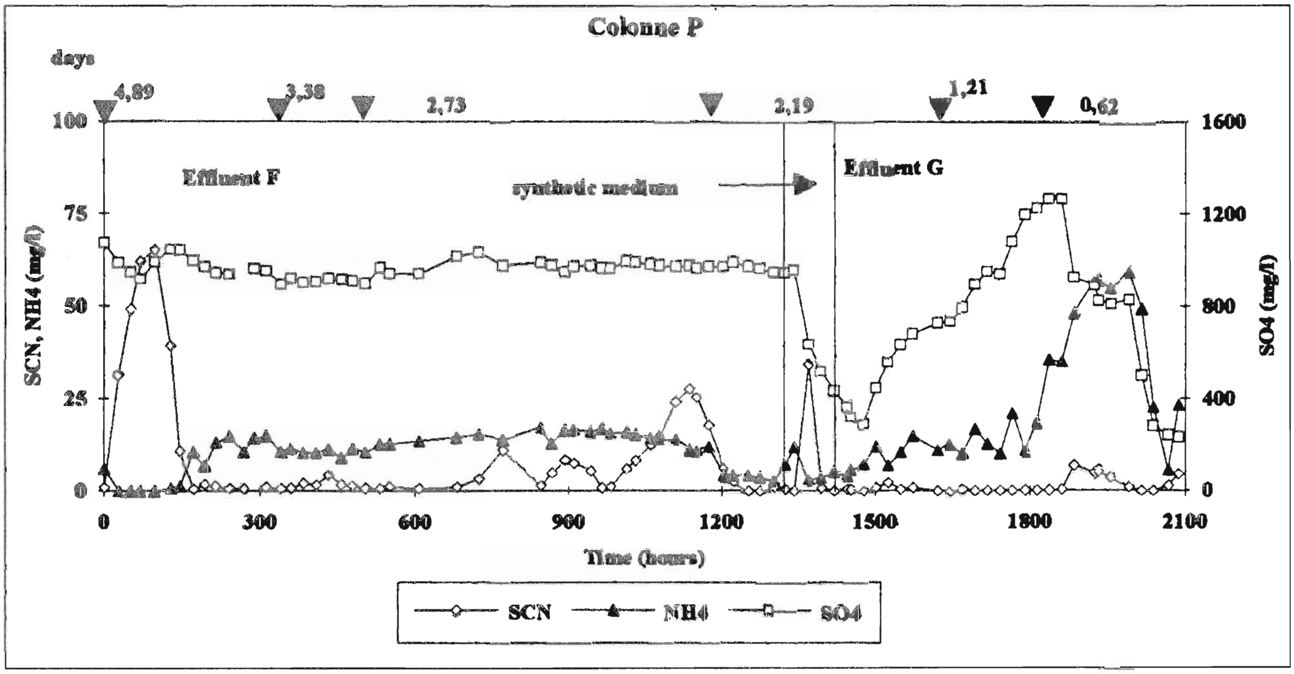

Fig. 5a. Support pouzzolana. Evolution of thiocyanate concentrations and its degradation by-products at decreasing residence times.

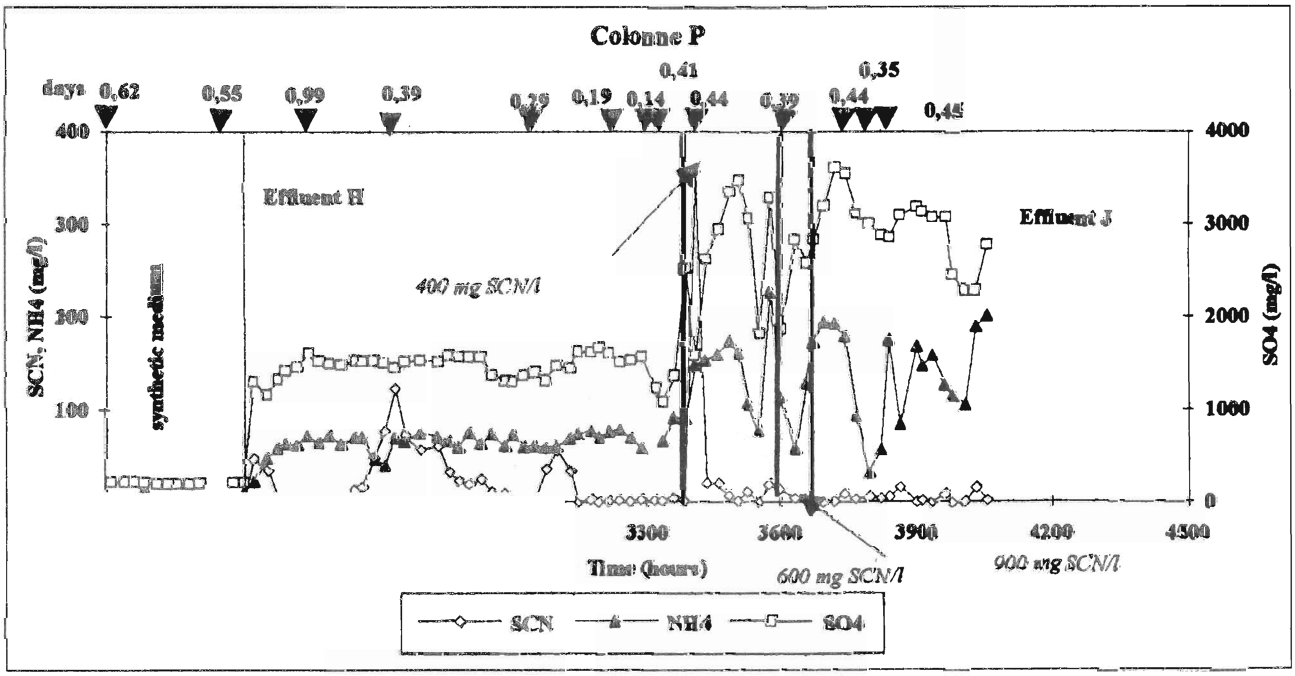

Fig. 5b. Support pouzzolana. Evolution of thiocyanate concentrations and its degradation by-products at decreasing residence times, increasing thiocyanate feeding concentrations.

time down to 0.42 day, induced an accumulation of $NH_4$, whose level reached a plateau around 50 mg $l^{-1}$. After 3100 hours of continuous experiment, production of $NO_2$ was detected for residence times between 0.42 and 0.13 day (Fig. 4b). The increase in thiocyanate feeding concentration generated a rise of ammonium concentration, this $NH_4$ being partially converted into nitrite. With a SCN concentration of 900 mg $l^{-1}$, the nitrification process was inhibited as neither nitrite nor nitrate was detected.

*Microbial support P*

After a transient accumulation of SCN, this compound was entirely decomposed when the residence time was 4.89 or 3.38 days (Fig. 5a). For a 2.73 days residence time, some variations in SCN outflow concentration were obser-

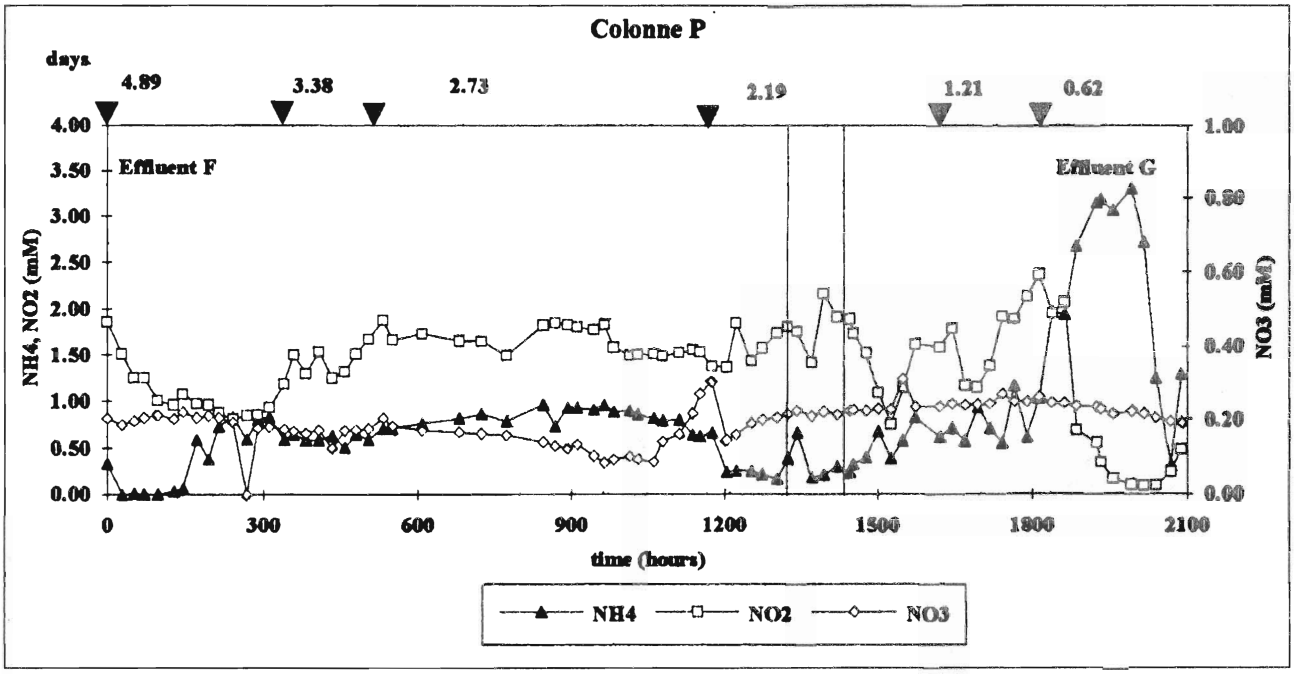

Fig. 6a. Support pouzzolana. Evolution of nitrogen forms at decreasing residence times.

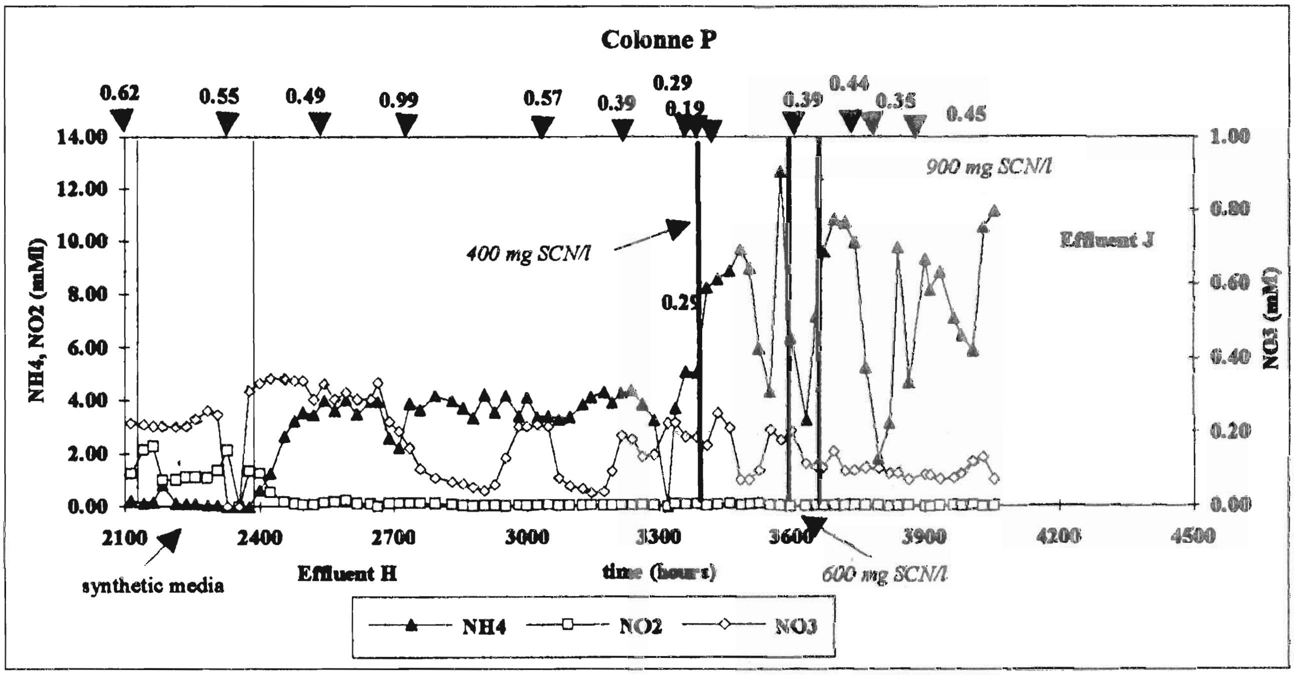

Fig. 6b. Support pouzzolana. Evolution of nitrogen forms at decreasing residence time and increasing SCN feeding concentration.

ved, although the quality of the feeding effluent did not change. During this period, thiocyanate accumulated up to 25 mg l$^{-1}$. The bacterial population might have been affected by the evolution of the ambient temperature: this step of the experiment was performed in winter, and the room temperature occasionally fell down to 12 °C. The subsequent results showed that this column could efficiently degrade SCN at residence time shorter than 2.73 when the ambient temperature was maintained around 20 °C. Nevertheless, transient accumulations of SCN were regularly obtained each time the working conditions were modified. On this support, the bacteria need an adaptation time of 3 - 10 days before reaching a steady-state corresponding to more than 90 % of thiocyanate being decomposed in the column.

The behaviour of the bacteria fixed on pouzzolana toward the increases in thiocyanate and cyanide concentrations was satisfactory (Figs. 5a and 5b). The residual SCN in the outflow was less than 10 % of the inflow concentration, even when the feeding contained 900 mg $l^{-1}$ thiocyanate. This apparent improvement of the bacterial efficiency may be the consequence of either an increase in the total biomass fixed on the support, or the adaptation of the microorganisms to their toxic substrates. Nevertheless, althought the bacteria were able to decompose SCN at the higher feeding concentration, the equilibrium of the biological system was less stable in this condition than it was when the inflow contained 180 mg $l^{-1}$ SCN. Subsequently to the increase in feeding concentrations, the stability of the column was greatly disrupted by each change in residence time. Ammonium and sulphate concentrations in the outflow displayed variations of significant amplitude, whereas SCN biodegradation efficiency did not seem to be affected.

During the first phase of the experiment, when the residence time was higher than 2 days (Fig. 6a), the nitrogen was equally distributed between $NH_4$ and $NO_2$ forms. Since the remaining $NH_4$ was not negligible, its oxidation was incomplete. Less than 10 % of the total nitrogen was converted to nitrate: the nitrification process was blocked at the $NO_2$ step. The successive increases in feeding flow-rate and pollutants concentrations induced a drop in $NO_2$ production. When the residence time reached values lower than 0.5 day (Fig. 6b), the nitrification process was almost entirely stopped. More than 90 % of the total nitrogen remained in the $NH_4$ form. The pouzzolana did not promote the fixation, development, and activation of the bacteria responsible for the nitrification process. The behaviour of the column when a synthetic medium was used was interesting to note. This medium, containing SCN but no cyanide, temporally replaced the real effluent between 2000 and 2400 h (Fig. 6b). During this period, the $NH_4$ concentration was very low, in other words the ammonium was efficiently oxidized. This result suggests that the first step of nitrification may be inhibited by cyanide. This could explain why $NH_4$ accumulated when the feeding flow rate and the cyanide concentration in the inflow were increased. Nevertheless, the nitrification process was stopped at the $NO_2$ form, even when the synthetic medium was used.

### *Comparison of the microbial supports according to degradation of cyanide forms*

With an initial feeding thiocyanate concentration of 180 mg $l^{-1}$, 98 - 100 % of SCN could be degraded at 0.09, 0.05 and 0.19 day of residence time for PPZ, CA and P respectively (Tab. 1). Concerning total cyanides, for a residence time of 0.42 day, the degradation level reached 74.5 % with the microbial support PPZ. The activated carbon seemed to be the most efficient in cyanide degradation, with a 100 % elimination of thiocyanate, total CN, and wad CN, at a 0.41 day residence time (Tab. 1).

At a constant residence time, thiocyanate concentration in the feeding medium was increased from 180 to 900 mg $l^{-1}$. Results concerning this phase are given in Tab. 2.

Tab. 1
Degradation levels and minimal residence time reached with the feeding medium containing 180 mg $l^{-1}$ SCN

| | PPZ | | CA | | P | |
|---|---|---|---|---|---|---|
| | deg. level (in %) | res. time day | deg. level (in %) | res. time day | deg. level (in %) | res. time day |
| SCN | 98.0 | 0.09 | 100.0 | 0.05 | 99.0 | 0.19 |
| CN wad | 89.0 | 0.42 | 100.0 | 0.41 | 100.0 | 0.49 |
| total CN | 74.5 | 0.42 | 100.0 | 0.41 | 77.0 | 0.49 |

Tab. 2
Comparison of microbial supports. Effects of increasing thiocyanate concentration in the feeding medium on thiocyanate degradation level

| | PPZ | | CA | | P | |
|---|---|---|---|---|---|---|
| SCN in feeding mg $l^{-1}$ | deg. level (in %) | res. time day | deg. level (in %) | res. time day | deg. level (in %) | res. time day |
| 180 | 98.0 | 0.09 | 100.0 | 0.05 | 99.0 | 0.19 |
| 400 | 71.0 | 0.13 | 88.3 | 0.08 | 86.4 | 0.44 |
| 600 | 78.5 | 0.13 | 98.5 | 0.13 | 98.5 | 0.39 |
| 900 | 95.0 | 0.16 | 99.0 | 0.76 | 99.4 | 0.45 |

For PPZ, at a residence time between 0.09 and 0.16 day, degradation level of SCN ranged from 71 to 95 % when the feeding concentration was increased.

For the same range of residence time, 98.5 % of thiocyanate was degraded in the CA column with an initial SCN concentration of 600 mg $l^{-1}$. When the feeding contained 900 mg $l^{-1}$ SCN, the CA column was working at higher residence time than the two other columns because the washing operation had disrupted the system. However, 99 % of the thiocyanate could be removed by adjusting the residence time to 0.76 day.

Concerning microbial support P, the SCN degradation level reached values between 86 and 99 %, although the feeding concentration was increased from 180 to 900 mg $l^{-1}$.

With an feeding containing 900 mg $l^{-1}$ SCN, 99.5 % and 97.7 % of total cyanides were degraded for PPZ and P microbial supports respectively. No WAD cyanide was detected in the columns PPZ and P outflow.

## Conclusion

The treatment of the cyanidation effluent was continuously performed during 6 months. The results of this experiment showed that the bacterial mixed inoculum, previously selected by the INRA laboratory, could be efficiently fixed on different supports. The immobilized bacteria showed their ability to withstand increasing feeding flow-rate and pollutants concentrations. More than 90 % of the feeding thiocyanate was biologically decomposed into $NH_4$, $CO_2$ and $SO_4$ in the three reactors. The elimination of free and complexed cyanides was performed, probably throught the combination of precipitation and biological degradation. Indeed, the analysis proved that the precipitates accumulated at the bottom of the column contained complexed cyanide. However, some observations suggest that cyanide was almost partially biodegraded: when the real effluent was introduced in place of the synthetic medium, a peak of cyanide in the outflow was observed, as if the bacteria needed an adaptation time. Moreover, the elimination of cyanide through the column was more complete, when the flow-rate was increased, than at the beginning of the experiment. This phenomenon might signify that the bacterial metabolism of CN was activated by either adaptation to cyanide or an increased availability of this substrate. The precipitation of complexed cyanide might also be promoted by the bacteria.

The most concentrated feeding, containing 900 mg $l^{-1}$ SCN and 100 mg $l^{-1}$ total CN, was equivalent to a non-diluted industrial effluent. Nevertheless, the characteristics of the wastewater produced by a mining plant undergo fluctuations. These variations are related to the instability of the ore-processing steps, and to the rainfall conditions which determine the dilution in retention pools. Thereby, analysis of the successive samples of mining effluent which were used to feed the columns proved that the SCN and CN concentrations could vary by more than 100 %. The minimum and maximum values for SCN content were respectively 500 and 2000 ppm. According to these variations, the biological reactor should imperatively be able to work in a large range of concentrations, and to withstand a sudden change in effluent composition. The three fixed bed reactors showed a satisfactory behaviour toward fluctuations in CN-feeding concentration: after the change from a SCN-synthetic medium without cyanide to a real effluent, less than 24 hours were sufficient to restore the CN-degrading ability of the reactors. However, the activated carbon-containing column was the more resistant to changes in feeding quality. No accumulation of SCN was observed with this support when a new effluent, recently received from the mining plant, was used to prepare the feeding. Concerning the nitrification process, the CA column also was the most efficient. Activated carbon was the only support which allowed the complete oxidation of $NH_4$ into $NO_3$, during the first phase of the experiment. With pouzzolana and pumice stone-zeolite, the nitrification was either blocked at the $NO_2$ or at the $NH_4$ step. The microorganisms responsible with the oxidation of ammonium seemed to be affected by cyanide. In the three columns, the nitrification process was entirely inhibited when the feeding concentration was increased. Setting aside the optimum flow-rate for SCN elimination, the toxicity of the $NO_2$ molecule could justify the use of the only support which prevented its accumulation, namely activated carbon. This support is more expensive than pouzzolana, pumice-stone, and zeolite. Nevertheless, activated carbon is commonly used in cyanidation processes, and could be easily available near the biological treatment unit.

Two hypothesis may be proposed to explain why activated carbon is much more efficient than the two other bacterial supports. First, it provides more fixation sites to bacteria, thanks to its high specific area. Furthermore, the residence time of the pollutants might be increased by the adsorption capacity of the carbon. Further experiments will be necessary to better understand the interactions between the CN- and SCN-degrading bacteria, the nitrifying population, and the supports.

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# Microbiological processes for cyanide purification in the waste water at the gold-extracting factories

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## Abstract

The present paper studies the relationship between the thermodynamic characteristics of cyanide complexes of zinc, copper, silver, iron and the rate of their assimilation by the bacterial culture of *Pseudomonas* genus. The differences were specified in cell metabolism depending on the properties of coordinating metal of the complex. It has been demonstrated that the efficiency of cell-complex interaction is determinated, on the one hand, by the degree of culture adaptation to cyanides and heavy metals and its capability to transform the toxic components into the low- and nontoxic forms and, on the other hand, by the state of complex salts in the solution. The extent of influence of various parameters on the process kinetics, such as pH, excess concentration of cyanide and metal, characteristics of electric field, has been also determined. It has been revealed that the rate of assimilation of $NaAg(CN)_2$ and $K_4Fe(CN)_6$ with electrically treated cells appeared to be higher than in the case of treatment with native cells. There were discussed possible mechanisms of intensifying the process of microbial destruction of cyanides in the electric field.

**Key words:** cyanide, complex cyanide, waste water, microbial purification, electric field

### Účasť mikroorganizmov na čistení odpadových vôd z extrakcie zlata od kyanokomplexov

V našej štúdii sme hľadali vzťah medzi termodynamickými vlastnosťami kyanokomplexov Zn, Cu, Ag, Fe a rýchlosťou ich asimilácie baktériami *Pseudomonas genus.* Zistili sme metabolické odchýlky v závislosti od vlastností koordinovaného kovu. Ukázalo sa, že miera interakcie medzi komplexom a bunkou závisí od nasledujúcich faktorov: odolnosti bunky voči kyanokomplexom (adaptovateľnosti na ne) a ťažkým kovom, schopnosti bunky biotransformovať kyanokomplexy a chemickej formy kyanokomplexov v roztoku. Ďalej sme skúmali vplyv pH, nadbytku kyanidov, iónov ťažkých kovov a vlastností vonkajšieho elektrického poľa na rýchlosť asimilácie kyanokomplexov bakteriálnymi bunkami. Ukázalo sa, že rýchlosť asimilácie možno zvýšiť pôsobením vonkajšieho elektrického poľa na bunky baktérií, a preto sme sa ďalej zamerali na odhalenie možných mechanizmov tohto javu.

## Introduction

The actuality of present study is determined by the extensive application of the technologies for the processing ores and metals with sodium cyanide as highly effective solvent being used therefor. The involvement of cyanide in the above technologies results in contaminating effluents with great amount of cyanide. The biochemical processes of decontaminating the cyanide-containing effluents of non-ferrous metallurgy plants are attractive due to their ecological safety as well as to the possibility of using the complex approach that is, providing the simultaneous destruction of cyanides and accumulation of the recovered metals (Whitlock and Mudder, 1986). A lot of enzymes involved in the processes of metabolic transformation of cyanides into non-toxic products have been lately separated and identified (Harris, Bunch and Knowles, 1987).

Unlike free cyanides, which could be destructed under the influence of ambient conditions such as air oxygen, UV-irradiation, pH variation, the cyanides bonded in the form of complex salts are more resistant to the effect of above factors. Furthermore, the recovery of coordinating metal during cyanide destruction not only causes the additional contamination of effluents with heavy metal ions but also exerts an oligodynamic effect on the culture-destruction.

The problem of interaction between microorganisms and cyanide complexes of transition metals studied within the context of general model of bacteria metallophilicity has a number specific features. These features are, first of all, connected with the effect of cyanides on physiologic activity and degree of energization of cells in bacterial suspensions (Yakubenko, Podolska, Vember and Karamushka, 1955) as well as with the durability of cyanide complexes and the nature of coordinating metal (Shpak, Podolskaya, Ulberg & Shpak, 1995). The present paper deals with the interrelation between the metabolic activity of *Pseudomonas fluorescens* strain bacteria and the parameters determining the state of cyanide metal complexes in solution as well as with the analysis of some physicochemical factors, in particular, the exterior electric field affecting the efficiency of interaction between the cell and the solution of cyanide complex compounds of copper, silver, zinc, iron, gold.

## Materials and methods

$Na_3Cu(CN)_4$, $Na_2Zn(CN)_4$, $NaAg(CN)_2$ cyanide complexes were synthesized according to the procedures specified in Brauer and Weigel (1986). Sodium cyanide and potassium ferrocyanide were received as commercially produced compounds.

*Pseudomonas fluorescens* B-5040 strain separated from the slime of tail deposit of gold-extracting Uzbekistan plant was used for studies. Cells have been cultivated under aerobic conditions for 18 hours in 200 ml of synthetic 5M medium (0.2 % $KH_2PO_4$ + 0.1 % $K_2HPO_4$ + 0.05 % $Na_2CO_3$ + 0.03 % $MgSO_4$ + 0.01 % NaCl + 0.2 % glucose + 0.05 % pentone + 0.01 % NaCN) at a temperature 28 °C. Being the cells at logarithmic growth phase the suspension was centrifuged. The sediment was used as seeding material and suspended in model waste water including the synthetic 5M medium and one of the cyanide complexes. There was used the colorimetric technique of determining the total cyanides using pyridine and barbituric acid (American Society for Testing and Materials, 1972).

For treating cyanide-containing solutions and bacterial suspensions by the direct electric field there was used the impulse potentiostat PI-50-1-1 (Russia). The solutions were treated in 50 ml cells, with working and auxiliary electrodes being made of platinum and as a reference one being used Ag/AgCl electrode of potential 0.201 V (NHE).

Aminoacid analysis of cultural liquid was carried out with BIOTRONIC-LC500 intrument (Japan) using Ninhydrine sorbent.

## Results

### *Biochemical interaction between the microbial cells and metal complexes*

Oxygenize mechanism of cyanide destruction to ammonia and $CO_2$ in the presence of *Pseudomonas fluorescens* has been earlier discovered by Harris and Knowles (Harris, Bunch and Knowles, 1987). Fig. 1 demonstrates the kinetic relationships of destruction of cyanides being included in the composition of complex salts and NaCN in the suspensions of *Pseudomonas fluorescens* B-5040 cells. As it is seen from this figure, the cyanides are most easily destructed in the solutions of NaCN and $Na_2Zn(CN)_4$. The dynamics of cyanide concentration reduction is very similar in this case. Cyanides to be included in the complexes with copper and silver were destructed more slowly. For 48 hours of contact with bacteria cells there has been destroyed only 5 % of potassium ferrocyanide.

There has been specified the specific reaction of cells to adding of cyanide silver complex into the bacterial suspension. In four hours of contact between cells and cyanide silver complex salt pH value has been more than 2 units decreased. The higher was the content of complex anion, the more pH value reduced. The addition of copper complex in most cases resulted in slight protoxydation of culture liquid following the first day of contact and in pH rise during the second day of contact. There were no substantial variations of pH value in the case of zinc and iron cyanide complexes. The amino-acid analysis of culture liquid to be formed in the process of culturing cells on cyanide-containing substrates was also performed. The obtained results evidence the differences of amino-acid composition depending on the kind of salt to be added thereto, although there are some regularities in this process. It was revealed that the growth of cells on the nutrient medium with NaCN was attended by the accumulation in the culture liquid of aminoacids of increased content of basic groups, with these groups constituting about 51 % of total content of functional groups and acid groups being present in an amount 6.29 %. The interaction of cells with $Na_3Cu(CN)_4$ and $NaAg(CN)_2$ was attendant by 2.5 fold increase of the content of acid and aliphatic groups, mainly, due to the presence of aspartic and glutamic amino-acids. At the same time, the content of basic groups was 5 - 6 fold reduced. The increase of contact time from 24 to 48 hours resulted in two-fold increase of acid group content. The metal content was controlled simultaneously with controlling the cyanide content in bacterial suspensions the experiments. It has been shown that on interaction between the cell and $NaAg(CN)_4$ there occurred the substantial reduction of silver concentration correlating to that of cyanide.

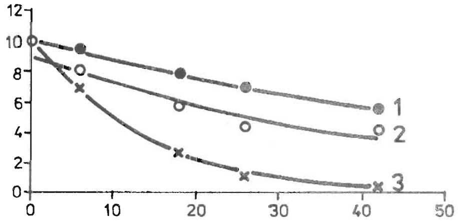

Fig. 1. Effect of solution treatment procedure on kinetics of cyanide destruction in $NaAg(CN)_2$ solution. 1 - electrical treatment at potential -0.3 V (Ag/AgCl); 2 - microbial destruction by *Pseudomonas fluorescens*, 3 - simultaneous microbial destruction and electrochemical treatment at above given conditions.

The ratio of [$CN^-$] and [$Ag^+$] was really about 2,3 for 48 hours of contact. The reduction of copper concentration in the solution of its complex salt was significantly lower than that of silver complex. The substantial reduction of zinc concentration in $Na_2Zn(CN)_4$ solution when culturing the microbial cells is in smaller extent connected with zinc accumulation by microbial cells and in greater extent is due to the formation of slightly-soluble precipitates.

### *Treatment by electric field*

The experiments on cyanide destruction by the microbial cells in 5M medium under the effect of direct and impulse electric field were carried out. At Figs. 1 and 2 are presented kinetic relationships of the $NaAg(CN)_2$ and $K_4Fe(CN)_6$ destruction respectively. These are following: assimilation with bacteria; treatment by impulse electric field; assimilation with bacteria alongside with the electric field treatment. It has been demonstrated that the highest rate of cyanide destruction was observed in the third variant where the electric stimulation of microbial destruction took place. The treatment either by the direct current field or by the impulse electric field gave closely agreed results.

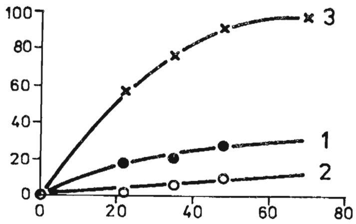

Fig. 2. Effect of solution treatment procedure on kinetics of $K_4Fe(CN)_6$ decomposition. 1 - electrical treatment at 0.5 V/cm; 2 - microbial treatment by *Pseudomonas fluorescens*, 3 - simultaneous microbial destruction and electrochemical treatment at above given conditions.

Some electrochemical investigations allow to explain the nature of discovered phenomenon. At the voltametric curves there were no found peaks corresponding to direct anode oxidation of cyanides. The reversible waves corresponding to the reduction of cyanocomplexes have been found at the curves recorded in the solution of silver and copper complexes with the potential values being -0.51 V and -0.70 V (vs. Ag/AgCl) respectively. The preparative electrolysis revealed low reduction of cyanide concentration in undivided cell at the potential of working electrode being in this case 0.2 V displaced to the anode region in relation to the potential of cyanocomplex reduction. The obtained results are presented in Tab. 2. Therefore, the effect of electrochemical destruction of metal complex under the conditions of treating biocolloid suspension including *Pseudomonas fluorescens* and $NaAg(CN)_2$ solution at the potential of -0.3 V (vs. Ag/AgCl) has been reduced to minimum.

## Discussion

As it is evident from the obtained data on the rate of cyanide destruction by *Pseudomonas fluorescens* cells, the metal complexes are placed in the following order:$NaCN > Na_2Zn(N)_4 > Na_3Cu(CN)_4 > NaAg(CN)_2 > K_4Fe(CN)_6$. It could be noted that one of estimated mechanisms of interaction between the microbial cells and cyanide metal complexes is assumed to be the displacement of equilibrium of the reaction of complex anion dissociation due to assimilation of cyanide ligand according to one of the mechanisms of enzyme kinetics (Harris, Bunch and Knowles, 1987). The rate of destruction is the higher, the lower is pH value of medium. At pH drop the dissociation of complexes is increased and at the rise of pH the dissociation reduced. As it was demonstrated (Shpak, Podolskaya, Ulberg and Shpak, 1995) at pH 5 the equilibrium concentration of silver in 0.01 M solution of $NaAg(CN)_2$ constitutes $1.5.10^{-6}$ M and at pH 7 it reduces to $6.8.10^{-8}$. This regularity is, however, true only at low concentration of complexes in the solutions. With the concentration increase the hydrolysis could take place. In this case the equilibrium of the complex dissociation reaction may be displaced towards the formation of dissociation products due to the removal of metal ions in the form of heavily soluble hydroxide. It is noteworthy that the pH value should not be outside the limits of physiologic pH values for specific bacteria culture, that is 5.5-9.5. Physiologic response of cells to the addition into the medium of some cyanides, in particular, copper and, especially, silver cyanides is expressed in pH reduction, it displaces the equilibrium of complex dissociation and facilitates assimilation of cyanides by the cells. As follows from Tab. 3, the rate of microbial destruction of complexes is well correlated with the line of their durability with its basic feature being the equilibrium concentration of metal and ligand. The apparent discrepancy between the low rate of microbial assimilation of ferrocyanide complex (Tab. 1) and its low durability (Tab. 3) may be well explained by the kinetic inertness of this complex (Chadwick and Sharpe, 1966). The obtained results demostrate that the higher is the equilibrium concentration of metal and ligand in metallocomplex solution and the more quickly this equilibrium achieved, the higher is the rate of destruction of said complex.

The accumulation in solution of excess amount of metal ions to be released after assimilation of cyanides with the cells results in the reduction of complex dissociation degree and has an inhibiting effect on microorganisms. Metals could be removed from the contact medium by one of below-mentioned techniques: accumulation by cells, production of high-strength complexes with the products of metabolism, formation of insoluble or low-soluble sediments, etc. As we have noted, the first of above mentioned mechanisms is true for $NaAg(CN)_2$. This specific interaction between the cell and cyanide complex of silver reduces the oligodynamic effect of metal and rises the limit of its toxicity for bacteria. The second of said mechanisms is most probably realized during the contact of cells with $Na_3Cu(CN)_4$. In this case copper mainly remains in the solution in the form of organocomplexes. The increase of oxygen content in the medium due to intensification of aeration process enhances the displacement of redox potential to positive region as well as the oxidation of organic components of the solution to the simplest mineral substances and the removal of copper from the solution as water insoluble sediments. Zinc included into the composition of complex salt is very easily hydrolyzed in neutral and weakly-alkaline pH region. The presence in the medium of phosphoric acid salts contributed to sediment production. At the same time, in spite of pH value being 6.5 - 7.5, under the conditions of oxygen deficit due to forming of mobile metal-organic composition with the products of cell metabolism in the solution there were accumulated water-soluble zinc compounds. The logic conclusion based on the above data is that the intensive aeration needed to realize the biochemical treatment of cyanide-containing solutions including the transition metal cyanides.

The irreversible displacement of equilibrium due to removing cyanides from the reaction medium is enhanced by treating the bacterial suspension in cyanide solution by low in-

Tab. 1
Variation of metal and cyanide-ion concentration vs. time of contact between complex compounds and *Pseudomonas fluorescens* dispersion

| Contact | Concentration (mg/l) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_4Fe(CN)_6$ | | $NaAg(CN)_2$ | | $Na_3Cu(CN)_4$ | | $Na_2Zn(CN)_4$ | |
| time (h) | $[Fe^{2+}]$ | $[CN^-]$ | $[Ag^+]$ | $[CN^-]$ | $[Cu^+]$ | $[CN^-]$ | $[Zn^{2+}]$ | $[CN^-]$ |
| 0 | 4.3 | 10.7 | 10.7 | 5.2 | 5.5 | 9.25 | 20.8 | 13.4 |
| 4 | 4.2 | 10.7 | 8.2 | 4.3 | 5.2 | 1.9 | 6.4 | 1.4 |
| 18 | 4.1 | 10.5 | 2.5 | 1.7 | 5.0 | <0.1 | 0.9 | 1.4 |
| 28 | 4.0 | 10.4 | 2.1 | 1.0 | 4.9 | <0.1 | 0.5 | 1.0 |
| 48 | 3.9 | 10.2 | 2.2 | 0.4 | 4.2 | <0.1 | <0.1 | 0.29 |

Tab. 2
Variation of cyanide concentration during the preparative electrolysis of $NaAg(CN)_2$ in 5M medium

| Time of treatment | Cyanide concentration (ppm) | | | |
|---|---|---|---|---|
| | Undivided cell | | Divided cell | |
| | | | Cathode compartment | Anode compartment |
| h | 1 | 2 | 2 | 2 |
| 0 | 9.2 | 9.6 | 9.1 | 9.1 |
| 2 | 9.0 | 8.4 | 7.9 | 8.9 |
| 6 | 8.9 | 6.2 | 5.6 | 8.4 |
| 10 | 8.4 | 4.0 | 3.4 | 7.8 |
| 16 | 7.6 | 0.8 | 0.2 | 6.9 |

1 - At cathode potential -0.3 V (vs. Ag/AgCl); 2 - At cathode potential -0.7 V (vs. Ag/AgCl)

Tab. 3
Calculated data on equilibrium concentrations of metal ions and ligand in the solutions of complex salts

| Compound | $K_{ins}$ [7] | [Me], M | $[CN^-]$, M |
|---|---|---|---|
| $NaAg(CN)_2$ | $8.10^{-22}$ | $6.8.10^{-8}$ | $1.4.10^{-7}$ |
| $Na_3Cu(CN)_4$ | $5.10^{-31}$ | $2.2.10^{-6}$ | $8.8.10^{-6}$ |
| $K_4Fe(CN)_6$ | $1.10^{-24}$ | $1.0.10^{-4}$ | $6.0.10^{-4}$ |
| $Na_2Zn(CN)_4$ | $1.3.10^{-17}$ | $1.0.10^{-4}$ | $4.0.10^{-4}$ |

Procedure for performing calculations is described in Shpak, Podolskaya, Ulberg and Shpak (1995).
Calculations are made for $1.0.10^{-4}$ M solutions of complex salts, pH 7.

tensity electric field. It was established that the application of electric field to a microbial suspension accelerates the biodestruction of weak and average strength complexes and initiates the biological destruction of the strong and inert complexes. Total effect of the microorganisms and electric field action has the synergetic character, i. e. considerably exceeds the sum of each factor action separately. This is especially noticeable for the iron cyanocomplex. As it follows from Tab. 1 the bacteria practically do not destruct the potassium ferrocyanide ions. The electric field application in the absence of the cells for two days leads to the 24 % destruction of ferrocyanides. At the same time, the electric field application in the presence of bacteria results in the 93 % complex ferrocyanide destruction. Thus the given phenomenon can be considered as the stimulation for the process of the microbial cyanide destruction. The electric field stimulation action was observed while applying very weak electric fields excluding the electrochemical cyanocomplex destruction.

We have also discovered that the rate of assimilation of $NaAg(CN)_2$ with the bacteria to be treated by the electric field appeared to be 25 % higher than that of assimilation with the native cells. During the subsequent multiple seeding of electrically treated bacteria on cyanide-containing media there was observed the considerable biomass increase exceeding that of control tests.

## Conclusions

1. On the example of cyanide complexes of transition metals the present study demonstrated that the efficiency of cell-complex interaction is determined, on the one hand, by the degree of adaptation of bacteria culture to cyanides and heavy metals and its capacity to transform the toxic components into low- and non-toxic forms and, on other hand, by the state of complex salt in the solution. Such parameters as pH value, excess concentration of metal and cyanide are capable to cause the reversible displacement of equilibrium of complex dissociation. In the process of microbiologic bonding of cyanide and treating the microbial suspension by the electric field there occurs the irreversible displacement of equilibrium due to the removal of cyanide from the reaction medium.

2. This study also discusses the effect of electric field on cell-metal cyanide solution. It was revealed that the intensification of cyanide destruction is not a simple combination of the processes of electrolysis and assimilation of cyanide by cells, but a complex mated system of interrelated phenomena, which include the electrostimulation and electroadaptation of microorganisms to cell toxins and growth inhibitors, displacement of dissociation equilibrium due to the removal of one of the components from the reaction medium, etc. It is well understood that the application of the exterior electric field can cause both the intensification of the process of assimilation of cyanides with cells and the death of bacteria culture as well as the deterioration of process characteristics due to incorrectly chosen electrostimulation condition.

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# Microbial detoxification of heavy metals in soil

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## Abstract

A soil contaminated with heavy metals, mainly copper, zinc and cadmium in the form of the relevant sulphides, was subject of detoxification by means of an in situ treatment system. The soil was initially inoculated with acidophillic chemolithotrophic bacteria and the microbial growth and activity were enhanced by suitably changes of some essential environmental parameters. The metals were solubilized as a result of the bacterial oxidation of the sulphides and the metal ions were transferred from the upper soil horizons (A and B1) to the deeply located horison B2 by washing with acidified water. Then the soil pH was increased to about 4.5 - 5.5 and soluble organics were provided as sources of carbon and energy to the anaerobic sulphate-reducing bacteria inhabiting this soil horizon. The hydrogen sulphide produced by these bacteria precipitated the metals as the relevant insoluble sulphides.

**Key words:** soil remediation, in situ rehabilitation, toxic metals, metals detoxification, acidophillic chemolithotrophic bacteria, sulphate-reducing bacteria

### Detoxifikačné odstránenie ťažkých kovov z pôd činnosťou mikroorganizmov

Detoxikácií úpravou in situ sa podrobila pôda znečistená ťažkými kovmi vo forme sulfidov. Medzi ťažkými kovmi dominovali Cu, Zn a Cd. Na začiatku pokusu sa pôda naočkovala acidofilnými chemolitotropnými baktériami a počas trvania pokusu sa regulovala aktivita a rast mikroorganizmov vhodnou voľbou parametrov prostredia. V dôsledku bakteriálnej oxidácie sulfidov sa kovy previedli do roztoku a následne sa okyslenou (acidifikovanou) vodou zmyli z vrtných vrstiev pôdy A a B1 do nižšej vrstvy B2. Potom sa pH pôdy upravilo na 4,5 až 5,5. V roztoku obsiahnuté organické látky slúžili zároveň ako zdroj uhlíka a energie pre anaeróbne baktérie redukujúce sulfát.

Činnosťou baktérií redukujúcich sulfát sa uvoľnil $H_2S$, ktorý sa vyzrážal s prítomnými ťažkými kovmi na príslušné sulfidy.

## Introduction

Pollution of soil by heavy metals arises as a result of varied activities, largely industrial, although sources such as agriculture and sewage disposal also contribute (Barrow, 1994). In most cases the main source are the acid drainage waters which are generated as a result of the oxidation of pyrite and other sulphide minerals in open-pit and underground mining works, waste rock and low-grade ore dumps, processing tailings, temporary stockpiles of sulphide concentrates as well as rich-in-pyrite coal and uranium mines. Soils around the flowpath of such waters are polluted with heavy metals, which are retained not only in the pore solution but also on the soil particles as a result of processes as adsorption, ion exchange and precipitation.

Another important way for soil pollution is the transportation by the air of metal-containing solid particles and gases.

Once in the soil, metals may undergo transformation into various mobile forms and/or immobilization in an environmental sink. In most cases these processes are connected with the activity of different soil microorganisms. These microorganisms immobilize, mobilize, or transform metals by extracellular precipitation reactions, oxidation and reduction reactions, methylation and demethylation, extracellutar binding and complexation, and intracellular accumulation (Paul and Clark, 1989; Beveridge and Doyle, 1989; Hughes and Poole, 1989; Brierley, 1990; Groudev, 1995).

As a result of the above mentioned reactions, the heavy metals are present in the soils in varied forms: as free ions (mainly cations) in the pore solution, as inorganic or organo-metallic soluble complexes, as ions or molecules absorbed on the soil particles, or as different solid metal-bearing compounds such as hydroxides, sulphides, etc. It must be noted that only some water soluble of the metals (the so called bioavailable forms) above certain concentrations are toxic for the living organisms in the soil. However, the metals can be turned from biologically inert to bioavailable forms as a result of chemical and, mainly, biological leaching.

The distribution of metals in the soil is not uniform. This distribution depends on the type and properties of the contaminated soil, the metal species, forms and content in the soil as well as on some essential environmental factors such as soil humidity, aeration, temperature, pH, redox potential, presence of nutrients for the soil microorganisms and plants.

The modern technologies for remediation of soils contaminated with heavy metals are based on the knowledge about the biogeochemical cycles of these metals, the biology of the soil microflora as well as on the properties of the contaminated soil. In this paper some data about field experiments on microbial detoxification of heavy metals in contaminated soil are present. This in situ treatment was connected with the transfer of the metals into the deeply located soil horizons where the soluble metal ions were turned into the relevant insoluble sulphides (Groudev, 1996). Both the transfer and precipitation of the metals were carried out by microorganisms related to different physiological groups, mainly acidophillic iron- and sulphur-oxidizing chemolithotrophic bacteria and anaerobic sulphate-reducing bacteria, respectively.

## Materials and methods

The soil field used in this study was located in the proximity of the Elshitza copper mine, Central Bulgaria. A detailed sampling procedure was carried out to characterize the soil and the subsurface geologic and hydrogeologic conditions of the site. Surface and bulk soil samples up to a depth of 2 m were collected by mechanical excavator. Drillhole samples were collected up to a depth of 8 m. Elemental assays in the samples were performed by digestion techniques and measurement of the ion concentration in solution by atomic absorption spectrophotometry. Mineralogical analysis was carried out by X-rays diffraction techniques. The main geotechnical characteristics of the site such as permeability and wet bulk density were measured in situ using the sand-cone method. True density measurements were carried out in the laboratory using undisturbed core samples. Such samples were also used for determination of their acid generation and net neutralization potentials using static acid-base accouting tests. The toxicity of soil samples was determined by the EPA Toxicity Characteristics Leaching Procedure (U. S. Environmental Protection Agency, 1990). The bioavailable fraction of the toxic metals was determined through leaching the samples by EDTA. The speciation of the heavy metals with respect to their mobility was determined by the sequential extraction procedure (Tessier, Campbell and Bisson, 1979).

The soil pore water level and quality in the site was monitored by means of piesometers installed in the drillholes. The parameters measured in situ included: pH, Eh, temperature, dissolved oxygen, conductivity and total suspended solids. Elemental analysis was done by atomic absorption spectrophotometry in the laboratory. The isolation, identification and enumeration of soil microorganisms were carried out by methods described previously (Groudeva, Ivanova, Groudev and Uzunov, 1993).

## Results and discussion

The soil was heavily contaminated with toxic metals, mainly copper, zinc and cadmium (Tab. 1). The metals were present mainly in the form of sulphide minerals, i.e. their mobilization was connected with a prior oxidation. This oxidation was connected with several electrochemical, chemical and biological reactions occurring in the presence of molecular oxygen, water and some acidophillic chemolithotrophic bacteria (mainly of the species *Thiobacillus ferrooxidans, Leptospirillum ferooxidans and Thiobacillus thiooxidans).*

The comtaminated soil contained its own indigenous microorganisms of the above-mentioned species. The number and activity of these microorganisms were limited, however, by some essential environmental factors such as the relatively high pH, shortage of oxygen inside the soil horizons, insufficient soil humidity during relatively long periods of time, absence of some important nutrients such as nitrogen and phosphorus sources. It was found that the inoculation of the soil with a mixed laboratory-bred microbial culture consisting of different active chemolithotrophic bacteria (mainly of the above-mentio-

Tab. 1
Characteristics of the soil treated in this study

| Characteristics | Before treatment | After treatment |
|---|---|---|
| Average density, g/cm$^3$ | 1.72 | 1.67 |
| Average wet bulk density, g/cm$^3$ | 1.32 | 1.28 |
| Average permeability, cm/s | $8 \times 10^{-2}$ | $9 \times 10^{-2}$ |
| pH | 4.5 - 5.5 | 4.4 - 5.3 |
| Content of toxic metals, ppm: | | |
| - copper | 240 - 770 | 65 - 210 |
| - zinc | 210 - 1220 | 45 - 205 |
| - cadmium | 8.2 - 23 | 1.7 - 8.2 |
| Bioavailable fraction, ppm: | | |
| - copper | 170 | 10 |
| - zinc | 210 | 14 |
| - cadmium | 3.2 | 0.5 |
| Sequential leaching (easily leachable fractions-exchangeable + carbonate), ppm: | | |
| - copper | 210 | 12 |
| - zinc | 255 | 17 |
| - cadmium | 4.1 | 0.6 |
| EPA TCLP test (riported solubilities), ppm: | | |
| - copper | 80 - 140 | 3 - 10 |
| - zinc | 95 - 170 | 8 - 23 |
| - cadmium | 0.1 - 2 | 0.1 - 0.3 |
| Pore water analyses: | | |
| - pH | 4.2 - 5.3 | 4.1 - 5.2 |
| - Eh, mV | 460 - 510 | 460 - 520 |
| - copper, ppm | 137 - 235 | 2.3 - 7.1 |
| - zinc, ppm | 170 - 275 | 5.0 - 12 |
| - cadmium, ppm | 2.8 - 4.2 | 0.3 - 0.5 |
| Net neutralization potential, kg $CaCO_3$/t | -50 | -10 |

Tab. 2
Concentrations of varios physiological groups of microorganisms in the soil before and after the treatment

| Microorganisms | Horizon A | | Horizon B | |
|---|---|---|---|---|
| | I | II | I | II |
| | Cells/g dry soil | | | |
| Aerobic heterotrophic bacteria | 7 x $10^8$ | 3 x $10^8$ | 6 x $10^6$ | 3 x $10^6$ |
| Oligicarbophiles | 6 x $10^7$ | 3 x $10^7$ | 1 x $10^6$ | 5 x $10^5$ |
| Cellulose-degrading microorganisms | 3 x $10^7$ | 1 x $10^7$ | 5 x $10^5$ | 3 x $10^5$ |
| Nitrogen-fixing bacteria | 2 x $10^6$ | 2 x $10^6$ | 5 x $10^4$ | 1 x $10^4$ |
| Nitrifying bacteria | 5 x $10^6$ | 3 x $10^6$ | 3 x $10^3$ | 4 x $10^3$ |
| Chemolithotrophic sulphuroxidizing bacteria | 9 x $10^6$ | 2 x $10^8$ | 5 x $10^3$ | 3 x $10^5$ |
| Anaerobic heterotrophic bacteria | 1 x $10^6$ | 1 x $10^6$ | 3 x $10^7$ | 2 x $10^7$ |
| Denitrifying bacteria | 8 x $10^5$ | 7 x $10^5$ | 5 x $10^6$ | 1 x $10^6$ |
| Anaerobic bacteria fermenting carbohydrates with gas production | 6 x $10^5$ | 3 x $10^5$ | 3 x $10^6$ | 1 x $10^6$ |
| Sulphate-reducing bacteria | 3 x $10^5$ | 1 x $10^6$ | 5 x $10^5$ | 1 x $10^7$ |
| Actinomicetes | 1 x $10^6$ | 5 x $10^5$ | 3 x $10^5$ | 1 x $10^5$ |
| Fungi | 1 x $10^6$ | 1 x $10^6$ | 7 x $10^5$ | 8 x $10^5$ |
| Total cells number | 9 x $10^8$ | 9 x $10^8$ | 5 x $10^7$ | 4 x $10^7$ |

Notes: I - Before treatment II - After treatment (the analyses were carried out immediately after the end of the immobilization phase, in the end of October 1993, i. e. before the remediation of the treated soil by grassing and additions of fertilizers, animal manure and line

ned species) enhanced considerably the rate of sulphide oxidation and metal solubilization. After the inoculation, the introduced microorganisms rapidly formed a stable community with the indigenous microflora. The treatment of the contaminated soil was carried out in situ by means of a flushing system. The soil was initially ploughed up (in March 1993) to a particle size less than 30 mm to enhance the natural aeration inside the upper soil horizons (A and B1). Then the ploughing was repeated several times, at least once per month, until the end of July 1993.

The microbial inoculum was added to the ploughed soil together with slightly acidified water (pH of about 3,0 - 3,5 with sulphuric acid) containing ammonium and phosphate ions. The irrigation of the soil with such solution was carried out to adjust the initial humidity of the soil to about 40 - 45 % and to provide the soil microorganisms with the most essential nutrents. Then the humidity was maintained at the desired level by periodical irrigation with above mentioned solution. During irrigation, subsurfase soil received oxygen dissolved in the solution. Then films of water were formed on the soil particles. These films were in contact with air, due to the high porosity of the soil, and oxygen diffused into the films. The oxygen transport was found not to be a rate limiting factor in this situ treatment operation.

It was found that the suitable changes of essential environmental factors in the soil ecosystem (optimum humidity, pH in the range 3,0 - 3,5, enhanced natural aeration, presence of nutrients) resulted in a considerable stimulation of the microbial activity, especially of the sulphide-oxidizing chemolithotrophic bacteria. This was connected with a steady decrease of the bioleachable metal fraction in the upper soil horizons and with an increase of the contents of soluble heavy metals in the pore solution. The soil was washed periodically with slightly acidified water to remove these soluble metals and to transfer them into deeply located soil horizons. An effective collection system was constructed to prevent solution migration and pollution of underground waters. The pregnant solutions collected by this system were treated to remove the soluble metals by means of sulphate-reducing bacteria growing in an anaerobic cell containing waste organic materials (spent mushroom compost, animal manure and straw) as sources of carbon and energy for these bacteria.

At the end of July 1993 most of the bioleachable metals were turned into mobile forms (mainly as the relevant sulphates) and were transferred into the deeply located soil horizons (mainly to the horizon B2). The treatment caused considerable changes in the composition of the soil microflora (Tab. 2) but the main physical and water properties of the soil were altered only to a small extent. The temperature of the soil was an essential factor affecting the microbial growth and activity. The highest rates of metal solubilization and removal were observed during the summer months (June-July 1993) when the temperature inside the soil profiles was the range of 17 - 32 °C. The process was efficient even at temperatures as low as 10 °C but practically stopped during the cold winter months (from December to February) as it was found by preliminary investigations carried out in another section of the same contaminated site.

After the above-mentioned stage of enhanced bacterial oxidation of sulphide minerals, the soil was washed with fresh water to increase the soil pH to its initial values of about 4,5 - 5,5. Then the soil was irrigated with water containing soluble organic compounds (wastes from the agriculture and paper industry). These organics-bearing aqueous solutions reached the soil horizon B2 and provided the anaerobic sulphate-reducing bacteria inhabiting this deeply located horizon with sources of carbon and energy. The hydrogen sulphide produced by these bacteria precipitated the soluble heavy metals in the form of the relevant insoluble sulphides. These precipitated sulphides were further immobilized by their sorption on the clay minerals present in the horizon B2. The duration of this metal immobilization phase was about three months (from the beginning of August to the end of October 1993). Then the grassing of the treated soil, the addition of certain fertilizers and animal manure as well as the periodical ploughing, liming and irrigation restored completely the physical, water and biological properties of the soil. No soluble forms of heavy metals in concentrations higher than the permissible levels were detected so far (May 1996) in the horizons A and B1 since the end of October 1993. The above-mentioned method seems especially attractive for treatment of acid soils with a high permeability and containing the metal contaminants mainly in the form of the relevant sulphide minerals. Its application depends on the presence of an impermeable geological barrier beneath the soil profiles. The treatment costs are markedly lower than those of the other in situ methods used for such purposes.

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# Bacteria membrane processes in the concentrating of heavy metals

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### Abstract

Influence of heavy metals (gold, zinc, cadmium) on the ATPase activity and transmembrane potential (ΔΨ) as integral index of bacterial cells membrane processes intensity has been studied. It was shown that studied membrane systems of bacteria are very sensitive to action of heavy metals and they can serve as an indicators of resistance or sensitivity of bacterial cultures.

**Key words:** heavy metals, membrane processes, transmembrane potential, ATPase activity

### Využitie bakteriálnych membránových procesov pri zakoncentrovávaní ťažkých kovov

Skúmal sa vplyv ťažkých kovov (Au, Zn a Cd) na aktivitu ATPázy a na hodnotu transmembránového potenciálu ako celkového ukazovateľa intenzity bakteriálnych membránových procesov. Ukázalo sa, že študované membránové systémy sú vysokocitlivé na vplyv a prítomnosť ťažkých kovov a môžu slúžiť ako indikátor citlivosti alebo odolnosti daného bakteriálneho druhu voči ťažkým kovom.

The heavy metals influence on various bacterium species manifests itself on two levels. The first level is associated with the metal shortage in the external medium that results in the functioning disturbance of the bacterium enzymes for which these metals are necessary as microelements. In this case not simple metal presence but the metal presence in accessible form for the utilization plays an important role (Sterritt and Lester, 1980; Collins and Stotzky, 1989; Gadd, 1992; Gadd and Griffiths, 1978; Gadd and White, 1989).

The second one is stipulated by the toxic action of the surplus metal quantity that causes the enzyme inactivation and/or the cell structure destabilization (Gadd and Griffiths, 1978; Karnachuk, 1995). In particular, the heavy metal toxicity can display itself by the cell permeability disturbance of membranes (Lebedev, Kuzovnikova and Phyodorov, 1987). The membrane enzymes in a system, first of all, sense the aggressive influence of surrounding medium and this affects the process run with their participation. Therefore, their sensibility can be used as an indicator of the heavy metal toxicity to a certain bacterium species, on the one hand, and can serve as the criterium of the microorganism resistance, on the other hand.

While studying the direct influence of heavy metal ions on the ATPase activity it was shown that the membrane ATPase of bacteria can be used during the assessment of the heavy metal toxicity and its mechanism as to the procariotic organisms (Gruzina, Balakina, Karamushka and Ulberg, 1996). At the same time, the indirect assessment methods for the metal toxicity based on the study of the functioning efficiency of the ATPase have been proposed ten years ago (Gadd, Mowll, White and Newby, 1986) and are successfully applied for the investigation on the interaction of the eucariotic unicellular organisms with heavy metals (Karamushka and Gadd, 1994; White and Gadd, 1987).

In order to develop the knowledge about the specific response of the bacterial cells on acting by heavy metals on them, the influence of ions of gold ($KAuCl_4$), zinc ($ZnCl_2$) and cadmium ($CdCl_2$) on the integral intensity index of the membrane processes - the transmembrane potential (Δ Ψ), one of the main generators of which is the ATPase was studied in the presented paper.

## Materials and methods

*Bacillus cereus* ATCC 14579, *Bacillus cereus* B4368 and *Alcaligenes eutrophus* CH34 bacterial strains were used in the work. The *B. cereus* B4368 strain was separated from the technogene waters contaminated by heavy metals and was capable to accumulate in considerable quantities some metals, in particular, copper and gold (Ulberg, Karamuska and Gruzina et al., 1992; Karamushka, Ulberg and Gruzina, 1990; Ulberg, Karamushka, Gruzina, Chopik and Dukhin, 1990). The museum strain *B. cereus* ATCC 14579 was taken for the comparison. The initial strain *A. eutrophus* CH34 contained plasmids determining the resistance to many heavy metals (Diels and Mergeay, 1990) and was kindly supplied by doctor L. Diels (VITO, Mol, Belgium).

The biomass of all cultures was concentrated by centrifugation and was reprecipitated in the medium containing 25 7 mM of tris-HCl, pH 7.5, 1 % of glucose (medium A). During the investigation of toxicity of the zinc, cadmium and gold chlorides (the gold chloride was in the tetrachloroaurate form, $HAuCl_4$) was used.

The plasmatic membranes were separated from the cell bacteria and were analyzed by previously described methods (Karamushka, Ulberg and Gruzina, 1990). The specific ATPase activity of the preparations was registrated as the increasing of the inorganic phosphate concentration (Pinorg) in the medium by the Fiske-Subbarow's method (Fiske and Subbarow, 1925). The results were represented in the relative units A/Ao, where Ao is the rate of the ATPase response of the intact plasma membrane, A is the same index for the membrane preparations modified by additions.

The measurement of the bacterium transmembrane potential was carried out by the penetrating ion methods (Skulachyov, 1989; Grinius, Daugelavichus and Alkimavichus, 1980).

The curves given in the Figures are typical in the series including not less than three repetitions.

## Results and discussion

Earlier (Gruzina, Balakina, Karamushka and Ulberg, 1996) we had investigated the sensivity of the membrane ATPase of the bacterial strains *A. eutrophus* CH34 as to the heavy metal row (Au, Cu, Zn, Co, Mn) and it was shown that the efficiency of the inhibition of the ATPase activity by the given metals coincided with the efficiency of their inhibiting influence on the growth of the bacterial cultures under investigation. In this connection we assumed that the ATPase can be one of the targets for the influence of heavy metals on the bacterial cells and the analysis of this parameter is important for the metal toxicity understanding. In this case, however, the use of the ATPase as an indicator of the toxicity is complicated by the necessity to obtain the membrane fractions and by the biochemical procedures. Therefore, we have assumed that other indices can be used as an indicator of the toxicity and the determination on which does not demand the cell destruction but which depends on the ATPase functioning and reflects the physiological state of an unicellular organism.

Such parameter can be the transmembrane potential ($\Delta\Psi$) which is formed on the plasmic membrane as a result of the ion redistribution between cytoplasm and the external medium during the ATPase and other generator functioning and reaches the values of 200 mV order (Skulachyov, 1989; Grinius, Daugelavichus and Alkimavichus, 1980). The $\Delta\Psi$ value is quite sensitive even to insignificant changes of the surrounding medium. For the *B. cereus* B4368 cells it is 170 ± 7 mV that was calculated on the base of our experimental data according to the TPP+ distribution taking into account its bonding by the cell components and with the assumption that the itracellular volume is 2 ml/mg of dry weight of bacteria (data for bacilli; Grinius, Daugelavichus and Alkimavichus, 1980). Also the *B. cereus* ATCC 14579 and *A. eutrophus* CH34 cells possessed the potential value close to the given one.

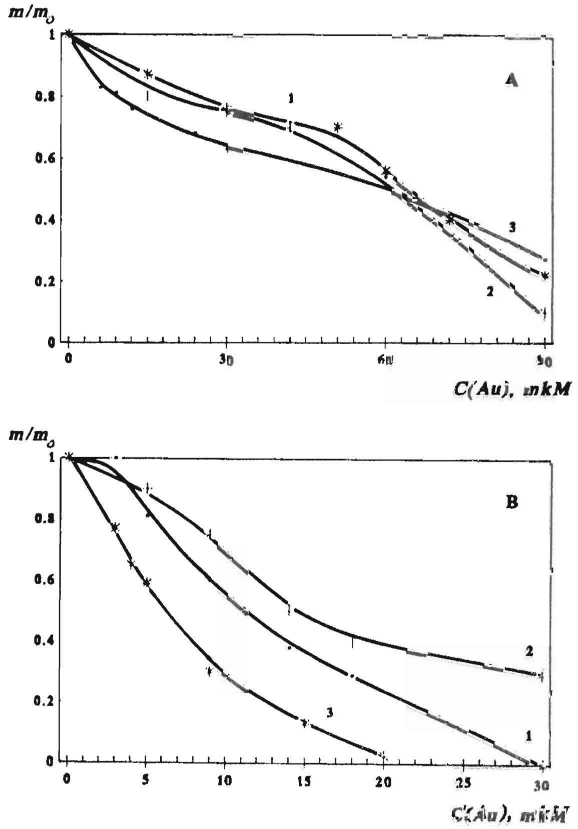

Fig. 1. The Au(III) influence on the intensity of the $TPP^+$ absorption by the *B. cereus* ATCC 14579 (1,1'), *B. cereus* OB4368 (2,2') and *A. eutrophus* OCH34 (3,3') bacteria. A - 1, 2, 3 - Au(III) is added in the medium of the $\Delta\Psi$ measurement (see Materials and methods), B - 1', 2', 3' - the cells are preincubated with the corresponding Au(III) concentrations for 10 minutes.

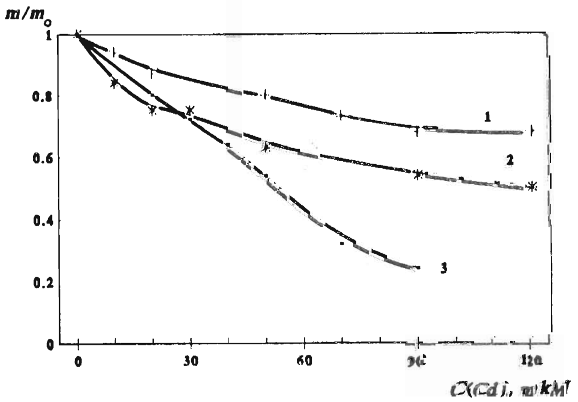

Fig. 2. The intensity of the TPP+ absorption by the *B. cereus* ATCC 14579 (1), *B. cereus* B4368 (2) and *A. eutrophus* CH34 (3) cells depending on the $CdCl_2$. The cells are preincubated with the metal for 10 minutes.

Trivalent gold introduced into the medium in the form of tetrachloroaurate rendered an oppressive action on the transmembrane potential (and consequently on the absorption of TPP+ by the bacterial cells that was experimentally registrated) of all investigated bacterium cultures

(Figs. 1 A, B). In this case the decrease in the Δ Ψ value depended on the metal order introduction. So, in the case when gold is in the medium of measurement and was in the contact with the cells during the TPP+ concentration registration, the sorption level of the latter decreased by 70-75 % for *B. cereus* ATCC 14579 (curve 1, A) and for *A. eutrophus* CH34 (curve 3, A) in the presence of 90 mM Au(III) and by 90 % for B. cereus B4368 (curve 2, A). When the cells were preincubated with Au(III) for 10 minutes, then were quantitatively transferred in cell for the potential measurement of the considerable decrease in the registrated parameter. So, already Au(III) 20 mM practically completely deprived the *A. eutrophus* CH34 of the ability to accumulate TPP+ (curve 3, B). The *B. cereus* B4368 cells looked to some extent more stable which were oppressed at the given Au(III) concentration by 60 %.

The study of the bacterial cell activity, preliminary incubated in the solution with the ions of the metals under investigation, has allowed to detect the following regularities. As it follows from Fig. 2, also in the presence of the cadmium ions, the dissipation of the transmembrane potential of the bacterium strains takes place. The toxicity of this metal, however, was substantially lower than Au(III). In particular, the ability of the *B. cereus* ATCC 14579 and *B. cereus* B4368 cells to absorb TPP+ (curves 1, 2) decreased by 30 and 50 % respectively at the final metal concentration 90-120 mM. The sensitivity of the gram-negative bacteria *A. eutrophus* CH34 (curve 3) proved to be higher (70 % oppression of their viability), in spite of their plasmide-determined resistance to a number of heavy metals (Diels and Mergeay, 1990).

The TPP+ accumulation by the *A. eutrophus* CH34 bacteria under the action of the zinc ions (Fig. 3, curve 3) decreased by 80 %. At the same time both strains of gram-positive bacilli again displayed great resistance in the investigated range of this metal concentration (curves 1, 2). Though the behaviour of these curves differs, the Δ Ψ dissipation for them did not exceeded 20-25 % at 100 mM concentration of the zinc ions.

The experiments of study of this metal influence on the ATPase activity, carried out on the membrane preparations, have shown that A. eutrophus ATPase (Fig. 4, curve 1) possessed the most sensitivity to the Au(III) action. The degree of the ferment inhibition grew with the zinc and cadmiun ion concentration increase, however, it did not exceeded 30 % of the initial activity (curves 2, 3).

For the comparision we used the *B. cereus* B4368 membrane preparations. As it is seen from Figure 4, B, all investigated metals decreased the rate of the ATP hydrolysis approximately only by 30 %. Thus, the experimental data indicate the inhibiting influence of Au(III), $Cd_{2+}$, $Zn_{2+}$ on the membrane ATPase that can be one of the reasons for the dissipation of the cell transmembrane potential. In this case the gold ions were the most toxic for the bacteria among the investigated ions. This conclusion follows both from dissipation level of the metal inhibiting concentration and from the level of the Δ Ψ dissipation. The *A. eutrophus* CH34 bacteria on both criteria proved to be more sensitive as compared with the representatives of the *Bacillus genus.* Possibly less resistance of the gram-negative bacteria is connected with the peculiarities in the structure of cellular wall that was repeatedly discussed in the literature (Beveridge, Forsberg and Doyle, 1982). On the other hand, it is shown that on treating the cells by the copper ions, the decrease in the cell

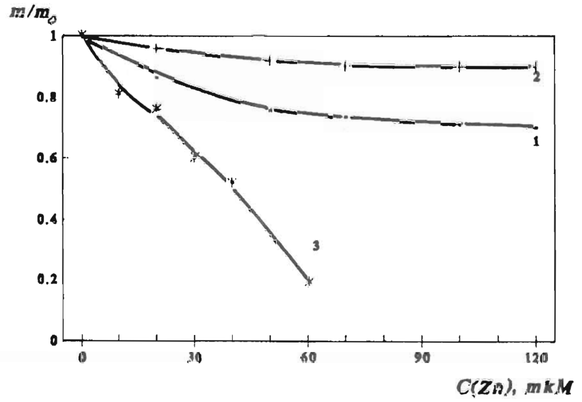

Fig. 3. The intensity of the TPP+ absorption by the *B. cereus* 14579 (1), *B. cereus* B4368 (2), *A. eutrophus* CH34 (3) in the presence of $ZnCl_2$. The cells are preincubated for 10 minutes.

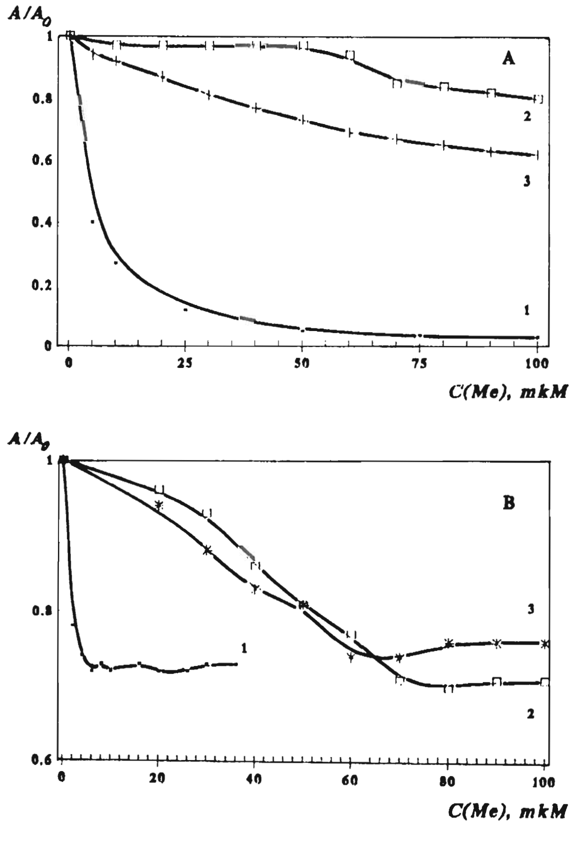

Fig. 4. The $HAuCl_4$ (1,1'), $ZnCl_2$ (2,2') and $CdCl_2$ (3,3') influence on the ATPase activity of the plasmic membranes of *A. eutrophus* CH34 (A) and *B. cereus* B4368 (B). Incubation medium: 10 mM of tris-HCl (pH 7.8); 3 mM of $MgCl_2$; 3 mM of ATP.

transmembrane potential of the gram-negative *E. coli* occurred as a result of the membrane barrier property disturbance and increase in the membrane conductance for the cations (Lebedev, Kuzovnikova, Kornev and Phyodorov, 1987; De Rome and Gadd, 1987). Au(III), as it was shown previously (Gruzina, Balakina, Karamushka and Ulberg, 1996; Karamushka, Ulberg and Gruzina, 1991), exceeds the copper ions in the row of the efficiency of the growth inhibition and the bacterium ATPase activity. Therefore, its expressed toxicity can display itself, on the one hand, directly in the inhibiting influence on ATPase and other main $\Delta\Psi$ generators (Karamushka, Ulberg and Gruzina, 1991) and on the other hand, in the destabilization of the plasmic membrane and in the disturbance in the process of oxidizing phosphorescing.

All above said allows to suppose that the described membrane processes of the bacteria are quite sensitive to the heavy metals action and can be used in the assessment of their toxicity and while explaining their mechanisms.

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# Applicability of cultures of higher fungi to biosorption of cadmium

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## Abstract

Fungal pellets (diameters ranging from 2 to 10 mm) were obtained from submerged cultivations on glucose/corn-steep medium. Native and processed pellets of wood-rotting basidiomycete *Phanerochaete chrysosporium* were used for a comparison of cadmium removal from 100 ppm solution. Native and autoclaved pellets showed only negligible difference in Cd uptake, as well as pellets previously cultivated in the presence of Zn. The treatment of autoclaved pellets with NaOH strongly increased their binding capacity, while the treatment with HCl was not effective.

### Možnosti využitia bunkových kultúr vyšších húb na biosorpciu Cd

Pelety s obsahom húb (priemeru 2 - 10 mm) sa získali submerznou kultiváciou húb v médiu s obsahom glukózy a kukuričného výluhu. V štúdii sa využila drevokazná bazidiomycétna huba *Phanerochaete chrysosporium.* Pelety sa získali zo živých alebo usmrtených a následne spracovaných buniek. Biosorpčná schopnosť sa testovala pri počiatočnej koncentrácii kadmia (od 100 ppm). Medzi živými a usmrtenými bunkami a bunkami kultivovanými v médiu s prídavkom Zn neboli zásadné rozdiely. Biosorpčná schopnosť usmrtených (autoklávovaných) buniek bola stimulovaná pôsobením NaOH. Prídavok HCl po autoklávovaní viedol k zníženiu sorpčnej schopnosti.

## Introduction

Biosorption may be used as an additional step in chemical removal of toxic metals from industrial water. This process involves in binding heavy metals to the outer structures of cells. Different biological material has been tested so far, including filamentous bacteria, yeasts, algae or fungi (Voleský and Holan, 1995). Filamentous bacteria or filamentous fungi, generated as waste by-product of large-scale industrial fermentations served as sources of highly effective and economic metal biosorbents in many studies (Siegel et al., 1990; Fourest et al., 1994; Brady and Tobin, 1995). Only several investigators have worked on metal accumulation using mycelium of higher fungi (e. g. Nakajima and Sakaguchi, 1993; Sanglimsuwan et al., 1993; Gabriel et al., 1994).

The aim of this work was to compare biosorption of cadmium to native and processed mycelium of wood-rotting basidiomycete *Phanerochaete chrysosporium.*

## Material and methods

*Fungus and cultivation.* The basidiomycete *Phanerochaete chrysosporium* (CCBAS 571) was cultivated on liquid glucose/corn-steep medium (Gabriel et al., 1994). Pellets from exponential phase of the growth were harvested, washed and immediately used for biosorption experiments. Pellets from stationary phase of the growth were harvested, autoclaved and then washed with water. Part of autoclaved pellets was then treated with either 5M NaOH or 1M HCl for 12 h at laboratory temperature. After washing with water (to neutral pH) the pellets were used for biosorption experiments. Zinc pre-treated pellets were obtained from submerged cultivation in the presence of 1 mM or 0.1 mM zinc acetate. Dry weight of all types of pellets was determined.

*Biosorption.* Cd uptake was studied in 250 mL Erlenmeyer flasks. Pellets (5 g wet weight) were incubated with 25 ml of 100 ppm cadmium nitrate (pH 5.90, unbuffered). Samples (0.5 mL) were taken after 0, 5, 10, 15, 30, 60 and 120 min of incubation and were centrifuged before analysis.

*Cadmium determination.* Concentration of cadmium in solutions was determined chromatographically as a complex with diethyldithiocarbamic acid using a reversed-phase stationary phase as described previously (Gabriel et al., 1996).

## Results and discussion

Wood-rotting fungi similarly to other filamentous fungi form branching mycelium. When cultivated submergedly, wood-rotting fungi give pellets with diameter ranging from 2 mm to 2 cm. Electron microscopic photography of mycelial pellet shows individual hyphae

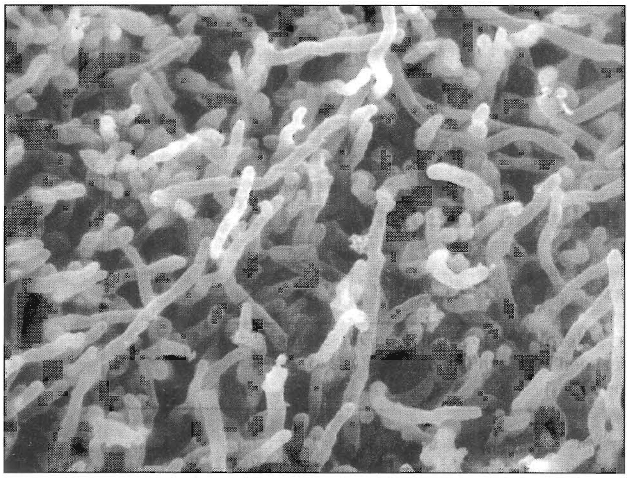

Fig. 1. Surface of *Phanerochaete chrysosporium* pellet from a 6-d submerged cultivation (Magn. 1350 x).

(Fig. 1). Mechanical properties of pellets of wood-rotting fungi are similar to those of lower fungi, and they can be easily cultivated on various sugar containing industrial wastes. Contrary to mycorrhizal or other terrestrial species they can be found in high yields in submerged cultivation.

In our previous work, cadmium biosorption to native pellets of 20 species of wood-rotting fungi was studied (Gabriel et al., 1996). In some basidiomycetes, cadmium uptake was higher than 100 mg Cd/g dry biomass which is considerable higher value than that achieved with *Rhizopus* sp., *Penicillium* sp. or yeasts (Voleský and Holan, 1995). Here, we report different biosorption of cadmium to native and processed pellets of the white-rot basidiomycete *Phanerochaete chrysosporium.*

Tab. 1
Cd removal from solution after 2 h of incubation at 25 °C
(initial concentration 100 ppm)

| Biosorbent (P.chrysosporium) | Cd removal (in %) | Cd content in pellets (mg Cd/g d.w.) |
|---|---|---|
| Native pellets | 59.0 | 10.89 |
| 1.0 mM Zn pre-treated | 64.0 | 7.17 |
| 0.1 mM Zn pre-treated | 64.2 | 11.26 |
| Autoclaved pellets | 62.7 | 7.11 |
| 5M NaOH treated | 100.0 | 9.43 |
| 1M HCl treated | 14.0 | 1.36 |

Native pellets were obtained from a 6-d cultivation on nutrient rich liquid medium. Biosorption of Cd to dead mycelium was performed with autoclaved pellets from a 20-d cultivation. In addition, some autoclaved pellets were underwent to further treatment with NaOH or HCl as described in Material and Methods. Possible effect of biogenic metals as "inductors" of metal binding sites was tested with zinc supplemented to the culture medium before inoculation.

Under the conditions described, equilibrium concentration was reached within 1 - 2 h. Efficiency of Cd removal was calculated from samples taken after 2 h of incubation. Cd content in mycelia was calculated from the Cd content in solution (followed by HPLC) and from the dry weight, which ranged from 2.6 to 5.3 % of the wet weight. No sorption of cadmium on glass flasks was observed. Each sorbent was tested in triplicate.

Native pellets of higher fungi have been reported as efficient biosorbents for precious metals such uranium (Nakajima and Sakaguchi, 1993) or toxic metals such cadmium (Gabriel et al., 1996). Our results indicate further possibilities of improvement of heavy metal biosorption by mycelial biomass of higher fungi. Addition of zinc to the culture medium enhanced only slightly metal binding capacity of pellets. Cadmium uptake was significantly affected by the acidic or alkaline treatment of the autoclaved pellets. 5M NaOH treated pellets accumulated 90 % Cd from the solution during 1 h. No cadmium was detected after 2 h (Tab. 1). Reduced uptake was observed in the case of autoclaved mycelium treated with 1M HCl, probably due to partial destruction of binding sites.

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# Metallophilic microorganisms from metal contaminated sources: properties and use in mineral biotechnology

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### Abstract

Metallophilic microorganisms (MM) are those which possess at least one of the properties mentioned below i) inability to live under low metal concentration in the medium (so called hallophiles); ii) capability to survive under relatively high metal concentration (resistant/tolerant microorganisms) and iii) capability to concentrate metal from water and/or soils by any possible mechanism. Collection of MM has been created in the Institute of Biocolloid Chemistry, Kyiv.

Collection includes bacteria, cyanobacteria, microalgae and fungi obtained from technogenic water (waste of juvelery and gold enterprises, ore water of mining factories, etc.) and natural sources (Charnobyl zone soils, gold ores from Middle Asia and Russian Far East, deposits of tungsten and other metals, etc.).

Some properties of microorganism have been investigated. It was shown that MM included in the Collection can be used in biotechnological processes for i) biosorbtion of heavy metals, ii) enrichment of raw material which contains precious metals by bioflotation and for iii) biodestruction of metallocomplexes (first of all, cyanocomplexes).

The some results of properties investigation of MM from the Collection and experiences of MM use in the processes of metals removal from contaminated water and raw materials treatment are discussed.

**Key words:** metallophilic microorganisms, heavy metals, biosorption, bioflotation

### Vlastnosti a biotechnologické využitie metalotrofných mikroorganizmov zo zdrojov kontaminovaných kovmi

Metalotrofné mikroorganizmy (MM) sú také, ktoré vykazujú aspoň jednu z týchto vlastností: 1. schopnosť prežívať a rásť iba v médiach s určitými minimálnymi koncentráciami kovov (tzv. halofily); 2. schopnosť prežívať (a rásť) aj v médiach s extrémne vysokými koncentráciami kovov (rezistentné alebo tolerantné mikroorganizmy); 3. schopnosť ľubovoľným mechanizmom akumulovať alebo koncentrovať kovy z vôd a pôd. V Inštitúte biokoloidnej chémie v Kyjeve bola vytvorená zbierka MM. Zbierka obsahuje baktérie, cyanobaktérie, mikroskopické riasy a huby izolované z technogénnych vôd (napr. z podnikov na výrobu bižutérie a spracovanie zlata, podnikov na ťažbu rúd, atď.) a prírodných zdrojov (pôd z oblasti Černobylu, ložísk zlatých rúd zo Strednej Ázie a ruského Ďalekého Východu, atď.). Skúmali sa už aj niektoré vlastnosti MM. Ukázala sa možnosť ich využitia na biotechnologické účely, a to: biosorpciu ťažkých kovov, bioflotačné obohacovanie rúd obsahujúcich drahé kovy, biodeštrukciu metalokomplexov (najmä kyanokomplexov). Článok zhŕňa poznatky o vlastnostiach MM a ich biometalurgickom využití.

## Introduction

It is well known that many aquatic microorganisms can accumulate dissolved heavy metals and radionuclides from their surroundings (Greene and Darnall, 1990; Gadd, 1988; White and Gadd, 1990). Moreover, some microorganisms can take up metals and their insoluble compounds in fine dispersed form (Weinrigth, Grayston and De Jong, 1986). It was shown that such processes can be quite selective (Ovcharenko, Ulberg, Pertsov, Kogan and Garbara, 1987). Microorganisms capable to be resistant or tolerant to heavy metals, to accumulate metals in dissolved form as well as to aggregate with colloidal and fine dispersed mineral particles and those inable to live under low metal concentration in the medium (so called hallophiles) were called "metallophilic" (Ovcharenko, Ulberg, Pertsov, Kogan and Garbara, 1987). To date, such microorganisms have many implementations in the processes of metal containing water purification because biosorption and bioaggregation are of importance for the removal of potentially toxic and/or valuable elements from natural and waste waters. Biotechnological processes of water purification and mineral resourses treatment can not fully substitute physicochemical techniques developed. However, due to some advantages (relatively low cost, environmental and economical profit, possibility to recycle extracted metals, reuse of biosorbent regenerated, etc.), biotechnology seems to be promising and effective for the solution of certain concrete problems.

The paper presents some results of technogenic metallophilic microbial strains formation, investigation and using.

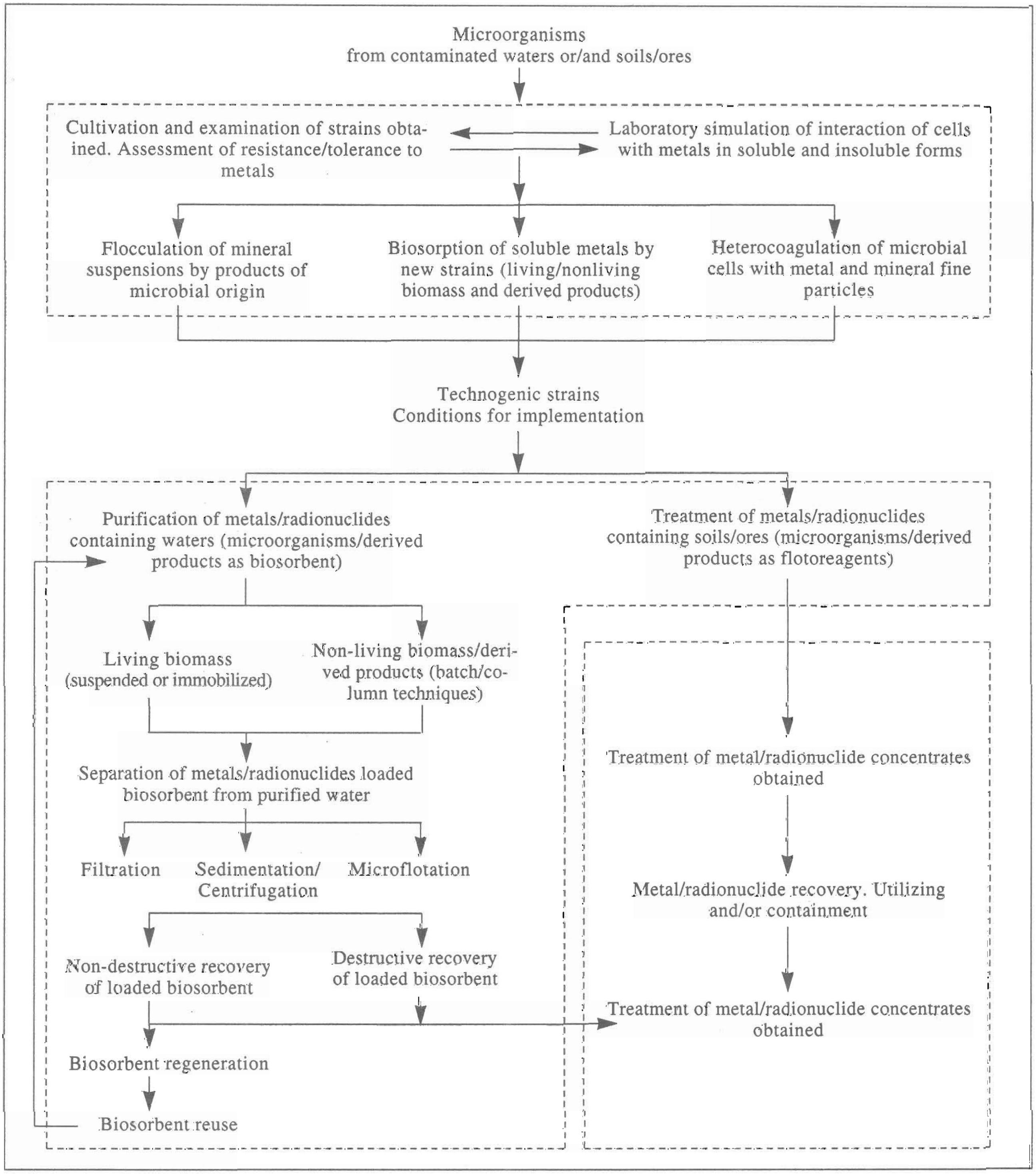

Fig. 1. Generalized scheme of the removal of heavy metals/radionuclides/compounds from aquatic (waste/natural waters) and solid (soils/ores) sources.

## Methodology

Methods of Bacteria and Algae strains separation, purification, identification, cultivation, characterization as well as methods of biomass preparation are described in the papers (Karamushka, Gruzina and Skljarov, 1992; Garbara, Stepura, Ulberg and Pertsov, 1992; Ulberg and Garbara, 1990).

Description of the methods of investigation of microorganism/metal interaction, flotation and relevant analytical procedures are presented in details in the previous publications (Ulberg, Karamushka, Vidybida, Sericov, Dukhin, Gruzina and Pechenaya, 1992; Karamushka, Gruzina and Skljarov, 1992; Garbara, Stepura, Ulberg and Pertson, 1992; Stepanenko and Garbara, 1992).

### *Technogenic microbial strains*

The scheme depicted in Fig. 1 shows that general approach to the creation of new biotechnological processes in combination with other techniques for metal containing waters and soils/ores treatment consists of three stages. Formation of the specific technogenic strains is first one of them. This stage includes separation of microorganisms from contaminated waters and/or soils/ores, their cultivation, examination, identification and laboratory simulation of the processes of soluble metal biosorption, coagulation of cells with metal/mineral disperse particles and mineral suspensions flocculation by products of microbial origin. The most effective strains obtained on this stage are the technogenic ones. They are used in the real processes of water purification (biosorption technologies) and the treatment of metals containing soils (ores) (bioflotation technologies) (second stage). The metal concetrates obtained are subjected non-biological treatment to get final product on stage 3.

### *Biosorption properties of microorganisms*

As can be seen from the data presented in Fig. 2, living cells of certain strains can rapidly accumulate the ionic gold introduced into the medium at low (subletal) concentrations. Free metal concentration in the medium, after sharp decrease, remains unchanged and an apparent equilibrium in the system is reached within a few minutes. But at first, the sorptional efficiency of different strains are very diverse (curves 1, White and Gadd, 1990; Weinrigth, Grayston and De Jong, 1986; Ulberg, Karamushka, Vidybida, Sericov, Dukhin, Gruzina and Pechenaya, 1992; Ovcharenko, Ulberg, Pertsov, Kogan and Garbara, 1987). At second, value of this parameter for microbial cells inactivated by heating on the water bath is much lower (curves 1-2). The data obtained indicate that we are dealing with a complex process, which cannot be regarded as a solely physico-chemical sorption. There are many factors influencing accumulation process. Most essential of them are i) type (strain) of microorganisms; ii) physiological state of microbial cells/culture; iii) physico-chemical characteristics of external medium (type and concentration of ions, temperature, pH, etc.). For example, the sorptional properties of biomass change sharply in mixed solutions (Fig. 3) and this feature can be used for biosorbent construction. Therefore comprehensive examination of microbial behaviour in metal ions solutions is necessary to choice most convenient biosorbent.

### *Microbial interaction with mineral particles*

It was revealed that some of the examined microorganisms possess an property to aggregate with metal sol

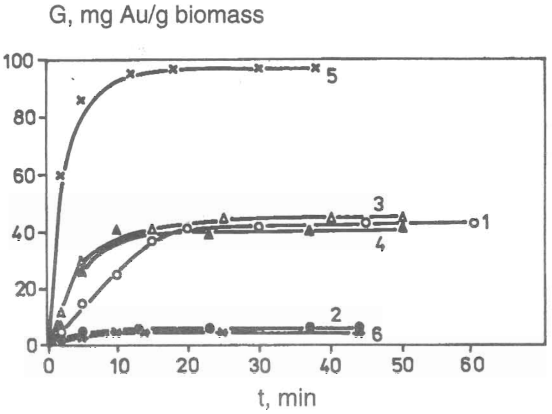

Fig. 2. Ionic gold accumulation by Bacillus cereus B4368. (1 - living, 2 - inactivated cells), Bacillus subtilis B1727 (3), Pseudomonas iodinum sp. (4), Chlorela vulgaris A10 (5) and Spirulina platensis sp. (6) in model batch systems. Initial gold concentration, 0.03 mM; biomass concentration, 120-130 (1-4, 6) and 80 (5) mg dry weight/L.

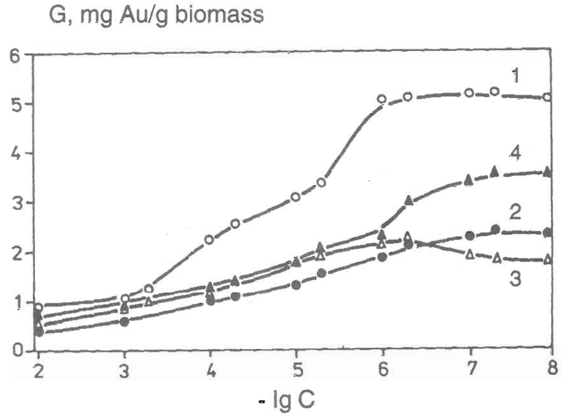

Fig. 3. Ionic gold accumulation by living (1, 2) and inactivated (3, 4) cells of Spirulina platensis sp. in the presence of manganese ions. Gold (tetrachloroaurate) was added before (1, 3) and 15 min after (2, 4) manganese.

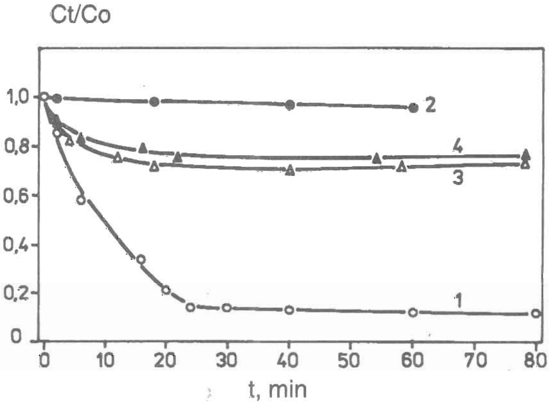

Fig. 4. Kinetics of the concentrating of gold particles by the bacteria. Co - initial gold sol concentration, Ct - concentration of gold sol not linked by the cells at the time moment t. Incubation medium: 2,5 mM Tris-HCl (pH 7.8), 7.35 mg of gold in 1 L (Co), 70 mg of cells dry weight in 1 L (1): 5 mM Na, K-phosphate buffer (pH 7.5), 12.75 mg of gold in 1 L (Co), 150 mg of cells dry weight in 1 L (2-4) as well as 0.001 mM gramicidin D (2), 0.00001 mM pentachlorophenol (3). Cells was washed after preincubating in the medium with 0.0001 mM PCP in the case (4).

particles in solutions and to form stable bioaggregates with finely dispersed particles. For example, Bacillus cereus B4368 living cells are quite effective in the process of interaction with colloid gold (Ulberg, Karamushka, Vidybida, Sericov, Dukhin, Gruzina and Pechenaya, 1992).

Special experiments on analyzing the stability of a biomineral aqueous suspensions of living microbial cells and mineral particles ascertained three essential facts. Firstly, arbitrarily selected microorganisms at incubation in a suspension with arbitrarily selected hydrosols are in number of cases capable of forming combined aggregates.

Secondly, at the existence of such an interaction living cells aggregate with sol particles much more effectively than inactivated cells of the same strain do. And, thirdly, the degree of heterocoagulation of cells of one and the same strain of microorganisms is substantially dependent on the nature of sol particles.

Among the microorganisms there turned out to be such ones that effectively fixed gold sol particles on their surface. The testing of wild and museum strains of bacteria, performed in our laboratory, demonstrated such strains to be encountered fairly often (Garbara, Stepura, Ulberg and Pertson, 1992). We selected from them the bacteria *Bacillus cereus* B-4368 for the model studies (Ulberg, Karamushka, Vidybida, Sericov, Dukhin, Gruzina and Pechenaya, 1992).

When these cells had been taken at the exponential phase of growth or at the beginning of the strationary phase, the nutrient medium had been washed off, and an aliquot of colloidal gold solution had been added to the suspension, after 30 minutes practically all the metal particles were fixed by cells, which then sedimentated slowly (Fig. 4, curve 1). It is important to note that process of heterocoagulation can be blocked by using of metabolic inhibitors (curves 2-4) and this feature we used for control of bioabsorption (Karamushka, Gruzina and Ulberg, 1995).

Tab. 1
Efficiency of flocculation of insoluble metal compounds by non-identified bacteria strains (Collection of Institute of Biocolloid Chemistry)

| Strain | Disperse phase | | | | | |
|---|---|---|---|---|---|---|
| | $CaCO_3$ | $SrCO_2$ | $UO_2$ | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ |
| R10-5 | - | - | ++ | - | - | - |
| R10-4 | - | - | ++ | - | - | - |
| Acr-9 | ++ | ++ | ++ | - | - | - |
| Ca-2 | ++ | ++ | - | - | - | - |
| D-13 | ++ | ++ | + | - | - | - |
| R10-6 | + | + | ++ | - | - | - |

- no flocculation, + - weak flocculation, ++ - intensive flocculation

As a rule, such interactions are specific (see Tab. 1) and therefore may be used for concentrating of certain compounds from mixed suspensions.

### *Microorganisms as flotoreagents*

The above-mentioned observations were assumed as a basis for the developed process of flotation of ultrafine gold from real industrial objects. As example, a high clay fraction of a kaolin-dickite ore, containing fine dispersed gold in amount of more than 85 %, was used in the experiments. Flotation was performed in two steps. At the basic flotation using traditional reagents, potassium butyl xanthogenate (PBX) and a foamer, gold floatable particles were transferred to the concentrate, after that, the control flotation was carried out using the biomass cells. Bacterial cells were introduced in the system in different states: the cells previously washed off from the nutrient medium residues and metabolites, and resuspended in tap water, native biomass of the cells. Another experiment was con-

Tab. 2
Indices of biofloccular flotation of fine dispersed gold. Bacillus cereus B-5039 biomass as flotoreagent

| No. | Flotation products | Yield (in %) | Gold content (g/t) | Extraction (in %) | | Flotation conditions |
|---|---|---|---|---|---|---|
| | | | | From the initial | After the step | |
| 1 | Basic concentrate | 6.9 | 78.67 | 49.8 | 49.8 | Without microorganisms |
| | Control concentrate | 6.4 | 12.77 | 7.5 | 14.9 | |
| | Tailings | 86.7 | 5.37 | Total = 57.3 | | |
| | Initial ore | 100 | 10.9 | | | |
| 2 | Basic concentrate | 7.1 | 72.11 | 48.3 | 48.3 | Washed off cells, 100 g/t |
| | Control concentrate | 6.3 | 21.20 | 12.6 | 24.4 | |
| | Tailings | 86.6 | 4.79 | Total = 60.9 | | |
| | Initial ore | 100 | 10.6 | | | |
| 3 | Basic concentrate | 7.4 | 79.37 | 50.2 | 50.2 | Washed off cells, 300 g/t |
| | Control concentrate | 6.7 | 25.84 | 14.8 | 29.7 | |
| | Tailings | 85.9 | 4.77 | Total = 65.0 | | |
| | Initial ore | 100 | 11.7 | | | |
| 4 | Basic concentrate | 7.0 | 81.92 | 51.2 | 51.2 | Washed off cells, 500 g/t |
| | Control concentrate | 7.2 | 23.33 | 15.0 | 30.7 | |
| | Tailings | 85.8 | 4.41 | Total = 66.2 | | |
| | Initial ore | 100 | 11.2 | | | |
| 5 | Basic concentrate | 7.2 | 76.93 | 49.9 | 49.9 | Cells (40 g/t) with nutrient medium |
| | Control concentrate | 7.0 | 29.02 | 18.3 | 36.5 | |
| | Tailings | 85.8 | 4.11 | Total = 68.2 | | |
| | Initial ore | 100 | 11.1 | | | |

ducted with the aim to check the influence of an eluate (a solution remained after the cell centrifugation) on the flotation indices. The flotation was carried out without medium regulators at natural acidity of the pulp (pH 7.3). The results are summarized in Tab. 2.

The obtained results convincingly testify to the positive effect of specific microorganisms on flotation of fine dispersed gold.

## Conclusions

Technogenic microbial strains for use in biosorption and bioflotation processes are presented in Collection of Institute of Biocolloid Chemistry, National Academy of Sciences of the Ukraine.

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# Preliminary characterization of bacilli isolated from old mining dumps

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## Abstract

The influence of bacterial strains of Bacillus genus on the structure of mineral samples in the form of polished sections, quartz and granulated mineral-processing products of the Hodruša deposit was studied in our experiments. These bacterial strains were isolated from soil samples taken on a 15th-century-bulgunniakhs site in "Lúky pod Tanádom" near Banská Štiavnica and inoculated individually as well as in mixture. The polished sections were of an allotriomorphic and granulated structure of mineral aggregates. Quartz and alumosilicates dominated in the polished sections. There were also traces of sphalerite, galenite, rhodonite, pyrite and gold aggregates in those polished sections. The pulverulent and granulated samples included the flotation concentrate (FC), the flotation waste (FW) and the gravitational concentrate (GC). In the FC dominated sulphidical minerals, namely pyrite, sphalerite and galenite, including gold prevailing above quartz mineral phase. The FW contained the big amount of quartz and alumosilicates with admixture of sulphidic minerals. The GC was dominated by quartz. Pyrite and chalcopyrite were found in the GC quartz. The ability of studied bacteria to destruct some silicates in the presence of metal cations was confirmed by morphological changes of mineral surface in comparison with control sample after 20 days of bioleaching.

The presence of vegetative bacterial cells in Erlenmayer flasks was detected by light microscopy after their Gram staining and the spores were stained by malachite green.

The main metabolites of our bacterial strains were detected by capillary isotachophoresis method. There were detected acetic acid, butyric acid, pyruvic acid, lactic acid and formic acid. The biodegradation ability of our strains was confirmed also by the X-ray analysis as well as by the atomic absorption spectrometry.

**Key words:** Bacillus, bioleaching, silicates

### Predbežná charakteristika baktérií rodu Bacillus izolovaných zo starých banských háld

V našich experimentoch sme študovali vplyv baktérií rodu Bacillus (jednotlivých kmeňov ako aj ich zmesí) izolovaných zo vzoriek odobratých z pingového poľa vytvoreného ťažbou v 15. storočí na Lúkach pod Tanádom pri Banskej Štiavnici na štruktúru nábrusov, práškového kremeňa a práškových - zrnitých produktov úpravy z ložísk Hodruša. Nábrusy boli allotriomorfno-zrnitej štruktúry minerálnych agregátov s prevládajúcim kremeňom a alumosilikátmi, v ktorých boli vtrúsené agregáty sfaleritu, galenitu, rodonitu, zlata a pyritu. K práškovozrnitým produktom úpravy patrili: flotačný koncentrát (FC), flotačný odpad (FW) a gravitačný koncentrát (GC). Vo flotačnom koncentráte prevažovali sulfidické minerály, a to pyrit, sfalerit a galenit s obsahom zlata nad kremennou minerálnou fázou. Flotačný odpad obsahoval veľké množstvo kremeňa a alumosilikátov s prímesou sulfidických minerálov. V gravitačnom koncentráte prevažoval kremeň, pyrit a chalkopyrit. Schopnosť baktérií zúčastňovať sa na deštrukcii vybraných silikátov v prítomnosti kovových katiónov bola potvrdená na základe morfologických zmien minerálneho povrchu v porovnaní s kontrolnou vzorkou po 20 dňoch biolúhovania. Prítomnosť baktérií sa sledovala priebežne svetelnou mikroskopiou po sfarbení podľa Grama (vegetatívne bunky) alebo malachitovou zeleňou (spóry). Izotachoforetickou metódou boli tiež zistené hlavné metabolity našich kmeňov, a to kyselina octová, maslová, pyrohroznová, mliečna a mravčia. Biodegradačná schopnosť našich kmeňov bola potvrdená aj röntgenodifrakčnou analýzou a atómovou absorpčnou spektrofotometriou.

Bacteria of Bacillus genus are ubiquitous and common soil microorganisms which are, at present, one of subjects of increasing interest of researchers. One of reasons of such interest are considerations concerning their possible industrial use in solid mineral waste biodegradation as well as in biosorption of heavy metals from solutions in future. These microbial species play an important role in silicates biodegradation during process of disintegration of rocks (Karavaiko et al., 1980). The results of their activity are both geochemical and structural changes of silicate minerals and rocks. Tesic and Todorovic (1952) have proposed that so-called "silicate bacteria" belong to the *Bacillus circulans* group. They can be isolated by placing small soil particles on nitrogen-free agar media. Pure cultures can be obtained by restreaking on a nutrient agar supplemented with 0.5 % (w/v) glucose. The mechanism of microbial destruction of silicates and alumosilicates by these bacteria is not explained yet, however, it is known that their activity leads for example to the decrease of Si content in bauxites of lower quality

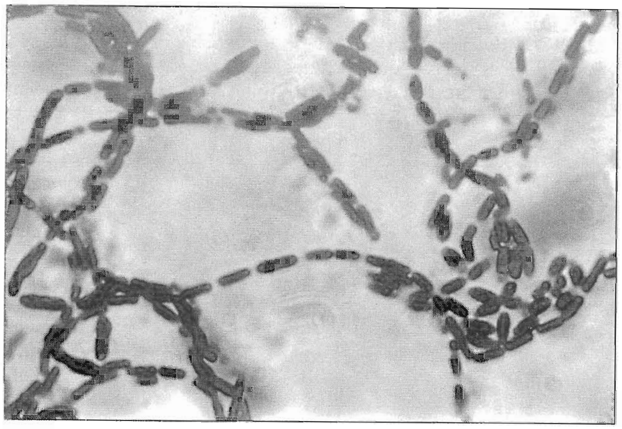

Fig. 1. Vegetative cells of Bacillus sp. after Gram staining.

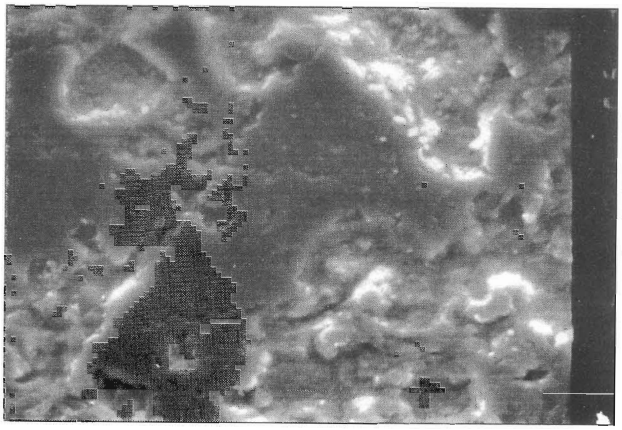

Fig. 2. The chemical destruction of quartz (magn. 2500x).

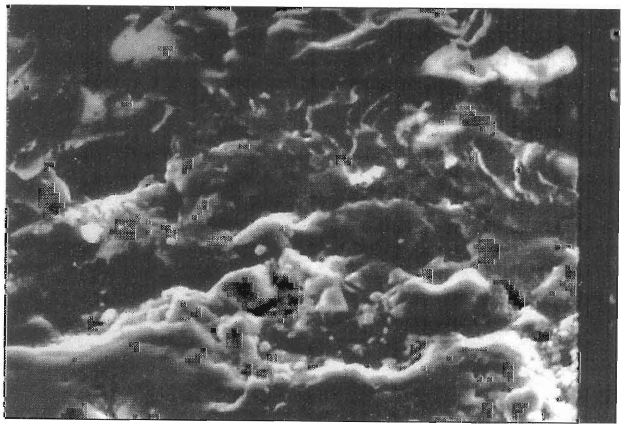

Fig. 3. The biological and chemical destruction of quartz (magn. 2500x).

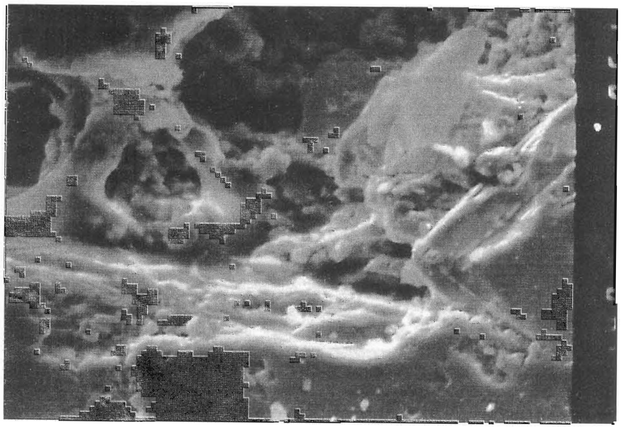

Fig. 4. The bacterial destruction of alumosilicates (magn. 1490x).

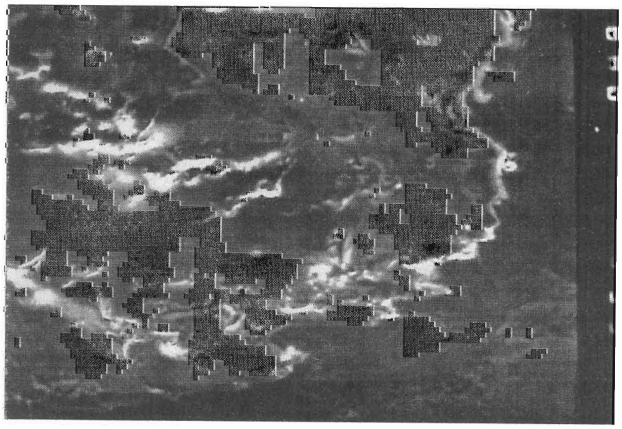

Fig. 5 A alumosilicate in abiotic control (magn. 650x).

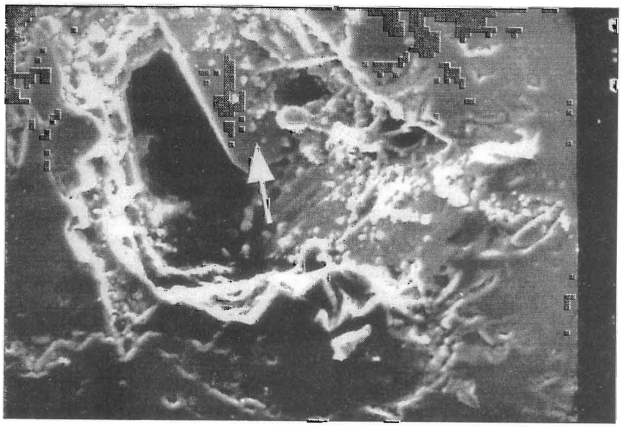

Fig. 6. Galenite visible after the biodegradation of alumosilicate (magn. 810x).

(Groudeva and Groudev, 1983), to extraction of Al, Ti, U, Au and other elements from silicates and alumosilicates (Groudev, 1990). The application of silicate bacteria in kaolin treatment may be also important, when there was observed an improvement of some physical-mechanical properties as whiteness, plasticity, firmness and decrease of fire-temperature after their activity (Groudev, 1990). There were written down also the positive results of the application of these bacteria in waste-water cleaning of toxic metals, when there were useful their bioaccumulation properties (Mullen, 1989).

Our bacterial strains of Bacillus species were isolated from soil samples taken on a 15th-century-bulgunniakhs site in "Lúky pod Tanádom" near Banská Štiavnica after

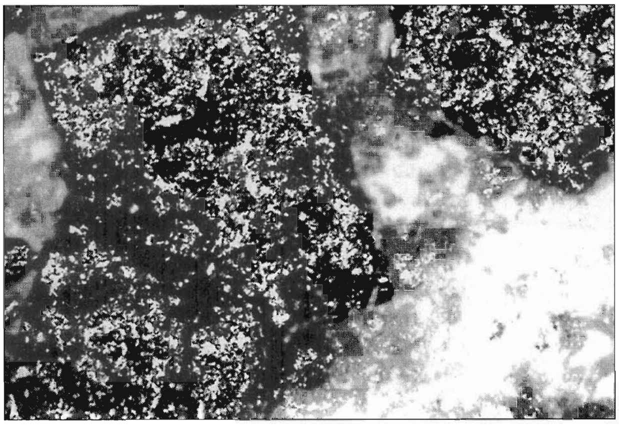

Fig. 7. Impregnated pyrites in a alumosilicate (1300x).

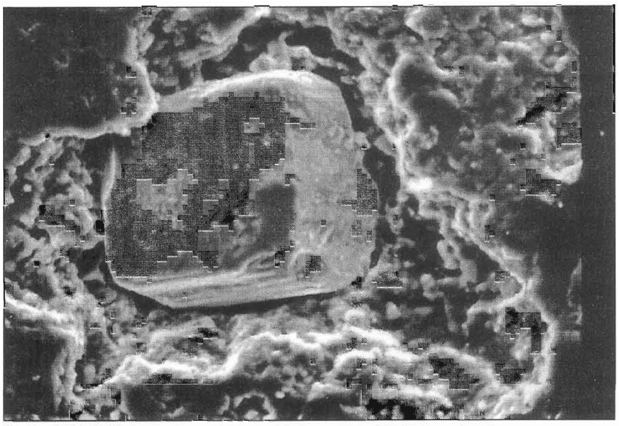

Fig. 8. The releasing of pyrite from alumosilicate by bacteria (magn. 1240x).

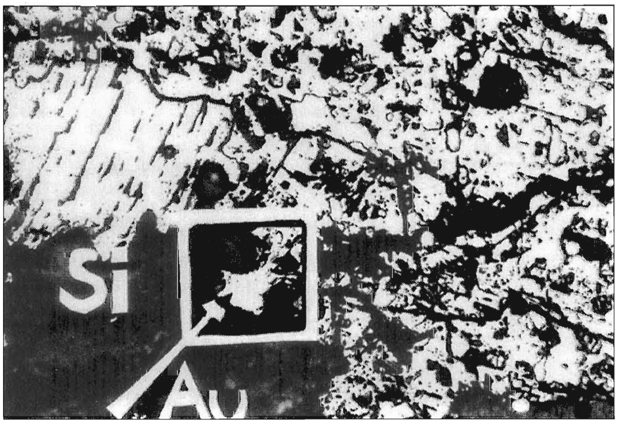

Fig. 9. The fine particles of gold in the quartz matrix (magn. 100x).

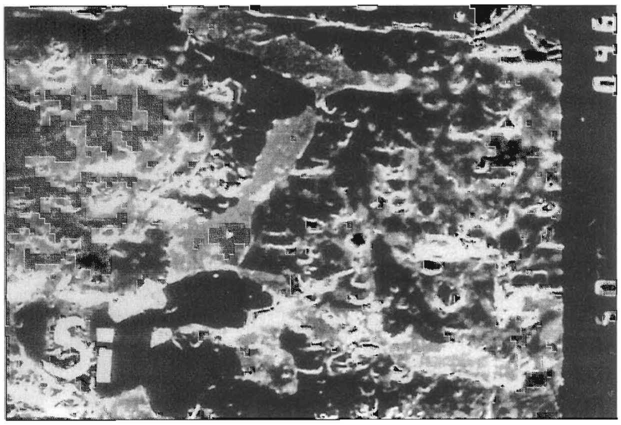

Fig. 10. Releasing of gold from the quartz matrix (magn. 500x).

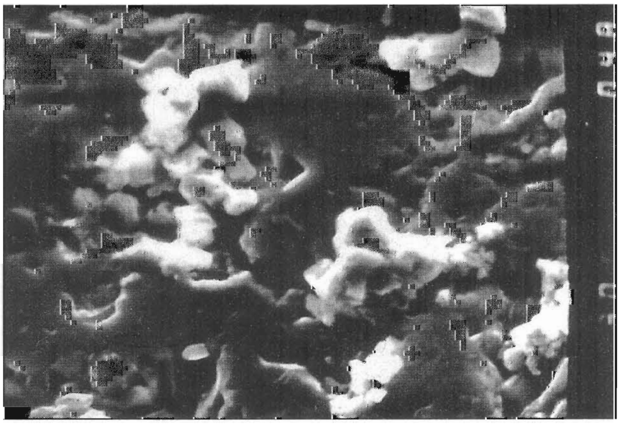

Fig. 11. Secondary chemical compounds after bacterial leaching (magn. 3000x).

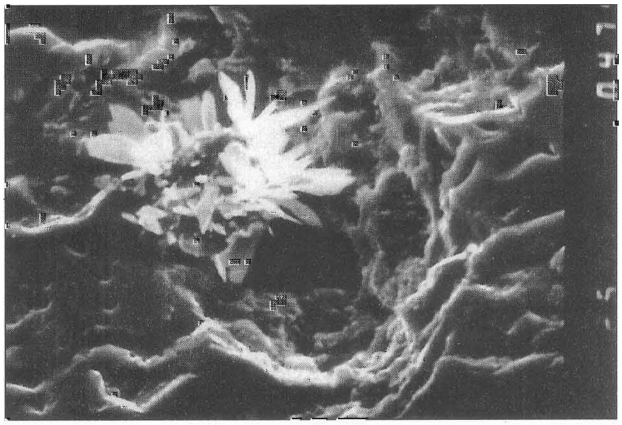

Fig. 12. Acantite was formed also after bacterial leaching (magn. 2500x).

their heating at 80 °C for 15 min to kill the non-sporoforming species. Individual bacterial strains were obtained by reisolation on Nutrient agar No. 2 (Imuna, Šarišské Michaľany) plates. Bacterial isolates formed on agar plates two types of colonies - ovoid and rhizoid. For experiment were chosen as ovoid as rhizoid colonies. These bacteria were grown in Nutrient broth No. 2 (Imuna) at 28 °C for 18 hours on a shaker with amplitude of 10 mm and turn frequency of 4 $s^{-1}$. Bacterial cells were subsequently centrifugated at 4000 r. p. m. for 15 minutes, then washed twice with saline (0.9 % NaCl) and individual strains as well as their mixture were added into Erlenmayer flasks with Ashby's solution including mineral samples.

We studied the influence of particular bacterial isolates on the structure of minerals. Mineral samples in these experiments used were in the form of:

- polished sections
- quartz
- granulated mineral-processing products of the Hodruša deposit.

The polished sections were of an allotriomorphic and granulated structure of mineral aggregates. Quartz and alumosilicates dominated the polished sections. There were traces of sphalerite, galenite, rhodonite, pyrite and gold aggregates in those polished sections, too. The pulverulent and granulated samples including the flotation concentrate (FC), the flotation waste (FW) and the gravitational concentrate (GC) were also examined. The FC was dominated by sulphidical minerals such as pyrite, sphalerite and galenite including gold in comparison with the quartz mineral layer. The FW was dominated by both quartz and alumosilicates with traces of sulphidical minerals. The GC was dominated by quartz. Pyrite and chalcopyrite were found in the GC quartz.

Bioleaching of the polished sections as well as pulverulent samples was performed in Erlenmayer flasks filled with Ashby's solution inoculated by individual bacterial isolates of Bacillus genus or their mixture. The abiotic controls were cultivated under the same conditions.

The presence of vegetative bacterial cells in Erlenmayer flasks was detected by light microscopy after their Gram staining (Fig. 1) and the spores were stained by malachite green.

The morphological changes of surfaces of individual minerals were investigated by scanning electron microscope and the changes of chemical composition by energy-dispersion analysis (EDAX) after 20 days of cultivation. The concentrations of extracted elements from pulverulent samples in the leach were determined by the atomic absorption spectrometry on a VARIAN spectrometer. The results of analyses of both leached substrates and leaches obtained by bacterial activity as well as the results of abiotic controls analyses (without bacteria) in experiments were presented earlier in the tables (Štyriaková and Kušnierová, 1995). There are seen the significant differences as among bacterial leaching of individual elements from several substrates as among leaching activities of individual strains on the same substrates. It is evident that our bacterial strains (forming ovoid as well as rhizoid colonies) intensified the extraction of many investigated elements as for example Al, Si, Pb, Zn, Cu, Au and Mn.

A part of leach of individual samples after removing of bacteria was analyzed on isotachophoretic analyser ZKI-001 (ÚRVTJ, Spišská Nová Ves) by capillary isotachophoresis method in suitable electrolytes system because of organic acids identification by our strains into leach produced. Individual samples (30 μl) were injected into the isotachophoretic analyser using a Hamilton syringe. The evaluation of organic acids was performed by method of standard addition (Boček et al., 1987). Standards of individual organic acids were purchased from Merck (Germany). Five organic acids were detected by capillary isotachophoresis method in different concentrations. The main metabolite of our Bacillus strains on each substrate was acetic acid (11-13 units). Other organic acids were produced in lower levels (butyric acid - 4 units; pyruvic acid - 3.4-3.6 units; lactic acid - 2.5-2.6 units and formic acid - 0.5-0.6 units). It is interesting to note that the organic acids production by our Bacillus strains was similar on all substrates tested. Only some non-significant differences among individual strains on several substrates were detected.

The biodegradation of the sulphidical minerals admixtures, mainly pyrite, was approved by the X-ray analysis of both the FW and the GC. As a consequence of the bacterial degradation, impregnated ultrafine particles of the sulphidic minerals were released from the dominating quartz matrix. Due to diminished granularity of the sample, the diffraction lines intensities after the bacterial leaching were twice as big as before. The FC analysis showed partial destruction of the structural plains of pyrite and sphalerite. The quartz structure was degraded by bacteria of Bacillus species to a certain degree. The destruction of the structural plain 100 was the most evident when the diffraction line intensity showed the biggest loss.

We managed to approve the ability of bacteria to destruct certain silicates in the presence of some metal ions in the medium. The evidence was given by surface morphology comparison of the silicates sample attacked by bacteria with a non-attacked control. The chemical destruction of quartz in abiotic system (Fig. 2) was less effective than the biological and chemical one after bacterial leaching (Fig. 3). The corrosive and enanatiomorphic holes are an outcome of the latter mentioned process. Bacterial destruction reached a higher degree by the Si-Al bonds cutting in the alumosilicates (Fig. 4). The alumosilicate surface was undamaged in the abiotic control (Fig. 5). The in-the-structure-impregnated sulphides (e. g. galenite on Fig. 6) were uncovered through the corrosive holes in the alumosilicates structure. Impregnated pyrites (Fig. 7) are released into the surrounding environment after the microbial attack (Fig. 8). The fine particles of gold are formed in the sulphide and the quartz matrix (Fig. 9). Gold is released from the quartz matrix (Fig. 10) to a larger amount than from the sulphide one. The biodestruction is parallel to another process. It is the crystallization of mineral products formed during the biodegradation and the formation of secondary chemical compounds (Fig. 11). Acantite (Fig. 12) is the only mineral product being identified so far.

Some years ago, only the autotrophic thiobacilli have been considered for metals recovery and detoxification of industrial waste products. Nowadays new methods are being developed for the extraction of valuable metals from oxide and silicate minerals and ores using heterotrophic microorganisms. The efficiency of heterotrophic microorganisms depends on metabolic compounds which are released into the culture medium and which will dissolve metal compounds mainly by chelating or formation of organic salts (Bosecker, 1985).

It is known, that bacilli which solubilize ores by reduction may also promote selective leaching. An example would be Bacillus GJ33 which selectively leaches Mn, Co, Ni and to some extent Cu from marine ferromanganese nodules without significantly solubilizing the iron in the nodules (Ehrlich et al., 1973).

We would like to hope that the importance of microbial leaching by heterotrophic bacteria (especially by bacteria of Bacillus species) will be continually increased. Microbial processes can be used for either solubilization of a metal value or concentration of metals. The perspective application of biotechnology in these areas will utilize native microbial species with control of process conditions to enhance their effectiveness. A long term goal will be also the genetic modification of the useful microbes to increase their utility.

Bioleaching of valuable metals from industrial waste products would not only contribute to an increase in the supply of raw materials in the future but would also be useful for detoxification of industrial waste products, thus overcoming some of our environmental pollution problems.

Although the present commercial application of microbial leaching is located outside our country, the biotechnology has the potential to become an indispensable part of the minerals industry including industrial waste biodegradation also in Slovakia.

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# Microfungi of acidificated region of Banská Štiavnica - Šobov

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### Abstract

In the contribution there are presented the results of mycological investigation of four biotops in former mining locality Šobov near Banská Štiavnica where are dumps of pyritizated material after quartz rock mining.

At present the locality is devastated by acidification. As the main pollution element is considered toxic $Al^{3+}$ in the concentrations of 76.5 to 540 $mg.kg^{-1}$ released by sulphuric acid from soil minerals into solution and water in fissure from the dump. Even heavy metals as Pb (98.9 - 181 $mg.kg^{-1}$), Cu (42.3 - 42.5 $mg.kg^{-1}$), Cd (0.09 - 1.76 $mg.kg^{-1}$) and As (19.1 - 34 $mg.kg^{-1}$) are released from soil particles into the soluble forms and the concentrations are over the limits for soils.

In the locality there were isolated microfungi from soil and water environments. The most genera were isolated from the soil biotop as follows: *Absidia, Cunninghamella, Mucor, Rhizopus, Zygorhynchus, Acremonium, Aspergillus, Paecilomyces, Penicillium, Scopulariopsis, Trichoderma, Verticillium, Cladosporium, Curvularia, Stachybotrys* and *Chaetomium.* In water environment there were isolated representatives of 3 genera: *Paecilomyces, Verticillium* and *Cladosporium.*

**Key words:** acidification, heavy metals, microfungi, toxicity

### Mikroskopické huby acidifikovaného regiónu Banská Štiavnica - Šobov

V tomto článku sú prezentované výsledky mykologického prieskumu 4 biotopov z bývalej banskej lokality Šobov pri Banskej Štiavnici. V tejto lokalite sa nachádza skládka obsahujúca pyritový materiál, odpad z ťažby kremeňa. V súčasnosti je táto lokalita zdevastovaná acidifikáciou, okyslením pôdy. Ako hlavný faktor znečistenia sú prítomné $Al^{3+}$ katióny v koncentráciách 76,5 až 540 $mg.kg^{-1}$. Sú vymývané kyselinou siričitou z pôdnych minerálov do vody odtekajúcej zo skládky. Z pôdy sú ďalej vymývané aj ťažké kovy prekračujúce najvyššie povolené koncentrácie v pôdach. Sú to: Pb (98,9 - 181 $mg.kg^{-1}$), Cu (42,3 - 42,5 $mg.kg^{-1}$), Cd (0,09 - 1,76 $mg.kg^{-1}$) a As (19,1 - 34 $mg.kg^{-1}$).

Z tejto lokality sa izolovali mikroskopické huby z pôdneho a vodného prostredia. V pôdnom biotope sa identifikovali rody *Absidia, Cunnighamella, Mucor, Rhizopus, Zygorhynchus, Acremonium, Aspergillus, Paecilomyces, Penicillium, Scopulariopsis, Trichoderma, Verticillium, Cladosporium, Curvularia, Stachybotrys* a *Chaetomium.* Z vodného prostredia sa izolovali zástupcovia troch druhov, a to *Paelomyces, Verticillium* a *Cladosporium.*

The acidification of environment that is caused by acidification esp. sulphur and nitrogen compounds can have considerable consequences during destruction of soil particles. The consequences are manifested at the places where the accumulation of acidificated substances was artificially done.

In 12th century Banská Štiavnica in middle Slovakia was well known as mining centre and activities during what many thousand meters of underground passages were done and on the surface milions of tons of deads were transported. The locality Šobov in the region has formed a dump od pyritizated material during quartz rock mining that serves as example of environment pollution by acidification.

The sulphuric acid is formed by the oxidation of pyrite in the quarry as well as in the dump and is considered as the source of pollution. The acid decomposes the structures of great amount of clay minerals and the toxic $Al^{3+}$ is released. Besides the release of $Al^{3+}$ the acidificated environment causes release even more cations from soil minerals esp. heavy metals that represent considerable ecological problem.

Because microfungi are considered as undemanding organisms with high adaptability to changed physiological conditions, they have unreplaceable role in circulation and degradation of organic matters in nature. Mainly in water environments and extreme physiological conditions (pH, some toxic compounds, heavy metals) which are toxic for organotrophic bacteria, fungi are considered as very important bioindicator of organic pollution. Even they have the ability to absorb heavy metals from environment into their thalli.

We have observed the occurrence and the presence of various genera of the microfungi in soil and water environments in the locality Šobov. On the eastern slope of the Malý Šobov hill, which is influenced by extremly high acid water (pH $H_2O/KCl = 2.11/2.0$), there were selected the places of sampling in the direction of increased acidity.

The characterization of sampling places:

1 - extremely acid water in the fissure (pH = 2.1) and it flows from the dump and causes soaking of soil in the places of sampling. It is not revitalized by common microflora of natural waters. It is considered as toxic waste water with content of heavy metals: Cd 152.6 ppb, As 3.31 ppb, Cr 593.64 ppb, Cu 16.19 ppb, Mn 139.0 ppb, Co 3.4 ppm (Forgáč et al., 1995).

2 - degradated meadow stand (0 - 2 plant species) with forming clearings 1.5 m from the erosion fissure.

3 - meadow stand (3 - 5 plant species) with necrotic Agrostis tennuis in the distance of 10 - 12 m from erosion fissure.

4 - rich meadow stand (up to 21 plant species) in the distance of 100 - 120 m from erosion fissure.

There is the soil type acid and very high acid Dystric Cambisol (KMd - FAO) with low quality of humus substances and with indecomposed unhumified organic matter. The basic microelements (Ca, Mg, K, P) are considerable flown out. The acidification caused significant increase of attainable $Al^{3+}$ (from 76.5 to 540.0 mg.kg$^{-1}$) that phytotoxically affected on it. The acidification is closely connected with the release of heavy metals into soil solution. The contents of heavy metals in soil exceeded the highest values of limits: Pb 1.2 - 2.2 times, Cu 1.2 times, Zn 1.5 - 1.8 times, Cd 2.2 times (at the place 4), As 1.2 times (at the place 1). However, increased contents of heavy metals in samples are likely caused by the occurrence of polymetallic mineralization which is typical for the region of Štiavnické vrchy (Šucha et al., 1995). From the region there were isolated and identified 16 genera of microfungi the representatives of classes Zygomycetes (5), Deuteromycetes (10) and Ascomycetes (1). The composition of fungi genera is poor (1 = 3, 2 = 8, 3 = 12, 4 = 15), Tab. 1. The representatives of the classes Deuteromycetes esp. the genera *Aspergillus, Penicillium* and *Trichoderma* isolated from all soil biotops are dominating. Only from two soil biotops there were isolated the genera *Paecilomyces, Cladosporium, Curvularia, Stachybotrys* and from the Ascomycetes the genus Chaetomium. The low occurrence of Mucorales (Zygomycetes) that require sufficient amount of easy decomposable organic substances reflects the deterioration of decomposing processes and the low quality of humus substances in soil. Their presence in per cent was the lowest (12.5 %) at the place 2 and it is represented by the genus *Absidia*. In investigated water Mucorales have not occurred. It is interesting that from water environment there were not isolated the most frequent microfungi of soil biotops of genera *Aspergillus, Penicillium* and *Trichoderma*.

Tab. 1
Genera of soil micromycetes in Banská Štiavnica - Šobov

| GENERA OF MICROMYCETES | Samples | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| ZYGOMYCETES | | | | |
| Mucorales - Mucoraceae | | | | |
| *Absidia* van TIEGHEM | | + | + | + |
| *Cunninghamella* MATRUCHOT | | | | + |
| *Mucor* MICHELI | | | + | + |
| *Rhizopus* EHRENBERG | | | + | + |
| *Zygorhynchus* VUILLEMIN | | | | + |
| DEUTEROMYCETES | | | | |
| Moniliales - Moniliaceae | | | | |
| *Acremonium* LINK ex FR. | | | | + |
| *Aspergillus* MICHELI | | + | + | + |
| *Paecilomyces* BAINIER | + | + | | + |
| *Penicillium* LINK ex FR. | | + | + | + |
| *Scopulariopsis* BAINIER | | + | | |
| *Trichoderma* PERS. ex FRIES | | + | + | + |
| *Verticillium* NEES | + | | | + |
| Moniliales - Dematiaceae | | | | |
| *Cladosporium* LINK ex FR. | + | | + | + |
| *Curvularia* BOEDIJN | | | + | + |
| *Stachybotrys* CORDA | | + | + | |
| ASCOMYCETES | | | | |
| Chaetomiales - Chaetomiaceae | | | | |
| Chaetomium KUNZE ex FR. | | + | + | |
| light sterile mycellium | | | + | + |
| dark sterile mycellium | | | + | + |

Despite the fact that the genera diversity of soil microfungi species in water was low, their survival in extremely acid water with the value of pH = 2.1 and with high content of heavy metals confirms their high adaptative ability under extreme physiological conditions. Simultaneously, there is pointed up the possibility of utilization of given characters in mentioned microorganisms during revitalization of devastated environment caused acidification.

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# Biofloccular flotation: Achievements and limitations in technology for extraction of noble metal ultrafine particles

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### Abstract

Polydispersivity and complex mineral composition of the processed raw materials as well as the association of the floated fine particles with various non-floated components are the factors hampering extraction of precious and rare-earth metals. In order to promote the solution of this problem, the use of microorganisms was proposed. It was revealed that strains of certain bacteria are able to form stable bioheteroaggregates (flocculi) on interaction with finely dispersed particles of gold, scheelite and other minerals comprising metals and metallic compounds. Such interaction can be quite selective and gives rise to the aggregates materially enriched in valuable component. The flocculi are efficiently separated from the mass of barren rock by flotation.

The experience of laboratory and commercial testing of biofloccular flotation for enrichment of gold containing sources (ores) originated from different deposites are discussed.

**Key words:** Noble metals, gold, extraction, biofloccular flotation, bacteria, bioflotoreagent, *Bacillus cereus*

### Pokroky a obmedzenia bioflokulárnych flotačných technológií využívaných na extrakciu ultrajemných častíc drahých kovov

Extrakciu drahých kovov extrémne sťažuje najmä prítomnosť ultrajemných častíc a komplexné zloženie nerastných surovín, a tiež asociácia jemných úžitkových flotovaných častíc s jalovými neflotovanými časticami. Zistilo sa, že niektoré bakteriálne kmene sú schopné tvoriť s určitými jemne dispergovanými minerálmi (zlato, scheelit a i.) selektívne stabilné bioheteroagregáty uľahčujúce flotáciu týchto minerálov.

Uvádzame prehľad laboratórnych a priemyselných aplikácií bioflokulárnych flotácií pri získavaní ultrajemných častíc drahých kovov.

## Introduction

At present, flotation and cyanation take leading place in gold mining due to constant technical improvement and high processing rate that enables large-scale production. Almost all sulphide ores particularly those which need fine dividing for opening grains, are processed by flotation. The last becomes increasingly urgent as rich and easy-enriched ores are depleted. Significant degradation of the environment stipulates reduction in the scope of cyanation, at least in processing of initial raw materials, and it is an additional stimulus for the flotation technology development.

In spite of large potentialities of flotation, certain factors adversely affect efficiency of flotation technology and thereby restrain achievement of high performance. Polydispersivity and complex mineral composition of the processed raw materials as well as the association of the floated fine particles with various non-floated components are among these factors hampering extraction of precious and rare-earth metals. Use of special microorganisms that selectively interact with finely dispersed particles of an ore, comprising metals and metallic compounds, promotes the solution of this problem.

Possibilities of the ultrafine particle flotation are substantially extended owing to the creation of a radically new model of flotation by means of special strains of microorganisms, so called biofloccular flotation. The technology has originated from a practical embodiment of phenomenon of selective heterocoagulation of microorganisms with mineral particles (Ovcharenko et al., 1985; Ovcharenko et al., 1987).

The discovered phenomenon attests that the interaction of this type may cause efficient migration and differentiated concentration of metals and their compounds in the form of microbiomineral aggregates. As differentiated from well known facts of microorganisms adhesion to various sorbents and carriers, which takes place, mainly at the expense of the molecular forces and is not specific, colloidal-bacterial interaction is characterized by the variety of forces and mechanisms as shown in (Ovcharenko et al., 1985; Ulberg et al., 1992). It was revealed that the formed aggregates are quite stable, that neither intensive agitation, nor washing with water causes separation of particles from cells.

Efficient extraction of bioheteroaggregates may be achieved by flotation after their additional hydrophobization. This possibility had been shown (Ulberg et al., 1988) in regards to the extraction of individual *Chlorella vulgaris* cells by means of modifying their surface with heavy metal cations, that caused changes of their electrokinetic potential and in related flocculation. Similar experiments were performed using bacteria cells (Bazhenov et al., 1988).

The data pertaining to the extraction of fine disperse and colloidal gold from the model systems and complex mineral suspensions are given. The results of the performed investigations reveal the perspectives of biofloccular flotation for the enrichment of ores containing precious and rare-earth metals, comprising great fraction of fine disperse particles.

## Experimental procedures

### *Microorganisms*

Microorganisms strains used in the study were bacteria obtained from existing collections as well as from natural and technogenic water containing metals and their compounds. Methods of Bacteria strains obtaining, purification, identification, cultivation, characterization as well methods of biomass preparation are described in the papers (Garbara et al., 1992; Ulberg and Garbara, 1990). Strains are deposited in the Collection of technogenic strains of microorganisms (Biocolloid Chemistry Institute, Kyiv; Ulberg et al., 1996). This paper reports the results of extraction of gold by flotation from systems comprising bacterial cells *Bacillus cereus B-5039.*

### *Ores*

Gold bearing raw materials originating from different deposits were mechanicaly treated in order to get high-disperse form (size of 65 - 90 % of particles was -0.074 mm) available for flotation.

### *Flotation*

Flotation process was performed in a pneumatic setup, comprising a glass column with a porous filter embedded in the bottom part of the column and impeller laboratory flotomashine. Potassium butyl xanthogenate (PBX) and pine oil emulsion was used as collector and foamer, respectively.

Purple hydrosol of gold was used in model experiments and prepared in accordance with standard Zsigmondi procedure.

Description of the flotation experiments with different type of ores and flotoreagents (including microbial biomass and derivates) as well relevant analytical procedures are presented in details in the previous publications (Ulberg et al., 1988; Stepanenko et al., 1992; Stepanenko and Garbara, 1992).

## Results and discussion

The data depicted in the Tab. 1 show results of model experiments and demonstrate that the interaction between potassium butyl xanthogenate as efficient gold collector and individual colloidal particles does not lead to the flocculation of the latters, but only large formations are separated in the concentrate. The cells introduced into the system in sufficient amount fix almost all the colloid gold in aggregates which nevertheless can not be transferred to the froth concentrate due to their enhanced hydrophilicity. An excessive amount of the biomass results in the formation of large flocculi, in which colloidal particles clusters are substantially blocked by the cells; flotation of such aggregates is also impeded. Preliminary modifying the cell surface with aluminium cations promotes formation of highly hydrophobic aggregates and their complete removal to the flotation concentrate.

Such observations were assumed as a basis for the process of flotation of ultrafine gold from real industrial object. A high clay fraction of a kaolin-dickite ore, containing fine dispersed gold in amount of more than 85 %, was used in the experiments. Bacterial cells were introduced in the system in different states: i) the cells previously washed off from the nutrient medium residues and metabolites, and resuspended in tap water; ii) the washed off cells treated with aluminium sulphate; and iii) native biomass of the cells.

Tab. 1
Efficiency of flocculation and of flocculi flotation in the system "gold sol + B. cereus B-5039 cells" against the relative amount of biomass and the presence of PBX

| Amount of biomass (mg/l) | Time of agitation with min | Amount of PBX (mg/l) | Gold content (in %) | | |
|---|---|---|---|---|---|
| | | | Froth concentrate | Filter | Solution |
| 2 | 2 | - | 7.4 | 18.2 | 74.4 |
| 2 | 10 | - | 7.6 | 30.3 | 62.1 |
| - | - | 20 | 0 | 0 | 100 |
| 2 | 2 | 20 | 36.2 | 8.5 | 55.3 |
| 5 | 2 | 20 | 61.4 | 6.7 | 31.9 |
| 10 | 2 | 20 | 80.8 | 6.4 | 12.8 |
| 30 | 2 | 20 | 89.3 | 5.1 | 5.6 |
| 60 | 2 | - | 44.9 | 50.7 | 4.4 |
| 60 | 2 | 20 | 92.8 | 3.7 | 3.5 |
| 120 | 2 | 20 | 83.2 | 15.6 | 1.2 |
| 60+Al(3) | 2 | 20 | 97.7 | 0.9 | 1.4 |

Another experiment was carried out with the aim to check the influence of an eluate (a solution remained after the cell centrifugation) on the flotation indices. The flotation was carried out without medium regulators at natural acidity of the pulp (pH 7.3). The results are summarized in Tab. 2.

As can be seen, obtained results convincingly testify to positive effect of microorganisms on the flotation indices of fine disperse gold. In the course of the experiments it was found that the efficiency of the flotation substantially depends on the state of the cell surface. Thus, thorough cell

Tab. 2
Indices of biofloccular flotation of fine dispersed gold. Microorganisms: *Bacillus cereus B-5039*

| No. | Flotation products | Yield (in %) | Gold content (g/t) | Extraction (in %) | | Flotation conditions |
|---|---|---|---|---|---|---|
| | | | | From the initial | After the step | |
| 1 | Basic concentrate | 6.9 | 78.67 | 49.8 | 49.8 | Without microorganisms |
| | Control concentrate | 6.4 | 12.77 | 7.5 | 14.9 | |
| | Tailings | 86.7 | 5.37 | Total = 57.3 | | |
| | Initial ore | 100 | 10.9 | | | |
| 2 | Basic concentrate | 7.4 | 78.34 | 51.3 | 51.3 | Washed off cells, 50 g/t |
| | Control concentrate | 6.5 | 14.26 | 8.2 | 16.8 | |
| | Tailings | 86.1 | 5.31 | Total = 59.5 | | |
| | Initial ore | 100 | 11.3 | | | |
| 3 | Basic concentrate | 7.0 | 81.92 | 51.2 | 51.2 | Washed off cells, 500 g/t |
| | Control concentrate | 7.2 | 23.33 | 15.0 | 30.7 | |
| | Tailings | 85.8 | 4.41 | Total = 66.2 | | |
| | Initial ore | 100 | 11.2 | | | |
| 4 | Basic concentrate | 7.3 | 73.76 | 49.4 | 49.4 | Modified cells by Al(/3), 50 g/t |
| | Control concentrate | 6.3 | 28.72 | 16.6 | 32.8 | |
| | Tailings | 86.4 | 4.29 | Total = 66.0 | | |
| | Initial ore | 100 | 10.9 | | | |
| 5 | Basic concentrate | 8.0 | 74.96 | 51.7 | 51.7 | Modified cells by Al(3), 100 g/t |
| | Control concentrate | 6.5 | 30.70 | 17.2 | 35.6 | |
| | Tailings | 85.5 | 4.22 | Total = 68.9 | | |
| | Initial ore | 100 | 11.6 | | | |
| 6 | Basic concentrate | 7.6 | 74.13 | 50.3 | 50.3 | Cells (20 g/t) with nutrient medium |
| | Control concentrate | 6.7 | 21.40 | 12.8 | 25.8 | |
| | Tailings | 85.7 | 4.82 | Total = 63.1 | | |
| | Initial ore | 100 | 11.2 | | | |
| 7 | Basic concentrate | 7.4 | 76.26 | 51.3 | 51.3 | Nutrient medium (5 ml/l) with metabolites |
| | Control concentrate | 8.5 | 8.93 | 6.9 | 14.2 | |
| | Tailings | 84.1 | 5.47 | Total = 58.2 | | |
| | Initial ore | 100 | 11.0 | | | |

washing from nutrient medium and metabolites as a matter of fact brings them in stress state and noticeably decreases their heterocoagulation properties. Best indices have been reached only at great biomass consumption. Washing is not so essential to the interaction between the cells and the gold sol because of the absence of complicating factors. Better results were obtained while using unwashed off cells, as compared with control experiment 1, total extraction grows by 11 %, whereas the extraction at the step of control flotation increases more than by 20 %. Modification of the bacterial cell surface with aluminium salts proved to be low-effective under real flotation conditions.

High residual gold content in the tailings shows that in order to extract successfully the fine gold from such complex systems as clay suspension, it is necessary to solve at least two problems. Firstly, to provide a contact of gold particles with microorganisms, and, secondly, to ensure sufficient hydrophobicity of the formed flocculi.

Significant adhesion of fine slimes, in particular clay particles, to fine dispersed gold makes it hardly accessible for flotation reagents and moreover for microbial cells. A model system prepared of kaolin and colloidal gold (gold-bearing kaolin) is extremely badly separatable by flotation. After suspension agitation with cells and added PBX the gold extraction in concentrate exceeded 20 %.

In this connection it is interesting to note the behaviour of the system and its constituents in an electrical field. Colloidal gold and quartz solutions exposed to the uniform electrical field of the intensity of 5 to 7 V/cm, factly coagulate, whereas dispersions of palygorskite or kaolin reveal only reversible concentration of particles at the anode without visible enlargement. The same behaviour in the applied electrical field is characteristic for a mixture of colloid gold and clay particles that indicates their strong binding. This adhesion interaction is not disturbed while adding bacterial cells and therefore selective separation, as in case of adagulation of colloid gold on large mineral particles, does not take place.

It is evident, one should search the solution of the problem in the combination of suspension treatment with mechanical dispersion-disintegration.

The pulp conditioning with sodium hexametaphosphate (smelted sodium polyphosphate - Graham salt, SHP) improves not only the concentrate quality, but other flotation indices. We have established that the positive effect is the most essential at joint supply of the biomass suspension and the dispersant. Earlier it was shown by the example of flotation of various samples with low initial gold content and a small number of complicating components. The results of the investigations of a clay-rich fraction are given in Tab. 3.

Prior to the basic flotation, the pulp was conditioned with sodium hydrocarbonate (80 g/t). SHP was added to the tailings of the basic flotation and the mixture was be-

Tab.3
Influence of preliminary pulp dispersing, dispersant content and hydrophobizing agents on gold extraction

| No. | Flotation products | Yield (in %) | Gold content (g/t) | Extraction (in %) From the initial | Extraction (in %) After the step | Flotation conditions |
|---|---|---|---|---|---|---|
| 1 | Basic concentrate | 7.3 | 80.36 | 51.4 | 51.4 | SHP - 20 g/t |
| | Control concentrate | 7.5 | 31.62 | 20.8 | 42.8 | PBX - 80 g/t |
| | Tailings | 85.2 | 3.71 | Total = 72.2 | | |
| | Initial ore | 100 | 11.4 | | | |
| 2 | Basic concentrate | 7.1 | 79.55 | 52.3 | 52.3 | SHP - 40 g/t |
| | Control concentrate | 7.3 | 39.06 | 26.4 | 55.3 | PBX - 80 g/t |
| | Tailings | 85.6 | 2.69 | Total = 78.7 | | |
| | Initial ore | 100 | 10.8 | | | |
| 3 | Basic concentrate | 7.6 | 74.58 | 52.0 | 52.0 | SHP - 60 g/t |
| | Control concentrate | 7.0 | 45.31 | 29.1 | 60.6 | PBX - 80 g/t |
| | Tailings | 85.4 | 2.41 | Total = 81.1 | | |
| | Initial ore | 100 | 10.9 | | | |
| 4 | Basic concentrate | 7.2 | 83.29 | 51.7 | 51.7 | SHP - 100 g/t |
| | Control concentrate | 6.8 | 51.0 | 29.9 | 6.9 | PBX - 80 g/t |
| | Tailings | 86.0 | 2.48 | Total = 81.6 | | |
| | Initial ore | 100 | 11.6 | | | |
| 5 | Basic concentrate | 7.3 | 80.24 | 52.3 | 52.3 | SHP - 60 g/t |
| | Control concentrate | 7.2 | 44.02 | 28.3 | 59.3 | PBX - 40 g/t |
| | Tailings | 85.5 | 2.54 | Total = 80.6 | | |
| | Initial ore | 100 | 11.2 | | | |
| 6 | Basic concentrate | 7.4 | 86.11 | 53.1 | 53.1 | SHP - 60 g/t |
| | Control concentrate | 6.9 | 51.65 | 29.7 | 63.3 | PBX - 120 g/t |
| | Tailings | 85.7 | 2.41 | Total = 82.8 | | |
| | Initial ore | 100 | 12.0 | | | |
| 7 | Basic concentrate | 7.1 | 83.33 | 51.9 | 51.9 | SHP - 60 g/t |
| | Control concentrate | 6.9 | 46.26 | 28.0 | 58.2 | PBX - 200 g/t |
| | Tailings | 86.0 | 2.66 | Total = 79.9 | | |
| | Initial ore | 100 | 11.4 | | | |
| 8 | Basic concentrate | 5.6 | 85.49 | 74.8 | 74.8 | Non-classified sample |
| | Control concentrate | 4.3 | 31.55 | 21.2 | 84.1 | SHP - 60 g/t |
| | Tailings | 90.1 | 0.28 | Total = 96.0 | | PBX - 80 g/t |
| | Initial ore | 100 | 6.4 | | | |
| 9 | Basic concentrate | 5.4 | 93.06 | 75.0 | 75.0 | Non-classified sample, |
| | Control concentrate | 4.1 | 16.83 | 10.3 | 41.2 | without microorganisms |
| | Tailings | 90.5 | 1.09 | Total = 85.3 | | |
| | Initial ore | 100 | 6.7 | | | |

ing mixed for 3 minutes at high speed of the impeller (3500 r/min), then the biomass was added, the speed decreased to 1700 r/min and the control flotation was carried out with adding a collector and a foamer. The SHP flow rate was changed from 40 to 200 g/tn at the step of control flotation. The results of the biofloccular flotation of non-classified ore sample ground to the grade - 0.074 mm (85 %) are given for comparison in the Tab. 3.

These results clearly demonstrate that the preliminary pulp dispersing with SHP significantly expands the possibilities of biofloccular flotation. Extraction of fine dispersed gold at the step of control flotation increases more than by 25 %, the concentrate quality improves, gold content in the tilings drops. The consumption rate of the hydrophobic agent at the step of biofloccular flotation within the investigated range does not influence the process of flotation. High indices reached for the non-classified material processing reveal expendiency of preliminary separating a clay-rich ore into slime and sand fractions. The joint presence of fine disperse particles and sand positively affects the flotation process. On the one hand, grains of large size act like "carriers" that promote flotation of the fine dispese particles, and on the other hand, the presence of solid sand fraction causes additional disintegration at the step of pulp dispersing leading to more full opening of gold particles and their interaction with a bioflocculant.

The carried out work permits to draw the following conclusions:

1. Selective interaction between the specific microorganisms and the fine dispersive gold is accompanied by the formation of large bioheteroaggregates (flocculi) which can be separated from the total mass of the ore suspension by flotation.

2. The efficiency of the selective flocculation depends on the state of the cell surface and the presence of free fine disperse gold in the ore.

3. A tendency showed by some microorganisms to form selectively bioheteroaggreates was observed not only in the systems, comprising pure metals in colloidal or ionic state, but also in the systems, comprising insoluble compounds of these metals, e. g., calcium tungstate.

This gives grounds to presume wide use of the specialized microbial cells for extraction of ultrafine particles of valuable ore components.

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# Selective coal flotoflocculation by *Rhodotorula glutinis*

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## Abstract

The paper deals with application of flotoflocculation by yeast *Rhodotorula glutinis* on the samples of hard coal sludges of the Darkov colliery in OKD. It was found from the mineralogic analysis that these sludges, deposited on the mud pit, have a high content of quality coal mass and therefore it is necessary to devote attention to their treatment. In this paper two technologies are compared: the classical flotation and flotoflocculation by yeast Rhodotorula glutinis. From the results there follows that flotoflocculation gives concentrates of better quality and the combined technology consisting of one basic and one cleaning-out flotation gives saleable concentrates with ash content under 10 %.

**Key words:** flotoflocculation, coal, Rhodotorula glutinis

### Selektívna flotoflokulácia uhlia kvasinkami *Rhodotorula glutinis*

Práca sa zaoberá aplikáciou flotoflokulácie s kvasinkou *Rhodotorula glutinis* na vzorkách čiernouhoľných kalov z odkaliska bane Darkov, OKD, a. s. Z mineralogicko-chemických analýz vyplynulo, že kaly deponované na tomto odkalisku obsahujú ešte veľké množstvo kvalitnej uhoľnej hmoty, a preto je aktuálne sa zaoberať ich úpravou. V práci su porovnávané dve možnosti úpravy: klasická flotácia a flotoflokulácia s kvasinkou *Rhodotorula glutinis.* Z výsledkov vyplynulo, že flotoflokulácia prináša lepšie výsledky v kvalite získaných čiernouhoľných koncentrátov a technológiou jednej základnej a jednej prečistnej flotoflokulácie je možné získať predajné koncentráty s obsahom popola pod 10 %.

## Introduction

The problem of fine-grained materials preparation becomes more and more important and new possibilities of their processing are being investigated. This paper deals with an actual problem of the Darkov colliery in OKD, namely the possibility of the preparation of hard coal sludges deposited on the mud pit "Novy York". Two technologies are compared: classical flotation and flotoflocculation by bioflocculant - the yeast *Rhodotorula glutinis.*

## Characteristic of the *Rhodotorula glutinis* microorganism

*Rhodotorula glutinis* is a hetherotrophic eucaryont microorganism belonging among fungi. It was given its name due to the ability to ferment monosaccharides and some disaccharides and even trisaccharides with resulting ethanol and carbon dioxide. *Rhodotorula glutinis* is an organism occurring in the nature in waste and sea waters, in soils and air but even in blossoms, olives, etc. It can also occur on human body incidentally but no pathologic ef-

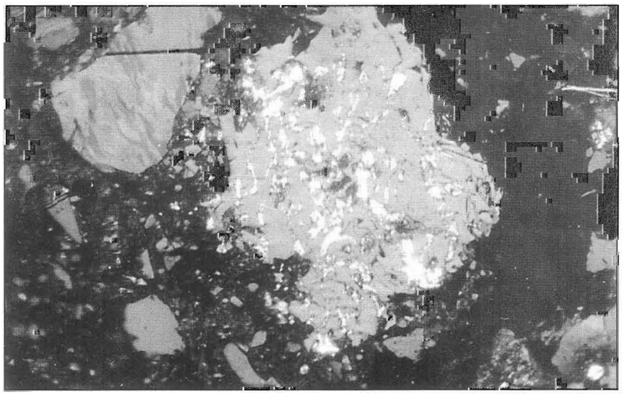

Fig. 1. The inertinite-fuzitized tissue with cells filled with ferric sulphide.

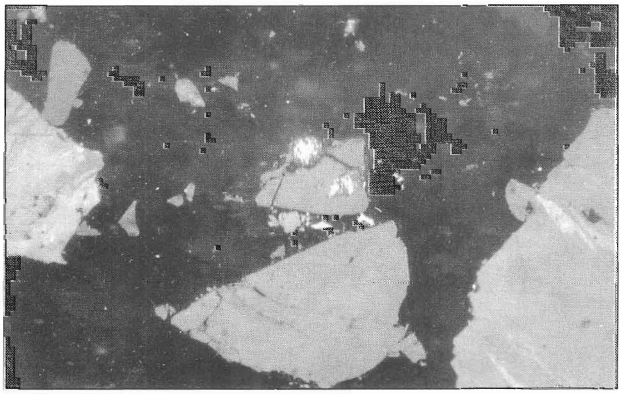

Fig. 2. The framboidal ferric sulphide in vitrinite.

Tab. 1
Results of flotation and flotoflocculation tests, sample No. 1 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 49.79 | 29.04 | 32.63 |
| Waste | 50.21 | 38.76 | 57.37 |
| Charge | 100.00 | 33.92 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 43.12 | 23.00 | 29.34 |
| Waste | 56.88 | 41.98 | 70.66 |
| Charge | 100.00 | 33.80 | 100.00 |

Tab. 2
Results of flotation and flotoflocculation tests, sample No. 2 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 60.36 | 18.16 | 38.11 |
| Waste | 39.64 | 44.91 | 31.89 |
| Charge | 100.00 | 28.76 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 44.09 | 14.09 | 23.23 |
| Waste | 55.91 | 36.71 | 76.77 |
| Charge | 100.00 | 26.74 | 100.00 |

Tab. 3
Results of flotation and flotoflocculation tests, sample No. 3 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 53.27 | 27.03 | 45.47 |
| Waste | 46.73 | 36.96 | 54.53 |
| Charge | 100.00 | 31.67 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 45.12 | 21.90 | 34.78 |
| Waste | 54.88 | 33.77 | 65.22 |
| Charge | 100.00 | 28.41 | 100.00 |

Tab. 4
Results of flotation and flotoflocculation tests, sample No. 4 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 72.58 | 18.88 | 46.83 |
| Waste | 27.42 | 56.75 | 53.17 |
| Charge | 100.00 | 29.26 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 48.18 | 18.48 | 58.05 |
| Waste | 51.81 | 35.88 | 72.46 |
| Charge | 100.00 | 25.65 | 100.00 |

Tab. 5
Results of flotation and flotoflocculation tests, sample No. 5 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 82.86 | 18.48 | 58.05 |
| Waste | 16.67 | 66.38 | 41.95 |
| Charge | 100.00 | 26.38 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 79.63 | 16.10 | 48.09 |
| Waste | 20.37 | 67.95 | 51.91 |
| Charge | 100.00 | 26.66 | 100.00 |

Tab. 6
Results of flotation and flotoflocculation tests, sample No. 6 (in %)

| Product | Yield | Content of ashes | Efficiency |
|---|---|---|---|
| | | Flotation | |
| Concentrate | 47.14 | 18.46 | 33.55 |
| Waste | 52.86 | 32.61 | 66.45 |
| Charge | 100.00 | 26.66 | 100.00 |
| | | Flotoflocculation | |
| Concentrate | 34.69 | 16.14 | 22.06 |
| Waste | 65.31 | 30.29 | 77.94 |
| Charge | 100.00 | 25.38 | 100.00 |

fects are known or supposed. The *Rhodotorula* genus differs from the others by its ability to synthetize carotenoid dyes, which gives the cultures the pink, crimson or red colours. The cultivation of *Rhodotorula glutinis* can be done on malt extract or on malt agar. During the first three or four days the cultures are of pink or light red colour. The cells are oval, 3 to 9 μms in diametre, and simple, forming only pairs or short chains. The cultures are hemispherically dished, smooth, lustrous, sometimes slimy trickling together like mucilage beads. The brims of the cultures are round and non-fibrous. Later (the seventh and following days) the cultures get light pink to red pink colour. The cells are nearly of the same size as during the previous days. The cultures are low and hemispherically dished to the centre, smooth and lustrous or semi-matte, slimy. The ability to form mucilages enables the utilization of *Rhodotorula glutinis* as natural flocculants.

## Characteristic of used coal sludges

The samples of coal sludges were taken from six sampling points at the mud pit "Nový York". The average sample was put through mineralogical-petrographical and chemical analyses. The results of maceral analysis at the

DPB Paskov company show that the average sample contains 51.0 % of vitrinite, 13.6 % of liptinite and 35.4 % of inertite. The mineralogical analysis focused on the bond of pyrite in the sample. According to this analysis, the content of pyrite is quite low, in most cases it occurs in the form of isolated grains of irregural shape. A relatively high content of ferric sulphide was found, mostly as the cell filling of fuzitized tissues. Sporadically the ferric sulphide was observed as the fissure filling, framboids and euhedra in coal grains. The inertinite - fuzitized tissue with cells filled with ferric sulphide - is shown in Fig. 1. The framboidal ferric sulphide in vitrinite is shown in Fig. 2.

The results of chemical analysis proved that the coal is of very high quality with 60.98 % of carbon and low content of ashes (19.59 %) and sulphur (0.45 %). According to the mesh analyses, the highest mass yield is cumulated in the range of less than 0,063 mms as well as the content of ashes.

## Flotation and flotoflocculation tests

The experiments were performed with the samples from all the six sampling points separately, 100 % of grains were of the size under 0.063 mms. The flotation tests were performed on the laboratory flotation machine VRF-2 (product of RD Příbram) with the flotation cell volume of 1 litre. The conditions were as follows:

- thickening: 50 grams per litre
- Flotakol NX collector charge: 300 gramms per ton
- agitation time: 1 minute
- flotation time: 5 minutes

Flotoflocculation tests were performed under the same conditions but firstly the yeast *Rhodotorula glutinis* was added and after one minute of agitation the Flotakol NX collector was added.

The results presented in Tabs. 1 to 6 show that the flotoflocculation tests provide the concentrates of much higher quality compared to classical flotation.

However, we did not achieve the demanded quality (less than 10 % of ashes) of concentrates by a simple flocculation. Therefore, the combined technology was applied in the next set of experimets, consisting of one basic and one cleaning-out flotations. The results of the combined technology are presented in Tab. 7, where only the quality of concentrates is presented.

Tab. 7
The qualities of various samples of flotoflocculation concentrates after the cleaning-out flotoflocculation phase

| Concentrate | Yield in % | Content of ashes in % | Efficiency in % |
|---|---|---|---|
| 1 | 28.16 | 11.83 | 9.96 |
| 2 | 39.00 | 7.82 | 9.82 |
| 3 | 18.79 | 10.69 | 7.18 |
| 4 | 33.73 | 8.22 | 10.39 |
| 5 | 62.83 | 8.26 | 19.01 |
| 6 | 16.87 | 8.83 | 5.76 |

According to the results presented in Tab. 7, it is possible to achieve the content of ashes lower than 10 % using the combined technology of one basic and one cleaning-out flotations. There are exception in samples No. 1 and 3 but taking into account the average sample, the average content of ashes equals to 9.28 % and therefore this technology provides a suitable means of the production of black coal concentrates in the needed quality.

## Conclusions

The objective of this research was to approve the suitability of flotation and flotoflocculation (using the *Rhodotorula glutinis* yeast) for processing the coal sludges deposited on the mud pit "Nový York" belonging to the Darkov colliery, OKD. According to the comparison of flotation and flotoflocculation tests, the concentrates of much better quality are provided using the flotoflocculation. Applying of the technology of one basic and one cleaning-out flotoflocculations, we can gain the concentrates of demanded market quality. Apart from the very good quality results, the filtrability of concentrates was improved as well.

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# The influence of biological-chemical factors on the structure of bentonite from Lastovce deposit

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## Abstract

The influence of chemolitotrophic soil microorganisms and their metabolites on the stability of structure of bentonitic clay from Lastovce deposit was observed. During the short-term 15 day contamination of bentonite by *Bacillus circulans (BC)* cca 20 % degradation of montmorillonite structure was achieved. The contamination by *Thiobacillus ferrooxidans (TF)* leads to 50-60 % degradation of montmorillonite structure and 20-25 % degradation of silicon structure. Modified medium on the base of *Aspergillus niger (AN)* metabolites caused a complete destruction of the montmorillonite structure and 50-60 % degradation of silicon structure.

**Key words:** biological contamination, biodegradation, montmorillonite, bentonite, *Bacillus circulans, Thiobacillus ferrooxidans, Aspergillus niger*

### Vplyv biologicko-chemických faktorov na štruktúru bentonitu z ložiska Lastovce

Skúmali sme vplyv chemolitotrofných pôdnych mikroorganizmov a ich metabolitov na stabilitu štruktúry bentonitického ílu z ložiska Lastovce. V priebehu krátkodobej (15 dennej) kontaminácie bentonitu s baktériami *Bacillus circulans (BC)* sa zistila cca 20 % degradácia štruktúry montmorillonitu. Kontaminácia s baktériami *Thiobacillus ferroxidans (TF)* viedla k 50 - 60 % degradácii štruktúry montmorillonitu a 20 - 25 % degradácii štruktúry kremeňa. Modifikované médium na báze metabolitov *Aspergillus niger (AN)* spôsobilo úplnú deštrukciu štruktúry montmorillonitu a 50 - 60 % degradáciu štruktúry kremeňa.

## Introduction

The processes of elements migration in litosphere are connected with degradation, transformation and constitutional procedures that run in the contact with biosphere and its various demonstrations that iniciate the course of chemical and biological-chemical reactions. The processes running in litosphere with the aim to maintain the environmental balance reside in mutual symbiosis of chemical, biological and biological-chemical procedures. They are, together with other corresponding physical and mechanical inhibitive resp. intensification factors in relation to mineral components, identified as weathering processes. They were and at present often are described as a result of absolutely chemical processes of alkalolysis, complexolysis and very often acidolysis. Consistent with the explanation of biological essence of weathering (biotransformation of sulphides and formation of deposits of supergenic enrichment) the important role of microorganisms in the weathering processes and biotransformation of other minerals and anorganic (as well as organic) substance is being gradually revealed. It can be assumed that the obtained information (as those about sulphides) will lead us to revelation and consequent industrial utilization of environmental biotechnological procedures of mineral processing which are going to be more developed from the point of view of ecology and economy. We can suppose that better knowledge enable us to regulate and maintain the environmental balance while deponing the waste of industrial orgin.

The above-mentioned reasons made us to start observing the influence of biological-chemical contamination of some industrally utilized clay minerals. The first information was obtained from experiments with bentonitic clay.

## Material

### *Microorganisms*

The changes of bentonitic clay caused by contamination by chemolitotrophic microorganisms that are present in larger or smaller amount in soil were studied. *Bacillus circullans* (Štyriaková and Kušnierová, 1995), *Thiobacillus ferrooxidans* (Kupka and Kupková, 1992) and metabolites of microscopic fungus *Aspergillus niger* (Kušnierová and Štyriaková, 1995) were used.

### *Sample*

The sample of bentonitic clay from Lastovce deposit (Slovakia) was used in the experiments. It comprised 40-50 % of montmorillonite, 10-20 % cristobalite, 20-30 % of amorphous phase, 3-10 % of silicon and 1-3 % plagioclase.

### *Methods*

To identify qualitative changes of bentonite, the methods of chemical analysis of aluminium and silicon in the leaching product using AAS were used. X-ray diffraction analyses were performed using DRON 2 equipment.

The contamination of bentonite samples by microorganisms and their metabolites was performed by short-term discontinuous leaching tests. The suspension density was 15 %, the temperature 28 °C and the continuous mixing was secured for 15 days.

### *Results*

The structural and qualitative changes, which were observed as a result of the contamination of bentonite sample by microorganisms and their metabolites are shown in Tab. 1 and Fig. 1.

The evaluation of the parts of X-ray photograms shows, that in spite of the fact that tests were extremely short (taking into consideration conditions of kinetics of biological-chemical reactions proceeding in situ), there are some changes in the structure of contaminated material. These changes were localized preferably when applying TF and BC into basal intermediate layer area of montmorillonite structure. The test with the modified agent of AN metabolites showed a complete destruction of the intermediate layer area of montmorillonite structure. The degradation of tetrahedrite structure was within the range of 40-50 %. During the experimental time the tests with BC showed relatively lowest changes, described as 20 % degradation of montmorillonite structure. Aluminium was preferably extracted into the leaching product. The 50-60 % degradation of montmorillonite structure and 20-25 % degradation of silicon structure were observed in the tests with TF. The structure of plagioclase seemed to be completely resistant. The presence of plagioclase increased as a result of degradation of montmorillonite and silicon. The small amount of silicon was in the leaching product. The most significant changes appeared in the tests with the modified agent on the base of AN metabolites. The montmorillonite structure was completely degraded and destruction of silicon was 50-60 %. Aluminium was preferably extracted, however, the silicon concentration exceeded the values recorded in the tests with BC and TF.

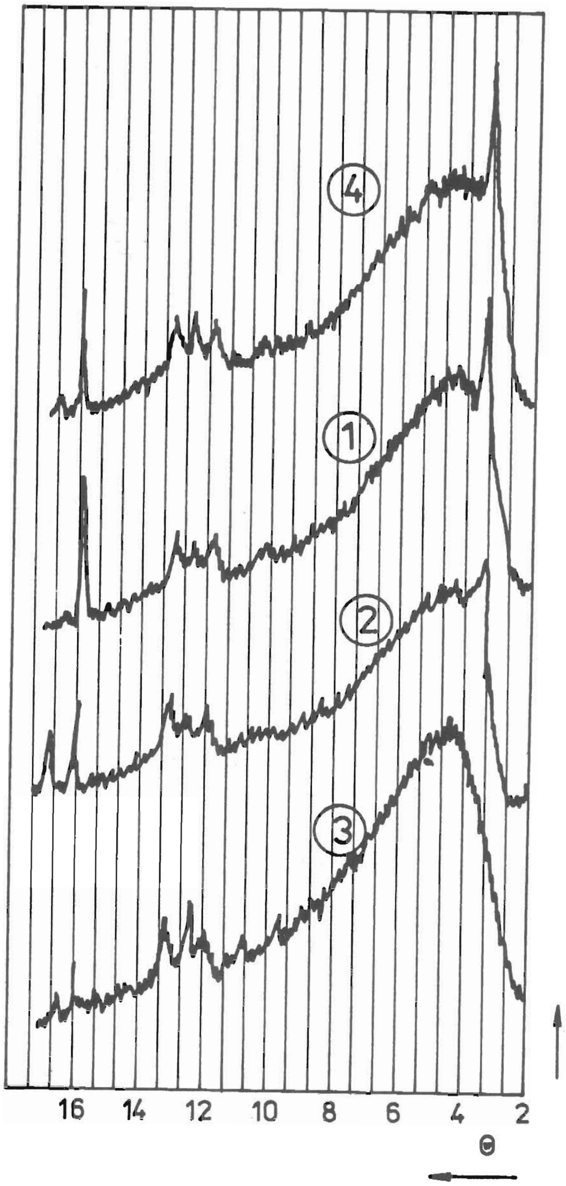

Fig. 1. Structural changes caused by biological contamination.

Tab. 1.
Al, Si concentrations in solutions after biological contamination

| Used microorganism | concentrations in solutions (g/l) | |
|---|---|---|
| | Al | Si |
| *Bacillus circulans* | 81.5 | 34.5 |
| *Thiobacillus ferrooxidans* | 76.0 | 87.2 |
| *Aspergillus niger* | 1802.5 | 194.0 |

## Conclusion

The results from the orientation tests of the biological-chemical leaching of bentonitic clay confirmed the assumption that chemolitotrophic soil bacteria and microscopic fungus can be, under in situ conditions at suitable places, the important catalyzers of biotransformation processes of bentonite and probably also other silicate and aluminium-silicate minerals. The biological-chemical degradation of bentonite structure preferably takes place in the basal intermediate layer area. The process of biological-chemical degradation of the mixture of minerals that form the bentonitic clay is selective. The montmorillonite structure is preferably destructed, the silicon destruction is consequent. The plagioclase structure during the short-term test seemed to be resistant.

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# Microbial leaching of a refractory pyrite/arsenopyrite gold-bearing concentrate

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### Abstract

A mixed pyrite/arsenopyrite gold-bearing concentrate was oxidized by means of acidophilic chemolithotrophic bacteria to liberate the gold from the sulphide matrix. The treatment was carried out under continuous-flow conditions by means of a unit consisting of five agitated reactors arranged in series. The pretreated concentrate was then leached in reactor with mechanical stirring under batch conditions by means of solution containing amino acids of microbial origin and thiosulphate as gold-complexing agents. It was found that the gold extraction depended on the degree of the preliminary sulphide oxidation. Sulphide oxidation in the range of about 50 - 60 % was sufficient for extraction of more than 90 % of the gold during the subsequent leaching.

**Key words:** gold leaching, bacterial pretreatment, gold-bearing sulphide concentrates, acidophilic chemolithotrophic bacteria, microbial amino acids

### Mikrobiálne lúženie ťažkospracovateľných pyritovo-arzenopyritových zlatonosných koncentrátov

Koncentrát sme podrobili biooxidácií činnosťou chemolitotrofných baktérií s cieľom uvoľniť Au v sulfidickej matrici. Proces bol kontinuálny a prebieha v sérií piatich kaskádovozoradených reaktoroch. Takto upravený koncentrát bol uvedený do reaktora obsahujúceho roztok so zlatokomplexujúcim činidlom, konkrétne zmes mikrobiálnych aminokyselín a tiosíranov. Zistila sa závislosť medzi výťažnosťou zlata a stupňom bakteriálnej oxidácie sulfidnej matrice. Výsledky potvrdili, že 50 - 60 % degradácia sulfidného matrixu biooxidácie postačovala na 90 % výťažnosť zlata.

## Introduction

Bacterial oxidation is an efficient method to liberate the gold encapsulated in sulphide minerals and to expose it for subsequent leaching (Van Aswegen, Godfrey, Miller and Haines, 1991; Brierley, 1995). This method can be applied on concentrates in agitated and aerated tanks as well as on ores in specially constructed heaps. Bacterial oxidation of refractory gold-bearing sulphide flotation concentrates is practised commercially in several plants located in different countries and the bacterial oxidation of refractory gold-bearing sulphide ores in heaps is now coming into use on industrial scale (Lawrence and Poulin, 1995; Brierley, Wan, Hill and Logan, 1995). After the oxidation, the pretreated concentrates and ores are leached, usually by cyanide solutions, to solubilize the exposed gold. However, cyanides are highly toxic and costly reagents which, in some cases, makes their use disadvantageous.

It has been shown that gold can be efficiently leached from oxide ores by means of slightly alkaline solutions containing both thiosulphate and amino acids of microbial origin as the gold-complexing agents as well as some ions acting as catalysts in the oxidation of the native gold and/or in the complexation of the gold ions formed as a result of this oxidation. Leaching with such solutions is characterized by increased rates of gold and silver solubilization compared with those obtained by cyanidation. The final extractions of these metals by both methods are similar. However, the reagents used in this combined chemico-biological method are not toxic and the method as a whole is economically more attractive than cyanidation. The method was applied under pilot scale conditions in two Bulgarian gold deposits to leach gold-bearing oxide ores by using the heap leach technique (Groudev, Ivanov, Spasova and Groudeva, 1995; Groudev, 1996) and a commercial scale gold heap leaching operation is to be commissioned this year at the Elshitza mine, Central Bulgaria.

The bacterial pretreatment followed by the combined chemico-biological leaching of the exposed gold has been applied to treat different gold-bearing pyrite concentrates (Groudev, Groudeva and Spasova, 1995; Groudev, Spasova and Ivanov, 1996). In this paper data from a study on the application of this method for treatment of a mixed pyrite/arsenopyrite concentrate are shown.

## Experimental procedures

A mixed pyrite/arsenopyrite flotation concentrate was used in this study. The weight ratio of these two sulphide minerals in the concentrate was close to 2:1. The concentrate contained 31.8 % sulphur, 32.5 % iron, 10.4 % arsenic, 90 g/t gold and 125 g/t silver. The gold was finely disseminated in the sulphide minerals and its concentrations in both the pyrite and arsenopyrite were similar. The concentrate was washed in acetone to avoid the presence of residual flotation reagents, which may adversely affect bacterial activity.

A mixed enrichment culture of mesophilic chemolithotrophic bacteria was used to oxidize the concentrate under batch and continuous-flow leaching conditions. The culture contained *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* as the prevalent microorganisms but *T. thiooxidans, T. acidophilus* and some acidophilic heterotrophic bacteria (mainly such related to the genus *Acidiphilium*) were also present. The culture was preliminarily adapted to the concentrate by consecutive transfers on slurries with increasing pulp density.

Batch oxidation was carried out in glass cylindrical buffled reactors of 5 l working volume agitated by stirring and aerated with air enriched in carbon dioxide. The continuous-flow oxidation was carried out by using a leach unit consisting of five bioreactors of the above type arranged in series. Concentrate and solution at the required ratio were fed into the first reactor which overflowed to the next and so on. Diluted sulphuric acid (with a pH of 1.7) supplemented with some nutrients (($NH_4SO_4$ - 0.5 g/l and $KH_2PO_4$ - 0.1 g/l) and containing $10^9$ cells/ml was used as feed solution. The temperature during the oxidation stage was in the range of 40-42 °C. Leached slurry was removed from the last reactors overflow and filtered daily. The pregnant solutions and leached residues were assayed at regular intervals to determine when steady state was reached.

Batch bacterial oxidation and subsequent leaching tests revealed that the extractions of gold and silver from the concentrate depended on the degree of sulphide oxidation (Tab. 1). Sulphide oxidation in the range of 50-60 % was sufficient to expose almost the whole amount of the precious metals enclosed in the sulphide matrix and to increase their final extractions to more than 90 % during the subsequent leaching. This was probably due to the fact that in most pyrite specimens the gold (and often the silver) is located mainly in the defect sites of the sulphide crystal lattice and these sites are preferentially attacked by the chemolithotrophic bacteria.

The optimum conditions regarding pulp density, stirring and aeration rates during the pretreatment stage were found to be 18-20 %, 600-800 rpm and 0.2 l air/l suspension. min, respectively.

The bacterial attack on the concentrate was initially connected with oxidation of arsenopyrite due to the lower rest potential of this sulphide mineral. The maximum arsenic solubilization rate achieved during the continuous-flow oxidation was as high as 134 mg/l. h and about 95 % of the arsenic were removed from the concentrate within 147 h. At that moment only about 10 % of the pyrite were oxidized to soluble products (ferric sulphate and sulphuric acid). Then the bacteria started an efficient oxidation of pyrite and the maximum iron solubilization rate achieved during this second oxidative phase was 293 mg/l. h. Pyrite oxidation of about 50 % was reached within 232 h from the beginning of the experiment.

Tab. 1
Effect of the degree of the prior bacterial oxidation of the concentrate on the gold and silver extraction during the subsequent chemico-biological leaching

| Sulphide oxidation<br>% | Metals extraction (in %)<br>Au | <br>Ag |
|---|---|---|
| 0 | 17.6 | 16.3 |
| 10 | 35.8 | 24.2 |
| 20 | 48.8 | 36.1 |
| 30 | 62.2 | 50.9 |
| 40 | 82.4 | 73.4 |
| 50 | 95.0 | 87.1 |
| 60 | 95.4 | 89.5 |
| 70 | 95.8 | 92.7 |

Tab. 2
Characteristics of the continuous bacterial oxidation of a gold-bearing pyrite/arsenopyrite concentrate

| Variable | Value |
|---|---|
| Pulp density (%) | 20 |
| Dilution rate ($h^{-1}$) | 0.00347 |
| Retention time (h) | 232 |
| Maximum arsenic extraction rate (mg/l.h) | 134 |
| Maximum iron extraction rate (mg/l.h) | 293 |
| Arsenic content in the outflow solution (g/l) | 14.5 |
| Iron content in the outflow solution (g/l) | 19.4 |
| Initial sulphide sulphur (%) | 31.8 |
| Residual sulphide sulphur (%) | 14.0 |
| Sulphide oxidation (%) | 56.1 |
| Mass of the pretreated concentrate (% from the initial mass) | 55 |
| Gold content in the pretreated concentrate (g/t) | 163 |
| Silver content in the pretreated concentrate (g/t) | 226 |

The maximum arsenic concentration in the leach solution during the treatment was 16.7 g/l. A part of the dissolved arsenic precipitated as iron arsenites and arsenates. This precipitation was enhanced during the subsequent pyrite oxidation when the ferric ion concentration in the leach solution was markedly increased and exceeded 25 g/l. The outflow solution at the end of the pretreatment contained about 15 g/l arsenic and less than 20 g/l iron (mainly in the ferric state). Only traces of soluble gold and silver were detected in this solution.

The pH of the leach suspensions decreased as oxidation continued and the final pH depended on the pulp density and the degree of pyrite oxidation desired. At an initial pulp density of 20 % and a pyrite oxidation of about 50 %, the final pH of the leach solution was lower than 1. At the same time, the redox (Eh) potential of the leach solution steadily increased and exceeded 600 mV at the end of the retention time.

The solid residues after pretreatment were washed with water and then were leached with solutions containing microbial protein hydrolysate - from 0.5 to 5.0 g/l, thiosulphate ions (added as ammonium thiosulphate) - from 10 to 100 g/l, and a mixture of ions-catalysts - from 0.5 to 5.0 g/l. The protein hydrolysate was a mixture consisting of protein hydrolysates from waste biomass of three different microbial species. The individual hydrolysates contained different gold - complexing amino acids and were mixed together in suitable proportions. pH of these solutions was in the range of 8.0-10.0. The leaching was carried out at different temperatures - from 20 to 50 °C and at stirring rates from 200 to 800 rpm.

The extraction of gold from the pretreated residues was very efficient. 96.1 % of the gold was solubilized within 14 hours from a residue in which 50 % of the sulphide sulphur was preliminarily oxidized by bacteria. The optimum concentrations of thiosulphate ions and of microbial protein hydrolysate in the leach solution were found to be 35-40 g/l and 3-5 g/l, respectively. The consumption of these reagents during the leaching amounted to 18.0 kg ammonium thiosulphate and 2.1 kg protein hydrolysate per ton of concentrate.

The optimum pH for gold leaching was about 10.0, and the optimum stirring rate was in the range of 600-800 rpm. The temperature coefficient $Q_{10}$ in the range of 10-50 °C was about 2.

The pregnant solutions after leaching were treated by cementation with metallic zinc. The degree of gold extraction from these solutions was higher than 95 %. The treatment was carried out by means of a fluidized-bed cementator and the consumption of metallic zinc was 0.17 kg per ton of concentrate. The products from the cementation were gold concentrates which contained also silver, copper and zinc as valuable components. The leaching of these concentrates by sulphuric acid at high temperatures (75-80 °C) and in the presence of oxygen resulted in selective dissolution of the copper and zinc. These non-ferrous metals can be recovered from the pregnant solutions after leaching by means of different methods. The contents of gold and silver in the final concentrates obtained after the removal of the copper and zinc were higher than 10 kg/ton. These concentrates were then processed by the conventional procedure for obtaining pure gold and silver.

A pilot scale operation to treat different gold-bearing sulphide concentrates by the above-mentioned method will be commissioned in the near future.

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# Microbial leaching viewed from the acpect of environmental protection

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## Abstract

Within the investigation of bacterial processing of low-grade ores, the possibility of utilization of mining waters was accentuated. Due to a natural enrichment of these waters by the process stimulation agents (bacteria, acidity, iron), reclamation of useful components (metals) is much more efficient.

In this work, the efficiency of bacterial leaching of copper and uranium ores, depending on a number of technological parameters, was investigated. This process was considered compared to the use of autochton bacterioflora, isolated from mining water and direct use of mining water as a leaching solution. The terrain investigations (the analysis of mining water and leach-out from the mining deposits) showed that there exists a correlation between the quality of mining water (acidity, oxidation degree, metal content) and quantitative presence of chemoautotrophic bacteria (belonging to *Thiobacillus genus*), i. e. all oxi-reducing processes determine the degree of natural leaching.

The final objective of investigations presented in this work is utilization of mining water for bacterial leaching and its possible practical application.

**Key words:** bacterial leaching, *Thiobacillus genus,* minig water

## Mikrobiálne lúženie z pohľadu ochrany životného prostredia

Dlhoročné laboratórne a poloprevádzkové pokusy s bakteriálnym lúžením kovov (Mo, Cu, Sb a U) poukazujú na možnosti jeho praktického využitia. V našich pokusoch sme skúmali možnosti využitia banských (odpadových) vôd v procese lúženia rúd chudobných na kovy, a tiež pri spracovaní odpadov z ťažby rúd. V lúžiacich pokusoch sme ako aparatúry použili sklenené kolóny s objemom 200, 800 a 1200 $cm^3$. Z baní s výskytom Cu, U a Sb boli izolované kmene baktérií *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* a *Thiobacillus genus*. Použité zásobné bakteriálne suspenzie mali koncentráciu $10^7$ až $10^8$ buniek/ml suspenzie. Banské vody použité v pokusoch mali koncentráciu biomasy $10^2$ až $10^5$ buniek/ml. Skúmali sme lúženie rúd s obsahom Cu a U. U ruda mala zrnitosť od 0,01 do 4,76 mm. Pri jej lúžení bola dosiahnutá 72 % výťažnosť uránu, a to pri použití 1900 ml Leathenovho média ako lúžiaceho roztoku inokulovaného 10 ml suspenzie biomasy. Počiatočné pH bolo 4,5 a počas pokusu kleslo na 2,5. Tým sa dokázala oxidačná aktivita baktérií. Na lúžení Cu rudy sa podieľal najmä bakteriálny druh *Thiobacillus genus*. Maximálne výťažky boli pri použití Leathenovho média ako lúžiaceho roztoku. Výťažnosť lúženia ešte zvýšila predlúhovacia úprava rudy klasickou hydrometalurgickou metódou pomocou $H_2SO_4$. Pri pokusoch s banskými vodami bola výťažnosť lúženia porovnateľná s výsledkami v Leathenovom médiu. V prvej polovici trvania pokusu došlo k nárastu počtu buniek pri použití banskej vody. Ku koncu sa počet buniek neodlišoval od pokusu s Leathenovým médiom.

## Introduction

The years-long investigations of bacteriological leaching of copper, uranium, antimony and molybdenum low-grade ores and copper tailings (i. e., already treated ores), carried out on laboratory and pilot-plant scales, pointed out at the possibility of it's practical application. On the basis of our findings and findings obtained elsewhere, nearly all significant parameters that provide for the efficiency and justification of this method application, are defined. One general attitude has also been established: each deposit (dump store) has it's own specificities, in form of abiotic and abiotic factors, which should be investigated in each individual case.

Over the last few years, these general investigations, associated with bacteriological leaching of low grade ores, became more complex. Microbial leaching was related with environmental protection and maximally intensified through utilization of all natural and technological factors. Since the natural bacteriological process (including an "additional" one, too) is relatively slow process, dependent on a number of parameters, particulary on quality of lixiviant (it's acidity and occurance of present bacterioflora), also that the mine drainage and seepage, originating from the places where natural leaching potential exists, are acidic, there should be taken care and such waters be utilized to this propose.

Uncontrolled microbial leaching (particularly in modified natural ore deposits or in tailing dumps) often induces intense ionization of formation seriously endangering water courses and soil. Although the concentrations of these pollutants are usually within tolerable limits, cummulative and sinergistic effects of individual compounds and ions should also be considered.

During realization of the projects dealing with reclamation of useful components from waste waters, it was found out that proposed solutions are accepted more readily if they emphasize the environmental aspect, as well (most probably because of the legal requirements). This "combined" approach of microbial leaching becomes more attactive if proposed technology points to the fact that returned value, obtained through reclamation of otherwise lost components, can compensate for a part of the costs invested into environmental protection.

In this work, we tried to present a realistic picture of the events occurring on the terrain, showing that significant values contained in tailings and waste waters are lost, contaminating further the water courses, although these values could be reclaimed by the appropriate technologies (including microbial leaching), thus preventing further pollution.

## Material and methods

While looking for the possibilities of more efficient utilization of mining water in the process of bacteriological leaching of the primary low grade ores or tailings (either in situ or in heap), the results of laboratory leaching of primary low grade ores were used, together with the investigation results of mining waters from the primary copper, uranium, nickel and molybdenum ore deposits (abandoned mines and research galleries) and mining waters from the secondary tailings dumps.

For laboratorial tests of bacteriological leaching of primary and secondary raw materials (ore and tailings), gass columns of various capacities (1200 cm$^3$, 800 cm$^3$, 200 cm$^3$ and flasks) were used. The parameters of bacteriological leaching were set up and adjusted, depending on the objective and used material. In these experiments (unless otherwise specified), bacterial cultures of hemoautothrophic, *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* bacteria, isolated from copper, uranium, molybdenum and antimony mines by the ordinary techniques, were used (Barbič, 1989; Bergey, 1989; Kuznetsov et al., 1962). A number of bacteria in the input solution (variant with bacteria) was between 10$^7$ and 10$^8$ per cm$^3$. In the variants with the "natural" mining water, the number of bacteria was determined immediately before leaching process and the population occurance varied between 10$^2$ and 10$^5$ per cm$^3$. During the laboratory experiments of leaching, a number of bacteria was permanently followed by a method of dilution (Kuznetsov and Romanenko, 1963). It has to be mentioned that on utilization of mining water (without subsequent intervention), there were also some other bacteria belonging to *Thiobacillus* genus, but in this investigation, they were not identified.

For investigation of effects of autochthon bacterioflora from mining water in laboratory processes of bacteriological leaching, the following materials were used:

1. Uranium material
1a. natural sample (PT-1)
1b. natural sample (PT-2)
1c. sample treated by hydrometallurgical method (PUR-1)
1d. sample treated by hydrometallurgical method (PUR-2)
2. Copper-bearing material
2a. ore (NR)
2b. sample, previously treated (PTR)

In order to reclaim copper, transferred into water courses in the region of the Bor mine ore deposits, tailings or technological processes, complete chemical analyses of Borska Reka and Krivajska Reka waters have been performed over a number of years. The investigations were carried out in various seasons, at various annual atmospheric falls.

## Results and discussion

Within the investigations of possibilities of bacteriological leaching of low grade ores and tailings (both primary and so called "technological" tailing), the terrain investigations were carried out at the localities of Bor-Majdanpek, Avala ("Šuplja Stena"), Bukulja (research operations) and Mačkatica (abandoned mine). From these localities, where oxi-reduction was evident, the ore samples and mine drainages were taken. On these samples, a detailed tes-

Tab. 1
Content of basic pollutants in blue mining water (g/dm$^3$)

| Components | Locality<br>Kriva Reka | <br>Jama - Zmajevo | <br>seepage from flotation tailings |
|---|---|---|---|
| Cu | - | 0.5200 - 0.2650 | 0.0030 - 0.0350 |
| Fe (total) | 0.0016 - 0.0040 | 0.0590 - 0.4570 | 0.0210 - 0.0280 |
| $SO_4^{2-}$ | 0.1030 - 0.7100 | 1.3690 - 3.806 | 0.2200 - 0.6530 |
| flow | 7.2000 - 16.5000 | 3.1200 - 3.4800 | 0.0350 -0.0380 |

Tab. 2
Microbial leaching of uranium ore (C sample)

| Large columns | C-1 | C-2 | C-3 | C-4 |
|---|---|---|---|---|
| Uranium in ore (g/t) | 595.700 | 595.700 | 595.700 | 597.700 |
| Uranium per column (g) | 0.511 | 0.511 | 0.511 | 0.511 |
| Leaching effect: | 0.080 | 0.090 | 0.006 | 0.003 |
| Cycle I (g/l) | 0.114 | 0.154 | 0.010 | 0.005 |
| total % | 28.180 | 30.140 | 2.000 | 1.000 |
| Cycle II (g/l) | 0.150 | 0.140 | 0.010 | 0.003 |
| total % | 0.250 | 0.221 | 0.014 | 0.005 |
|  | 48.800 | 43.300 | 2.800 | 1.000 |
| Cycle III (g/l) | 0.210 | 0.200 | 0.012 | 0.003 |
| total % | 0.322 | 0.281 | 0.016 | 0.005 |
|  | 63.000 | 55.000 | 3.100 | 1.000 |
| cycle IV (g/l) | 0.230 | 0.230 | 0.014 | 0.010 |
| total % | 0.340 | 0.322 | 0.179 | 0.013 |
|  | 66.500 | 63.100 | 3.500 | 2.500 |
| Leached out from | 443.5 | 413.4 | 29.8 | 14.9 |
| the ore (g/t) % | 72.8 | 69.4 | 5.0 | 2.5 |

ts were carried out in laboratory to determine the presence of bacteria (particulary of *Thiobacillus* genus) and the concentration of anions and cations in water samples. Water samples from these localities were also used in a specific variants of bacteriological leaching of ores from the same localities. The autochtone bacterioflora was used directly in leaching process, or a pure culture was obtained by certain techniques and then used for determination of oxi-reducing capacities of isolated bacteria.

In Tab. 1. three basic pollutants present in blue mining water are represented. Concentrations of this components are definitely dependent on the flow-rate, i. e. on the atmospheric falls.

Just as an illustration: based on observation of six characteristic places, it was registered that about 100 tons of copper is lost (at low flow-rate, in November), up to 535 tons (in April), and so is 186 - 963 tons of iron and 6600 to 9645 tons pf $SO_4^{2-}$. According to the same source, the content of copper in these waters was 10 to 300 times higher then the highest legally acceptable concentration, while the iron concentration was 10 to 1500 times higher.

Depending on time and place of sampling, the samples of mine drainages used in tests of bacteriological leaching varied both in chemical composition (concentration of anions and cations) and bacteriological composition (number of bacteria of *Thiobacillus* genus). In certain samples of mine drainage, collected after the abandoned mine research activities, the concentration of uranium varied up to 0.1 g/l, that of iron-up to 5 g/l, while the acidity was mainly between 2 and 3. Mine drainage from abandoned mercury mine contained about 0.3 - 1.1 g/l of nickel, up to 0.1 g/l of cobalt, up to 5 g/l of iron (over 80 % in two-valent state), between 9 and 12 g/l of sulphate ions, while the acidity was about 2.5. The concentrations of copper in mine drainage (seepage from tailing and "blue water") was occasionaly above 0.2 g/l (the average value was about 0.03 g/l), while the concentration of cations in these waters was about 3 kg/l. It is worth mentioning that the concentration of cations in these waters was directly dependent on qualitative and quantitative composition of hemoautothrophic bacteria.

The results of bacterial leaching of uranium ore with average uranium content (sample C) are presented in Tab. 2.

Granulation of investigated samples was in the range of -4.76 mm to -0.00 mm. In the first series of experiments (large columns), the ore was leached in the four variants:

C-1: 1900 ml of medium (by Leathen) +10 ml of the biomass

C-2: 1900 ml of medium (by Silverman) +100 ml of the biomass

C-3: 2000 ml of running water (control)

C-4: 1988 ml of destilled water +2 g HgCl (control)

In the first series of experiments (large columns), the maximal leaching effect of 72 % was achieved in C-1 variant (optimal initial acidity, with addition of ferrosulphate). In C-2 variant, this effects was somewhat lower, while in C-3 and C-4 variants (the control columns), it was 15 - 30 times lower. The effects of microbial leaching and bacterial oxidizing ability were also confirmed by pH value of the leaching solution. At the beginning of experiments, pH value of solution with bacteria was 4.5, falling to 2.5 at the of experiment. No change was registered in the control columns. Leaching effect was more or less stable, irrespective of granulation (71 - 91 %). It is evident that over 80 % of uranium was leached out in the first two cycles. It is necessary to point out that leaching solution was not replaced by the fresh one, as will be investigated in our future investigations.

In Tab. 3, the results of leaching of lower grade run-or-mine uranium ore (D sample with 364 g/t and E sample with 320 g/t), are presented.

This leaching performed under conditions similar to those for C-1 to C-4 samples, was done in the three variants:

D-1 and E-1: 1900 ml of medium (by Leathen) + 100 ml of the biomass

D-2 and E-2: 1950 ml of mining water +50 ml of the biomass

D-3 and E-3: control columns

Bacteriological leaching of copper ore (sample "NR" and ore that was already treated (technological tailing, "PTR" sample) by autotrophic bacteria of *Thiobacillus* genus in mine drainage, with the corresponding controls, is presented in Tab. 4. In both samples, the highest ex-

Tab. 3
Bacterial leaching of uranium ore (D and E samples)

| | D sample | | | E sample | | |
|---|---|---|---|---|---|---|
| | D-1 | D-2 | D-3 | E-1 | E-2 | E-3 |
| Initial uranium conc. (g/t) | 340.0 | 340.0 | 340.0 | 320.0 | 320.0 | 320.0 |
| Total leaching effect (g/l) | 313.0 | 263.5 | 33.5 | 270.7 | 257.3 | 40.6 |
| Left in ore after leaching (g/t) | 50.6 | 100.5 | 330.5 | 49.3 | 62.7 | 297.7 |
| Leaching effect (%) | 86.1 | 72.4 | 9.2 | 84.6 | 80.4 | 12.6 |

Tab. 4
Bacteriological leaching of copper

| | Sample "NR" | | | Sample "PTR" | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| Copper in ore (g/t) | 1140 | 1140 | 1140 | 280 | 280 | 280 |
| Leaching effect: cycle I (g/l) | 0.0735 | 0.0850 | 0.0050 | 0.0350 | 0.0410 | 0.0050 |
| Cycle II | 0.0910 | 0.0560 | 0.0065 | 0.0215 | 0.0185 | 0.0040 |
| Cycle III | 0.0435 | 0.0245 | 0.0050 | 0.0200 | 0.0100 | <0.0020 |
| Cycle IV | 0.0190 | 0.0480 | 0.0070 | 0.0170 | 0.0080 | <0.0020 |
| Taken for analyses (g/l) | 0.0120 | 0.0100 | 0.0024 | 0.0064 | 0.0050 | 0.0001 |
| Total (b+c) | 0.2390 | 0.2234 | 0.0290 | 0.1008 | 0.0826 | 0.0094 |
| Left in ore after leaching (g/l) | 656.6000 | 693.1000 | 1080.7000 | 78.1000 | 114.8000 | 261.2000 |
| Total copper extracted (g/l) | 483.4000 | 446.9000 | 59.3000 | 201.9000 | 165.2000 | 18.8000 |
| % of extraction | 42.4000 | 39.2000 | 5.2000 | 72.1000 | 59.0000 | 6.7000 |

traction is achieved in the variant where bacteriological Leathen medium was used as leaching solution, somewhat lower in the variant where mine drainage was used, while the weakest extraction was achieved in their controls (variant 3). The difference in extraction percentage, registered between the two samples, is quite significant. This is probably as due to the fact that "PTR" sample was previously treated by a standard hydrometallurgical method (by sulphuric acid) and, in that way, better prepared for bacteriological leaching, since it provided more favourable initial conditions for bacterial growth.

During bacteriological leaching of copper-bearing and uranium materials, we monitored the change in number of introduced bacteria. In all samples, considerable increase in number of bacteria is detected in the first half of the leaching period, in the first and the second recycling (the curve of the bacterial growth is steep), in those variants where mine drainage was used as lixiviant. Towards the end of the leaching cycle, these differences disappear, so the curve of the populations growth is getting the same form, i. e. the increase in number of bacterial units per unit of time is becoming approximately the same for all variants. This is explained as due to the fact that the initial conditions for bacterial growth and multiplication in the "natural" mine drainage are much more favourable, particulary if bacterioflora selected from that, or the neighbouring water is used, because there is a certain preadaptation of bacteria to the environmental conditions. This phenomenon, expressed in a form of improved conditions for bacterial growth, is also reflected upon the overall conditions that influenced bacteriological leaching effects (percentage of extracted metal, adicity of leaching solution, better expressed oxi-reducing process, higher redox potential).

A method of bacteriological leaching (applied to intensify the existing, natural processes, thus contributing to the environment protection) requires a thorough understanding of the situation on the terrain and development of the specific project design. Our experiences point out that it is necessary to collect the "output" waste waters in one place and to perform the primary extraction of metals, also recycling waters to the place of "process", in order to enrich the solution with bacteria. Bacterial leaching, significantly contributing to environmental protection, should be implemented in accordance with other technological processes. It is particularly important not to disturb the course of these waters, since it might additionally contribute to groundwater pollution.

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# Possibilities of recovery of dispersed metals occurring in walchia shale using fungi

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## Abstract

Northwest Poland has deposits of uranium-bearing, polymetallic walchia shale. This research was focused on the application of biological leaching for the extraction of trace amounts of dispersed metals in non-workable material characterized by alkaline gangue. Chemical and micro-biological research was conducted, which made possible the identification of the characteristics of the researched material. *Aspergillus niger* fungi were used for the detailed examination of the effectiveness of biological leaching. A 5-month research cycle was adapted, in a variety of environments. The degree of extraction of various metals was extremely varied, from 29.5 % to 83.3 %. Additionally, research was carried out on the influence of the bioleaching process on the leached solid stage.

**Key words:** biological leaching, *Aspergillus niger*, uran, lead, zinc, molybden

### Možnosti získania rozptýlených kovov z walchia bridlíc s použitím húb

Severozápadné Poľsko má ložiská uránových polymetalických walchiových bridlíc. Tento výskum sa zameral na aplikáciu biologického lúhovania za účelom extrakcie stopových množstiev kovov rozptýlených (vtrúsených) v odpadovom (nebilančnom) alkalickom materiáli. Bol urobený chemický a mikrobiologický výskum, ktorý umožnil určiť charakteristiky skúmaného materiálu. Pre podrobné zistenie účinnosti biologického lúhovania boli použité huby *Aspergillus niger.* Bol navrhnutý 5-mesačný pozorovací cyklus v rozdielnych prostrediach. Stupeň extrakcie rôznych kovov bol extrémne rozdielny, od 29,5 % do 83,3 %. Navyše bol skúmaný vplyv procesov biologického lúhovania na stupeň vylúhovania pevnej fázy.

## Introduction

In Poland, there are no technologies for the processing of mineral and quasi-mineral materials based on the use of biotechnical processes. However, the perspective of a need for them is indicated by the fact that currently there is research underway directly on the subject (Golab and Orlowska, 1988; Cwalina et al., 1990, 1992; Sztaba and Konopka, 1992, 1993, 1994) or indirectly related to it (Chmielowski et al., 1991, 1993). This type processes are effectively applied in other parts of the world, on an industrial scale, but only for strictly specified materials (Maturana et al., 1993; Cevole et al., 1993; Groudev, 1993; Solodov et al., 1994) and with the use of autotrophic microbes, represented mainly by *Th. ferroxidans.*

In the Polish context, the principal issue is the proposed development of a method for the recovery of trace amounts of metal -- in a situation where there are no other rational methods for enriching materials of unfavourable geochemical properties for the application of effective methods of both classic and hydrometallurgical processing.

## Research objective

The objective of the research was to evaluate the possibility of using the biological leaching method to recover trace amounts of dispersed metals in highly alkaline, uranium-bearing walchia shale, present in the grounds of Northwest Poland. It is a polymetallic material, characterized by higher than average content of metal: U - to 200 grams per ton; Zn - 3000 gpt; Pb - 400 gpt; Mo - 100 gpt; and many others. It is therefore justifiable to look for another biological factor which would be active in this alkaline environment.

That is why heterotrophic organisms, namely fungi, deserve some interest. They have a number of properties which can prove very useful for the research objective. They adapt very well in various environments. In favourable conditions, fungi grow extremely fast, and, being larger than bacteria, they produce much more biomass. The product of their metabolism - depending on their growing base - is a variety of organic acids, e. g. citric acid, oxalic acid, gluconic acid, and some other amino acids - all characterized by leaching qualities and the ability to complexate metals, which, to some degrees of concentration, are some of their nutrients. The most active fungi among those which were part of the research are *Aspergillus* and *Penicillium* sp. (Niu et al., 1993; Singal, 1994; Tzefaris, 1994; Vachon et al., 1994; Sayer et al., 1995; Sukla et al., 1993, 1995; Holan, 1994; Akthar et al., 1995)

Detailed research on the effectiveness of bioleaching of metals which are present in walchia shale involved the

Tab. 1
Chemical analysis results of 3 grain class samples of walchia shale (in %)

| class mm | | ash | roasting losses | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $SO_4$ ($S$-$FeS_2$) | $TiO_2$ | MnO | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| +10 | 1 | 76.00 | 24.00 | 19.53 | 4.00 | 7.90 | 31.92 | 2.10 | 2.56 | 6.16 | 1.04<br>(0.32-0.60) | 0.26 | 0.40 | 9.07 |
| 10-1 | 2 | 88.69 | 11.31 | 45.25 | 7.60 | 17.39 | 8.74 | 2.40 | 2.22 1 | 2.87 | 0.90<br>(0.30-0.56) | 0.49 | 0.48 | 7.78 |
| -1 | 3 | 88.58 | 11.15 | 45.26 | 8.40 | 17.05 | 7.26 | 2.60 | 3.03 | 2.90 | 0.90<br>(0.30-0.56) | 0.49 | 0.57 | 7.61 |

use of *Aspergillus niger* and *Penicillium chrysogenym* fungi.

## Experimental work

### *Chemical and micro-biological tests on the material: uranium-bearing walchia shale*

The acquisition of the research material involved sampling to the depth of 1 metre. Samples were taken at a site of the highest radiometric anomaly: 150 - 300 impulses, with the background level at 50 impulses, characterized by the highest concentration of uranium.

The material was divided into several broad grain classes: +10 mm, 10-1 mm, and -1 mm. Chemical tests were done to determine the chemical constitution of the basic gangue and the degree of metal concentration in each of the grain classes. The direct objective of the tests was to find a shale sample with initial chemical characteristics for more detailed tests focused on the effectiveness of leaching of small amounts of metals. A spectral analysis indicated the presence of the following metals (apart from the dominating gangue components): Mn, U, Pb, Ti, V, Zn, Cu (higher-than-average concentrations), Mo, B, In, As, Sn, Ga, Sr (low concentrations), and Ni, P, Cd, Ag, Cr (hardly detectable concentrations). The following metals were selected for further detailed tests: U, V, Mo, Zn, Pb, Mn, and Ti.

The chemical test results of several grain classes, in regard to various compositions of the base gaunge, are shown in Tab. 1, while Tab. 2 presents those results with regard to metal concentration degree (metalloferrosity).

Sample No. 3 was chosen for bioleaching research. It is characterized by the highest metal content (U - 90 ppm) and belongs to -1 mm grain class.

The research objective called then for micro-biological analyses of 4 samples of walchia shale, taken from their natural environment with utmost care for the sterility standards.

Generally, the tested walchia shale samples showed little biological life. Main forms of life include psychrophilic and mesophilic bacteria of the *Bacillus* genus and some bacteria active in the chemical processes involving nitrogen compounds: nitrifications and denitrifications. Fungi of the *Micromycetes* class were also found, albeit in very small amounts. That is why the decision was taken to introduce into the wachia shale environment some allochtonous (non-indigenous) microbes: the *Apergillus niger* and *Penicillium chrysogenum* fungi - heterotrophic microbes of well-known qualities which justify their various possible applications in the proces of metal leaching. And that was the objective of our research.

### *Tests on effectiveness of metal leaching with the use of the Aspergillus niger fungus - discussion of results*

As the tests showed that *A. niger* was more effective than *P. chrysogenum* in terms of leaching metals from walchia shale, there search conducted on just that fungus will now be presented .

The tests were done in conical flasks, with the use of 10 grams of *A. niger (P. chrysogenum)* suspension and 80 cubic cm of wort solution, or Czapek-Doxa solution, as nutrient. The experiment was conducted with partial exchange of the leaching solution: once a week 20 cubic cm of the leaching solution (along with the mycelium) was taken away and substituted with fresh solution. After each month of leaching, the leaching solution was replaced completely. The experiment took 5 months, and was conducted in various environments. On completion of that cycle, a large quantity of *A. niger* biomass was extracted from all of the leaching solution. Both the solution and the biomass were analysed for metal content.

Table 3 presents the results of metal leaching effectiveness with the use of *A. niger*, on wort nutrient medium

The analysis of the results concerning the effectiveness of metal leaching with the use of *A. niger* led to the conclusion that its controlled metabolism catalyses the leaching process, albeit it is still a very long process, even when best possible conditions have been provided. The environment underwent high degree of acidification, up to pH =

Tab. 2
Metal concentration degree in samples of 3 classes of walchia shale (grams per ton)

| Class mm | | Concentration degree (grams per ton) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | U | V | Mo | Zn | Pb | Mn | Ti |
| +10 | 1 | 49.6 | 60 | <1 | 800 | 200 | 3070 | 1630 |
| 10-1 | 2 | 71.3 | 150 | <1 | 2050 | 420 | 3750 | 2930 |
| -1 | 3 | 90.0 | 143 | 2 | 2500 | 440 | 4360 | 2950 |

Tab. 3
Results of metal leaching effectiveness with the use of *A. niger*, on wort nutrient medium.

| Conditions of the process | Analysed component | Metal extraction degree - recovery Σ (%) | | | | | | | Final pH |
|---|---|---|---|---|---|---|---|---|---|
| | | U | V | Mo | Zn | Pb | Mn | Ti | |
| 1 - room temperature | solution | 5.36 | 3.01 | 18.00 | 7.64 | 8.21 | 44.15 | 2.23 | |
| - static system | biomass | 25.82 | 26.08 | 25.00 | 51.00 | 21.14 | 21.67 | 11.70 | |
| | total effect | 31.18 | 29.09 | 43.00 | 58.64 | 29.96 | 65.82 | 13.93 | 5.60 |
| 2 - room temperature | solution | 2.57 | 12.42 | 39.00 | 10.40 | 6.62 | 38.58 | 3.23 | |
| - aerated culture | biomass | 34.91 | 28.53 | 34.00 | 45.62 | 16.64 | 44.72 | 26.27 | |
| | total effect | 37.48 | 40.95 | 73.00 | 56.02 | 23.26 | 83.30 | 29.50 | 4.30 |
| 3 - temperature 28 °C | solution | 5.08 | 9.86 | 41.50 | 11.26 | 6.48 | 32.25 | 1.90 | |
| - static system | biomass | 41.07 | 43.50 | 39.00 | 49.78 | 11.67 | 38.98 | 10.77 | |
| | total effect | 46.15 | 53.36 | 80.50 | 61.04 | 24.15 | 71.23 | 12.67 | 4.64 |

5.62-4.30, which is evidence of active biochemical processes in the leaching system, the measurable effect of which was the significant yield of metals as well as progressive changes in the leached solid stage. The following degrees of extraction were achieved for the various metals: U 46.15 %; V 53.40 %; Mo 80.50 %; Zn 61.04 %; Pb 29.95 %; Mn 83.30 %; Ti 29.50 %. The effect of leaching was assessed according to the total amount of metal (in relation to the theoretical potential amount) which went over to the leaching solution, with the provision that the term "leaching solution" in the experimental conditions means the solution proper plus the ample amount of *A. niger* biomass in it.

Chemical analysis of metal content showed that, in experimental conditions, a large part of the extracted metal - anywhere from 33 % to 90 % - was in the fungus biomass. A general conclusion may be that proper treatment of the fungus biomass presents a number of methodological problems, as it is impossible to find the exact division line between divisible biomass and that which stays in the solution. Nevertheless, it is beyond any doubt that, in experimental conditions, *A. niger* biomass shows a high degree of sorptiveness for all extracted metals and becomes their main carrier.

It is possible to intensify the leaching process by providing optimal conditions. The process of leaching metal with the use of *A. niger* from a walchia shale type material of given characteristics is not a selective process, at least for the metals taken into consideration in the research.

### *Tests on the effects of the leaching process with the use of A. niger on the condition of the leached solid stage - discussion of results*

The surface of the shale leached by *A. niger* was assesed with the use of a Yeol 5400 electron scanning microscope (image) and a Linc AN 10000 X-ray microanalyser (local analysis).

The microscope observation is shown in photographs 1 (a, b), and the results of the local chemical analyses are presented in Figs. 1, 2 and 3.

Photograph 1 shows the surface of a walchia shale before (photo a) and after 5 months of leaching (photo b). Biological leaching affects that surface: the scanned microscope image shows considerable reduction of grain size as well as some blurring of the sharp edges between the phases.

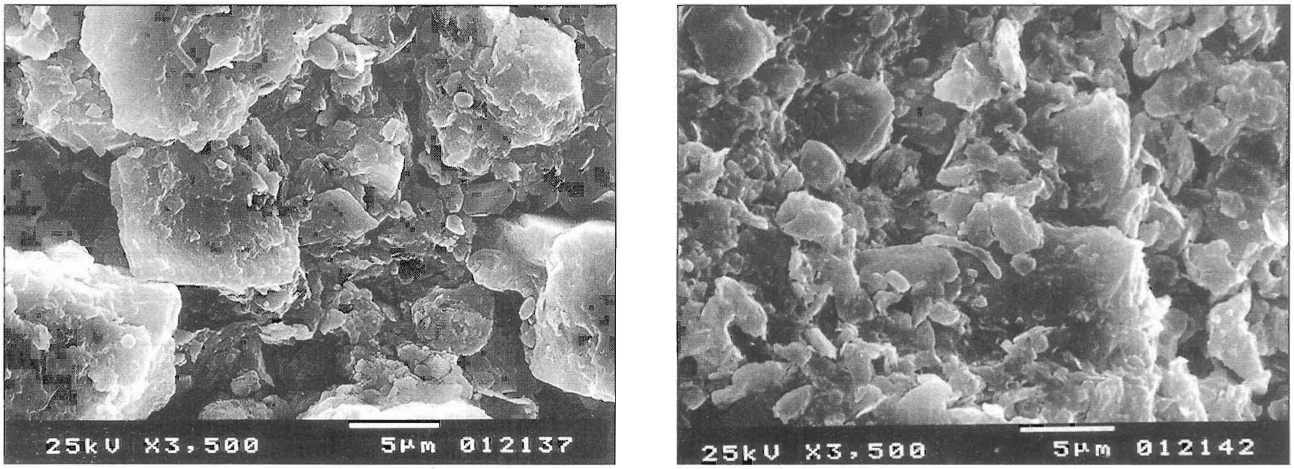

Photo. 1. Scanned microscope image of shale surface: a - initial stage, b - after 5 months of leaching with the use of *Aspergillus niger*.

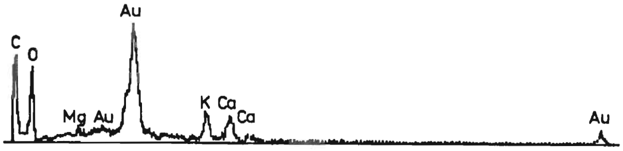

Fig. 1. Results of the X-ray local chemical analysis of the leached walchia shale sample in its initial condition.

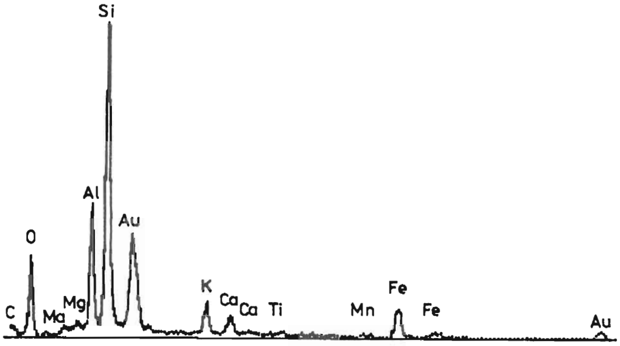

Fig. 2. Results of the X-ray local chemical analysis of lab-produced pure *Aspergillus niger* biomass.

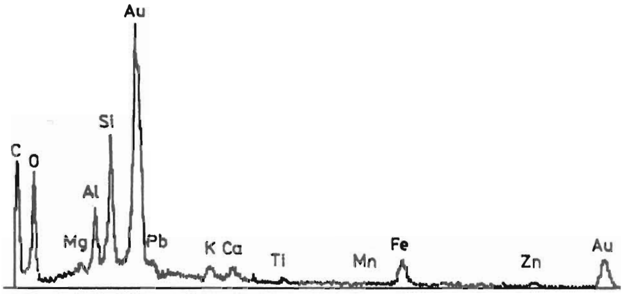

Fig. 3. Results of the X-ray local chemical analysis of the *Aspergillus niger* biomass sampled from the leachid environment.

Fig. 1 is a presentation of the results of the X-ray local analysis of the shale in the initial state, where, apart from the dominating components of the gangue plus Ti and Mn, no traces of other metals were found.

The leaching process with the participation of *A. niger*, as shown by the results of the local chemical analysis, can be evaluated on the basis of a comparison of Fig. 3, which presents the results of the analysis of *A. niger* biomass sampled from the leaching environment, with Fig. 2, which presents the results of the analysis of its pure biomass taken from a lab culture (bred for research). The lab culture *A. niger* biomass has a rather poor local analysis spectrum, both in qualitative and quantitative terms, which testifies to the contribution of the fungus biomass to the general effect of this type leaching.

Upon completion of the 5-month leaching cycle with the use of *A. niger*, an analysis of the grain composition of the leached sample was done. Data of the initial sample are also given for comparison.

The results are shown in Tab. 4.

As the data indicate, leaching with the participation of fungi is conductive to excessive reduction in grain size of the leached material in the whole grain size range: the percentage of the largest class decreases, while the medium-sized grain content increases, and then again the percentage of the smallest grains decreases, which may indicate that the smallest grain class is most susceptible to the leaching processes.

In order to assess the influence of long-term leaching with the participation of *A. niger* on the condition of the gangue containing the leached walchia shale, chemical tests of the leached solid stage were run following the completion of the 5-month-long leaching cycle. The data on the initial sample are also given for comparison.

The resulsts are shown in Tab. 5.

The results of the chemical tests of the gangue containing the leached shale allow one to conclude that leaching does take place and that it is accompanied by the process of solution of alkaline components, particularly CaO. Its content definitely decreases, from the initial 7.26 % to 1.34 %. What increases is the relative content of acidic components. X-ray tests have shown beyond any doubt the complete disappearance of calcite peak, which is another confirmation of the chemical tests results.

## Conclusion

The research objective was to recover trace amounts of metals dispersed in walchia shale, with the use of the method of bioleaching - as the only feasible one for this type of raw material.

Chemical tests have shown that the shale in question contains a number of economically desirable metals, including uranium. However, they are highly dispersed (grams per ton) - U 49.6-90.0; V 60-143; Mo c. 2; Zn 800-2500; Pb 200-440. Low metal concentration degrees, so characteristic of this type of geological deposits, often render effective research of the form of their presense practically imposible, and the minerals of most chemical elements never get isolated.

The gangue is alkaline, with a pH = 9.7-7.61, which results from the high content of alkaline components (CaO + MgO): from 10 % - 34 %.

With the overall research objective in mind, micro-biological tests of the shale were undertaken. They showed

Tab. 4
Results of walchia shale samples grain composition analysis: before and after leaching

| Class (μm) | Weight percentage of grain class | |
|---|---|---|
| | initial sample | sample leached by *A. niger* |
| +160 | 35.33 | 32.83 |
| 160-190 | 15.93 | 16.94 |
| 90-63 | 11.23 | 12.30 |
| 63-45 | 4.84 | 4.58 |
| 45-32 | 5.01 | 7.50 |
| 32-25 | 3.63 | 4.50 |
| 25-0 | 24.03 | 21.35 |

Tab. 5
Results of chemical analyses of walchia shale samples: before (W) and after 5 months of leaching by *A. niger* ($A_5$)

| Sample | Ash (in %) | Roasting losses (in %) | $SiO_2$ (in %) | $Fe_2O_3$ (in %) | $Al_2O_3$ (in %) | CaO (in %) | MgO (in %) | $K_2O$ (in %) | $Na_2O$ (in %) | $S_{total}$ (in %) |
|---|---|---|---|---|---|---|---|---|---|---|
| W | 88.85 | 11.15 | 45.26 | 8.40 | 17.05 | 7.26 | 2.60 | 3.03 | 2.90 | 0.30 |
| $A_5$ | 85.06 | 14.94 | 48.02 | 9.10 | 17.80 | 1.34 | 2.10 | 2.36 | 2.49 | 0.10 |

that rather scant biological life was present in it, so decision was taken to undertake bioextraction of metals with the use of *A. niger* fungi - allochtonous microbes which had proved effective in other environments.

The products of *A. niger* metabolism proved an effective factor in metal leaching. The degree of leach-based extraction varied for the various metals, ranging from 29.5 % to 83.3 %. A significant part of the extracted metal was found in the fungus biomass, which might indicate that the biomass has strong sorptive qualities and can become a targer carrier for the extracted metals in the future. The contribution of the biomass to the leaching process has been confirmed by X-ray local chemical analysis, which showed that bioextraction influences the intensification of the spectrum lines in comparison with lab culture biomass. The products of leaching are the reason for that. The leaching process under discussion is a very long one; however, there is a way of intensifying it.

The fact of biochemical process occurring in the researched environment, its effect being the leach-based extraction of metals, is proved by a considerable pH decrease, down to as low as 4.30, and the change of state of leached solid stage. The microscope image of the leached shale surface is evidence of the size reduction of the larger grain, which has been confirmed by the analysis of the grain composition. Chemical analysis showed that leaching is accompanied by the process of solution of the alkaline components, particularly CaO. Its content drastically decreases, from the initial 7.26 % to 1.34 % - and it is calcite. It was shown by X-ray tests, wherein complete dissapearance of calcite peak was observed in the leached material.

What has been proved is the positive role and justified use of *Aspergillus niger* fungus in the process of leaching metals from raw materials deposited in alkaline gangue.

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# Bacterial extraction of sulphur from preleached chalcopyrite

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## Abstract

In this paper the changes in surface properties and the leaching of chalcopyrite $CuFeS_2$ after ultrafine grinding are examined. The methods of surface area measurement and photoelectron spectroscopy (XPS) were used for characterization of the ground samples. Gradual diminishing of particle size from 32 µm for as received $CuFeS_2$ to 2 µm for sample ground for 60 minutes as well as increasing surface area from 0.23 $m^2g^{-1}$ to 2.68 $m^2g^{-1}$ for equal samples was observed. Analysis of the XPS line of sulphur S2p has shown the existence of sulphur in three different chemical forms: $S^{2-}$, $S^0$ and $S^{6+}$. The ground samples exhibited a greater proportion of higher oxidation states. The samples were chemically preleached with the acid solution of Fe(III) sulphate to equal conversion degree ($\varepsilon_{Cu}$ = 25 %), characterized and subsequently leached by bacteria *Thiobacillus thiooxidans*. While the rate of chemical leaching is proportional to the increase in $CuFeS_2$ surface area, the rate of subsequent bacterial leaching is limited by 15 minutes grinding. The different behaviour of the samples ground for a langer time may be explained by differences in chemical composition of surface layers.

**Key words:** *Thiobacillus thiooxidans,* chalcopyrite, sulphur, bacterial leaching

### Bakteriálna extrakcia síry z predlúhovaného chalkopyritu

Skúmal sa vplyv ultrajemného mletia na zmenu povrchových vlastností a proces chemického a bakteriálneho lúhovania $CuFeS_2$. S dobou mletia klesá stredný rozmer častíc z 32 µm na 2 µm a narastá ich povrch z 0,23 na 2,68 $m^2g^{-1}$. Analýza XPS línií síry potvrdila prítomnosť jej $S^{2-}$, $S^0$ a $S^{6+}$ foriem, pričom u mletých vzoriek bolo zastúpenie $S^{6+}$ vyššie. Následné bakteriálne lúhovanie kmeňom *Thiobacillus thiooxidans* ukázalo, že nárast jeho rýchlosti je limitovaný 15 minútovým mletím. Pokles reaktivity pri vyšších časoch mletia môže súvisieť s rozdielnym zložením povrchových vrstiev chalkopyritu.

## Introduction

Several agents have been tested for chemical leaching of chalcopyrite ($CuFeS_2$). Owing to refractory character of this mineral a sufficient recovery of copper requires application of strong oxidizing agents among which the solutions of trivalent iron have been especially utilized (Dutrizac, 1978; Munoz et al., 1979; Majima et al., 1985; Tkáčová and Baláž, 1988). Ferric sulphate reacts with chalcopyrite in the presence of sulphuric acid according to the equation

$$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S \qquad (1)$$

The elemental sulphur formed during leaching covers the particle surface and is therefore considered to be responsible for slowing down the rate of leaching (Dutrizac, 1989). Scientists and technologists are still searching for some method to suppress the above-mentioned unfavourable effect. One of the ways to this aim is to use bacterial leaching where the produced sulphur is oxidized to form sulphuric acid. In our previous investigation bacteria *Thiobacillus ferrooxidans* were used for subsequent leaching of chemically preleached chalcopyrite (Baláž et al., 1991). It has been found that the rate of bacterial leaching is a function of specific surface area of the preleached chalcopyrite and decreases with increasing amount of the sulphur, created on the surface by reaction (1). The retardation effect due to formation of the protecting sulphur layer is significant in bioleaching. Nevertheless, it is possible to eliminate this effect, i. e. by using other sulphur oxidizing bacteria, e. g. *Thiobacillus thiooxidans.* According to literature data (Waksman and Joffe, 1922) these bacteria oxidize elemental sulphur to sulphuric acid without accumulation of any intermediate oxidation product.

This process obeys the following reaction scheme

$$2S + 3O_2 + 2H_2O = 2H_2SO_4 \quad (2)$$

The objective of this study has been to determine the surface properties of preleached samples of chalcopyrite and to evaluate the feasibility of leaching these samples by *Thiobacillus thiooxidans.*

## Experimental procedures

### Materials

The investigations were carried out with a sample of chalcopyrite $CuFeS_2$ (Slovinky deposit, Slovakia) of the following composition: 31.55 % Cu, 31.44 % Fe, 32.54 % S, 4.11 % $SiO_2$, 0.24 % insoluble residue. The X-ray diffraction examination showed that the mineral components were chalcopyrite (JCPDS-ICDD, 9-423), pyrite (JCPDS-ICDD, 6-0710) and quartz (JCPDS-ICDD, 5-0490).

Ultrafine ground chalcopyrite samples were characterized by methods of surface area measurements and XPS analysis. Details are published in Baláž et al. (1996).

### Chemical leaching

The chemical leaching was investigated in a stirred 500 ml glass reactor where 300 ml of leaching solution (0.25M $Fe_2(SO_4)_3$ + 0.25 M $H_2SO_4$) were placed. After heating to the temperature of 90 °C (± 0.1 °C), 4g of $CuFeS_2$ were added and the leaching started at appropriate time intervals. Aliquots (1ml) of the solution were withdraw and subjected to determination of the percentage of dissolved copper by atomic absorption spectroscopy.

### Bacterial leaching

Bacteria *Thiobacillus thiooxidans* were used for leaching. The leaching was carried out under the following conditions: A culture of active bacteria was first centrifuged. Thus the heavier sulphur sedimented and the supernatant fluid containing the bacteria was filtered through a membrane filter of 0.40 µm pore size. Finally, the filter containing the bacteria was transferred into a sulphur free fresh medium (Waksman and Joffe, 1922). Then the chalcopyrite samples (2g) were subjected to leaching in 100 ml of the prepared bacterial suspension. The initial biomass concentration in the suspension was 8.97 mg of bacterial protein per liter. The leaching continued for 10 days at atmospheric pressure and 30 °C in a rotary shaker operating at 180 rpm. Aliquots (0.2 ml) of the solution were taken for determining $SO_4^{2-}$ by the nephelometric $BaCl_2$ method.

### Processing of recovery data

The kinetics of chemical leaching according to equation (1) has been described by the Ginstling-Brounstein equation derived for heterogeneous processes controlled by diffusion through solid product

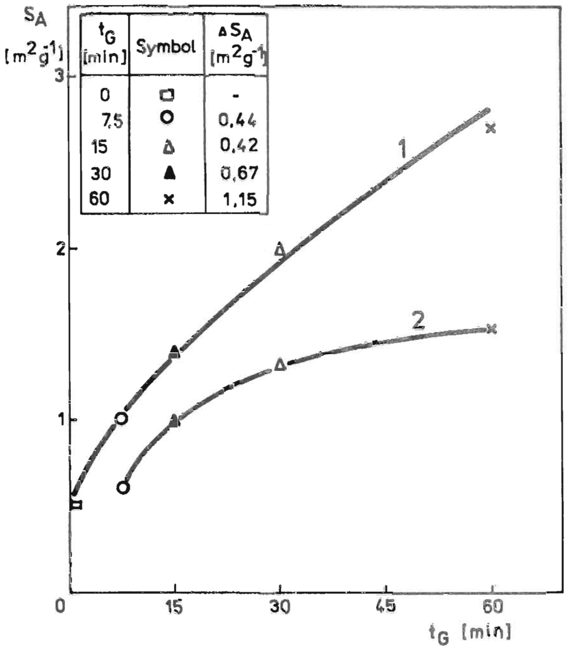

Fig. 1. Specific surface area, SA of $CuFeS_2$ vs. grinding time, $t_G$: 1- samples after ultrafine grinding, 2 - ground samples after chemical and bacterial leaching.

$$1 - 2/3\ \varepsilon_{Cu} - (1 - \varepsilon_{Cu})^{2/3} = k.t_L \quad (3)$$

where $\varepsilon_{Cu}$, k and $t_L$ are recovery of copper into leach, rate constant and time of chemical leaching, respectively.

The kinetics of bacterial oxidation of sulphur was characterized by the rate constant µ calculated from exponential stage of leaching governed by the equation

$$C = C_0.e^{\mu.t_{BL}} \quad (4)$$

where C, $C_0$, µ and $t_{BL}$ are concentration of the $SO_4^{2-}$ ions, concentration of the $SO_4^{2-}$ ions in the time moment $t_{BL} = 0$, rate constant (equivalent to specific growth rate) and time of bacterial leaching, respectively.

## Results and discussion

### Influence of ultrafine grinding on physico-chemical properties of $CuFeS_2$

In Fig. 1 the values of specific surface of $CuFeS_2$ are depicted as a function of grinding time. The surface of ground samples progressively increased from the original value of 0.50 $m^2g^{-1}$, corresponding to a non-ground sample up to more than fivefold value corresponding to a sample ground for 60 minutes (curve 1). Simultaneously the mean grain diameter $d_{50}$ decreased from the value of 32 µm to a few micrometers, corresponding to samples ground for 7.5 minutes and more. The presence

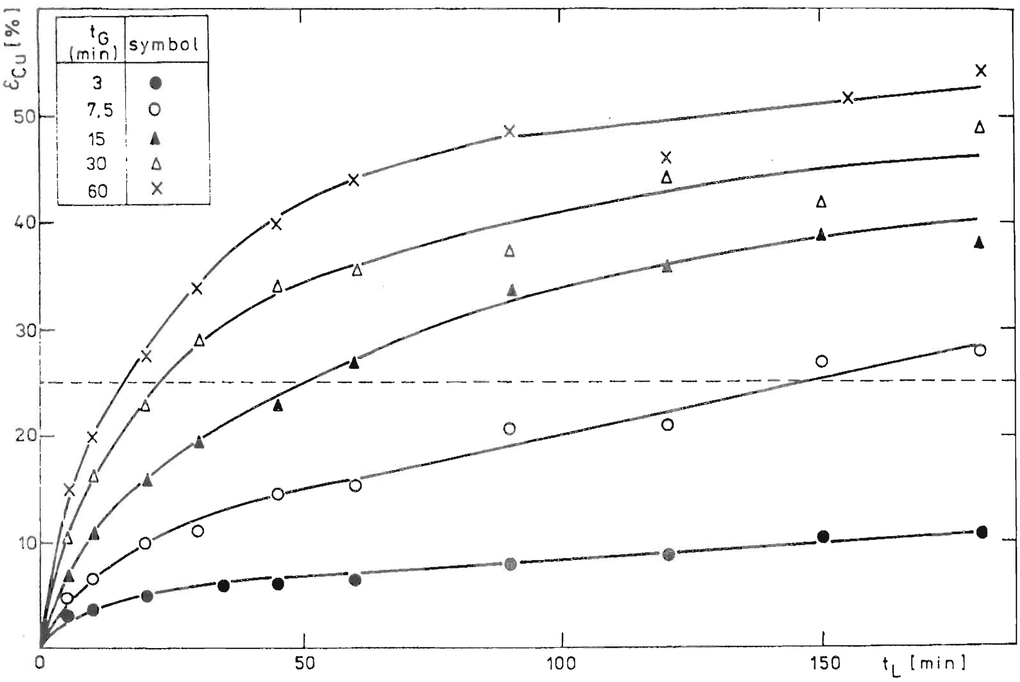

Fig. 2. Copper recovered in solution, $\varepsilon_{Cu}$ vs. duration of chemical preleaching, $t_L$ for $CuFeS_2$ ground in different times, $t_G$.

of individual elements in surface of $CuFeS_2$ samples was estimated by the method of photoelectron spectroscopy. The relative atomic concentrations of elements in a non-ground reference sample and in a sample ground for 15 minutes are given in Tab. 1. The results from the presented are data that sulphur occurred in samples in three chemically different forms, i. e. in sulphidic form, elemental form and in sulphate form. By fitting the spectra the following values of bond energy were found for individual forms of sulphur: $S^{2-}$ - 162.0 eV, $S^0$ - 164.2 eV and $S^{6+}$ -169.1 eV. For ground sample can be observed a higher proportion of higher oxidation degrees of sulphur which might be a consequence of surface oxidation of chalcopyrite in the course of grinding (Brion, 1980; Baláž et al., 1993).

The decrease in iron concentration of the ground sample indicates that some form of iron may arise at the surface of chalcopyrite which is able to be set free in the course of grinding in liquid medium. The occurrence of carbon and to a certain extent of oxygen in minerals is quite usual and is due to adsorption of carbon dioxide. The decrease in carbon concentration in a ground sample indicates that it is the surface carbon that is set free in the course of grinding.

Tab. 1
Relative atomic concentrations of elements in $CuFeS_2$ samples referred to copper concentration

| Grinding time (min) | S |  |  | Fe | O | C |
|---|---|---|---|---|---|---|
|  | total | $S^{6+}/S^{2-}$ | $S^0/S^{2-}$ |  |  |  |
| 0 | 3.5 | 0.24 | 0.14 | 0.88 | 6.7 | 11.5 |
| 15 | 3.9 | 0.35 | 0.32 | 0.81 | 6.6 | 7.4 |

### *Chemical and bacterial leaching of ultrafine ground $CuFeS_2$*

The samples ground for 3, 7.5, 15, 30 and 60 minutes were leached with ferric sulphate for 180 minutes. The course of kinetic curves of leaching is represented in Fig. 2. The experiments were repeated and the leaching continued until the recovery $\varepsilon_{Cu}$ = 25 % (dashed line) was attained. For the sample ground for 3 minutes, the recovery $\varepsilon_{Cu}$ = 25 % was not reached under the used experimental conditions. The solid residues of the samples ground for 7.5, 15, 30, and 60 minutes were filtered, dried and exposed to subsequent bacterial leaching. The results of bacterial leaching of $CuFeS_2$ ground for different times $t_G$ and chemically preleached to $\varepsilon_{Cu}$ = 25 % are represented in Figs. 3 and 4. While the rate of chemical leaching corresponds to the increase in chalcopyrite surface area, the bacterial leaching is effective only for the samples ground for 7.5 and 15 minutes.

As to the samples ground for a longer time, the effectiveness of bacterial leaching does not practically manifest itself, which is also consistent with the pH values of medium (Tab. 2). However, for all grinding times there is valid that the oxidation process of non-sulphidic sulphur to sulphate by bacteria according to equation (2) proceeds selectively with minimum solubilization of copper and iron (Fig. 5). This solubilization is a consequence of indirect leaching, i. e. chemical leaching of the mineral (Groudev, 1983). In this connection the zero content of

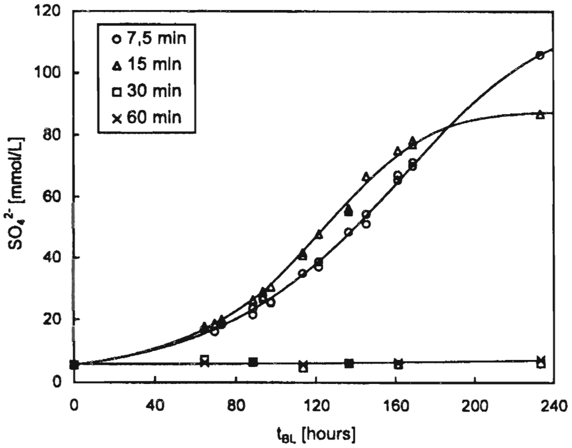

Fig. 3. Sulphate concentration, CSO$_4^{2-}$ vs. duration of bacterial leaching, $t_{BL}$ for CuFeS$_2$ ground in different times, $t_G$ and chemically preleached to $E_{cu}$ = 25 %.

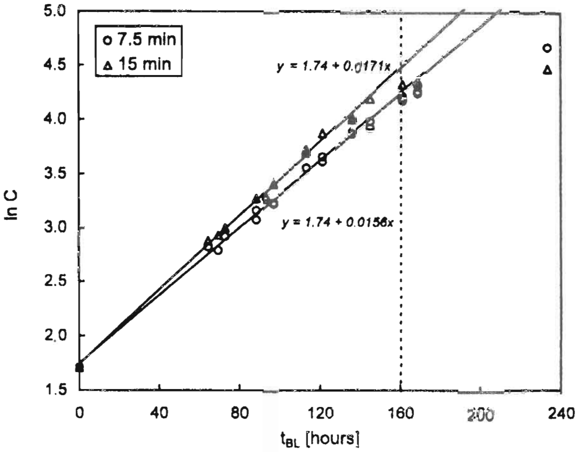

Fig. 4. Logarithm of sulphate concentration ln C vs. duration of bacterial leaching $t_{BL}$ for CuFeS$_2$ ground for 7.5 and 30 min. Eq. 4 becomes linear $\ln C = \ln C_0 + \mu . t_{BL}$ with intercept $\ln C_0$ and slope $\mu$. Linear regression was calculated only for data up to 160 hours (dashed line).

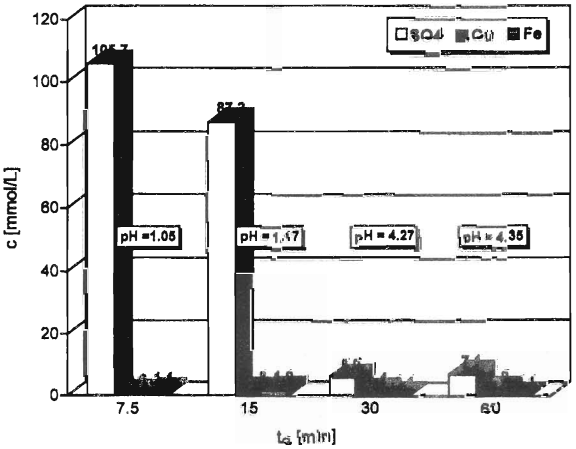

Fig. 5. Sulphate, copper and iron concentrations in solutions and final pH value after 10 days bacterial leaching of CuFeS$_2$ ground in different times, $t_G$ and chemically preleached to $\varepsilon_{cu}$ = 25 %.

soluble iron in the discussed samples is also remarkable. The heterogeneity of surface (Fig. 1, curve 2) also changes. While the samples ground for 7.5 and 15 minutes exhibit the surface difference ΔSa between original ground sample and sample after combined chemical and bacterial leaching $\Delta S_A \approx 0.4$ m$^2$g$^{-1}$; this difference indicates to 0.67 or 1.15 m$^2$g$^{-1}$ for the samples ground for 30 minutes or 60 minutes. This fact indirectly confirms a changed quality of the surface as well.

An explanation of the differences between the values obtained for differently ground samples (7.5 and 15 minutes grinding as opposes to 30 and 60 minutes grinding) can be furnished by analyzing the corresponding photoelectron spectra. The photoelectron spectra of sulphur S2p as well as of the CuFeS$_2$ surface of the samples ground for 7.5 min.(1) and 60 min. (3) and the equal samples subjected to combined leaching-spectra (2) and (4) are represented in Fig. 6. The relative atomic concentrations of elements in the surface are summarized in Tab. 3. From the view point of the found differences the information about sulphur and iron is important. The values found for sulphur correspond with the relations represented in Fig. 4 while the ratio S$^0$/S$^{2-}$ is equal to 2.9 (0.51:0.24) for the sample ground for 7.5 minutes and this value is equal to 2.9 (0.60:0.21) for the sample ground for 60 minutes. Thus the analysis of surface of the solid phase confirms that the bacterial leaching is more efficacious with respect to elemental sulphur in the sample ground for 7.5 minutes.

The deciding contribution to elucidation of the differences between differently ground samples has been provided

Tab. 2
Rate constant-μ, doubling time-*T* in the exponential phase and the final pH value of medium after 10 days bacterial leaching

| Sample<br>Grinding time (min) | μ [h$^{-1}$] | *T* [h]* | pH** |
|---|---|---|---|
| 7.5 | 0.0156 | 44.4 | 1.05 |
| 15 | 0.0171 | 40.8 | 1.17 |
| 30 | - | - | 4.27 |
| 60 | - | - | 4.36 |

* doubling time is the time taken for the bacterial population to double, it is the natural logarithm of 2 (0.639) divided by the specific growth rate (ln2/μ)
** initial pH value of medium was 4.3

Tab. 3
Relative atomic concentrations of elements in CuFeS$_2$ samples, concentrations of elements are referred to copper concentration

| Sample Grinding | Combined leaching | S | | Fe(O+S$^{6+}$) /Fe(CP) | Si | N |
|---|---|---|---|---|---|---|
| | | S$^{6+}$/S$^{2-}$ | S$^0$/S$^{2-}$ | | | |
| 7.5 | - | 0.56 | 0.24 | 6.15 | 0.63 | 0.00 |
| 7.5 | + | 0.26 | 0.51 | 4.84 | 2.17 | 2.25 |
| 60 | - | 0.64 | 0.21 | 6.41 | 0.68 | 0.00 |
| 60 | + | 0.29 | 0.60 | 2.34 | 1.55 | 0.35 |

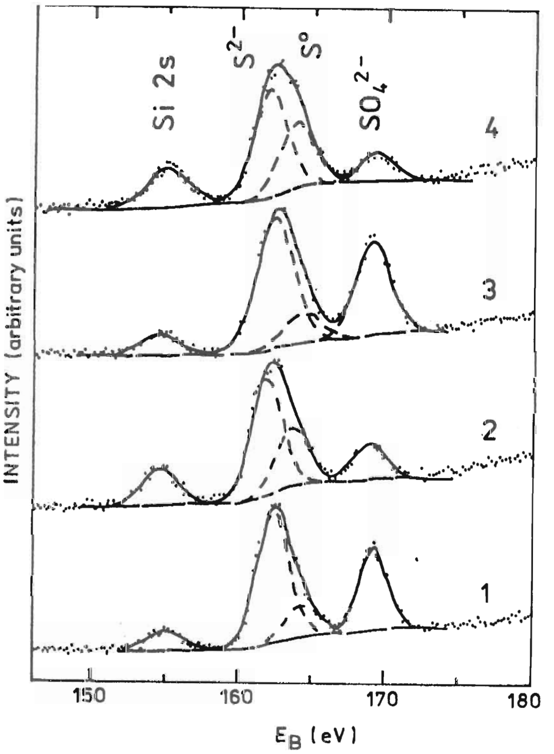

Fig. 6. XPS S2p spectra of $CuFeS_2$ samples: 1 - $CuFeS_2$ ground for 7.5 minutes, 2 - sample 1 after combined chemical and bacterial leaching, 3 - CuFeS2 ground for 60 minutes, 4 - sample 3 after combined (chemical and bacterial) leaching.

by the analysis of surface iron. Because of the closeness of the oxide (O) and sulphate ($S^{6+}$) lines of iron (Briggs and Seach, 1983), their differentiation was not feasible and for this reason only the ratio of Fe ($O+S^{6+}$) to iron in chalcopyrite Fe (CP) is given in Tab. 3. While this ratio is equal to 0.8 (4.84:0.15) for the sample ground for 7.5 minutes, it is equal only to 0.4 (2.34:6.41) for the sample ground for 60 minutes. It results from this fact that the sample (60 minutes) non-active from the viewpoint of bacterial leaching exhibits the twofold deficit of surface iron in the solid phase when compared with the active sample (7.5 minutes). However, the analysis of the liquid phase of this sample did not detect any iron at all (Fig. 5).

We can assume that not only the discussed change in surface heterogenity of the fine ground samples (30 and 60 minutes) but also a change in chemical surface composition has arisen. A compounds of the hydroxide or hydroxysulphate type is likely to be formed. For instance, Brion (1980) states that $Fe(OH)SO_4$ is present at the surface of chalcopyrite because of its long-term oxidation. A washing out of this compounds due to bacterial leaching could be responsible for the increase in pH of the leach (Fig. 5) as well as for the decrease in iron content in the solid phase (Tab. 3) for the samples ground for 30 minutes and more. A negative influence of fine fractions of other sulphides on the bacterial oxidation kinetics was also observed for leaching pyrite by *Thiobacillus ferrooxidans* (Baláž et al., 1991). In order to explain these phenomena in more details, a thorough study the mechanisms of microbial adhesion at various surfaces would be necessary.

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# Arsenic(III) inhibits more metabolic steps of iron(II) oxidation system in *Thiobacillus ferrooxidans*

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## Abstract

Kinetic analysis of Fe(II) oxidation by nongrowing cells of *Thiobacillus ferrooxidans* in the presence of arsenic(III, V) demonstrated both qualitative and quantitative changes in the inhibition pattern during several hours of incubation only in the case of arsenic(III). More complex inhibitory effect of arsenic(III) on the components of Fe(II) oxidation system was assumed, which was supported by results on growth culture inhibited by low arsenic(III) concentrations. The active culture growth was much less inhibited compared with the culture in the lag time. Consequences on bacterial leaching of arsenopyrite are discussed.

### Inhibícia niektorých komponentov $Fe^{2+}$-oxidačného systému T. f. $As^{3+}$

Analýza kinetiky oxidácie $Fe^{2+}$ prežívajúcimi (nerastúcimi) bunkami T. f. v prítomnosti As(III, V) poskytla kvalitatívne aj kvantitatívne dôkazy o inhibičných zmenách počas niekoľkohodinovej inkubácie T. f. iba v prítomnosti $As^{3+}$. V prípade $As^{3+}$ sme takýto vplyv aj očakávali. Tento predpoklad sa potvrdil rastom kultúry T. f. v prítomnosti nízkych koncentrácií $As^{3+}$. Inhibičný vplyv $As^{3+}$ sa prejavoval najmä v lag-fáze rastu kultúry T. f. V práci zároveň opisujeme vplyvy $As^{3+}$ na bakteriálne lúženie.

## Introduction

Relation of arsenic toxicity to biohydrometallurgy (Rawlings and Silver, 1995) is based on its influence on the rate of arsenopyrite oxidation by *Thiobacillus ferrooxidans*. Arsenic toxicity is highly dependent on its oxidation state. Generally, trivalent arsenicals are much more toxic than the pentavalent derivatives. Toxicity of arsenite is due to its binding to protein sulphydryl groups, arsenate is a toxic analog for inorganic phosphorylating activities (Cervantes, Ramírez and Silver, 1994). During arsenopyrite biooxidation, As(III) is approximately three times more toxic to leaching bacteria than As(V) (Barrett, Hughes, Karavaiko and Spencer, 1993).

The form of arsenic in the leaching solution depends on more factors. The primary process of arsenopyrite oxidation by *T. ferrooxidans* can be described as follows (Barrett, Hughes, Karavaiko and Spencer, 1993; Zeman, Mandl and Mrnuštíková, 1995):

$$\mathrm{FeAsS} \xrightarrow{O_2,\ \text{bacteria}} \mathrm{Fe(II)} + \mathrm{As(III)} + \mathrm{S(VI)}$$

This overall primary reaction has a complex stoichiometry and must occur in a number of stages (Barrett, Hughes, Karavaiko and Spencer, 1993). Secondary processes include bacterial Fe(II) oxidation and a possible chemical As(III) oxidation. According to another report (Monroy Fernandez, Mustin, deDonato, Barres, Marion and Berthelin, 1995), S(VI) formation has been considered as a secondary product of bacterial oxidation of elemental sulphur, the formation of which has been detected only during the chemical arsenopyrite oxidation (Zeman, Mandl and Mrnuštíková, 1995). In addition to As(III), earlier reports also suggested an As(V) formation during arsenopyrite oxidation (Karavaiko, 1985), which does not seem to be a primary process at present. A relation between arsenopyrite and its oxidation arsenical products is shown in Fig. 1.

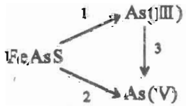

Fig. 1. Arsenic formation during biooxidation of arsenopyrite. 1 - major pathway, 2 - minor pathway(?), 3a - oxidation by Fe(III) under pyrite (Barrett, Ewart, Hughes and Poole, 1993; Mandl and Vyškovský, 1994) or chalcopyrite (Barrett, Ewart, Hughes and Poole, 1993) catalysis supported by mineral-surface-oxidizing bacteria; b - enzymic oxidation by thermophilic bacterial strain *Sulfolobus acidocaldarius* (Sehlin and Lindström, 1992).

Under acid mesophilic bioleaching conditions, oxidation of As(III) according to the stage 3a in Fig. 1 seems to be a general pattern resulting in a relatively detoxification effect. In dependence on the rates of above As(III) formation and As(III) oxidation, both the arsenic ions can appear in

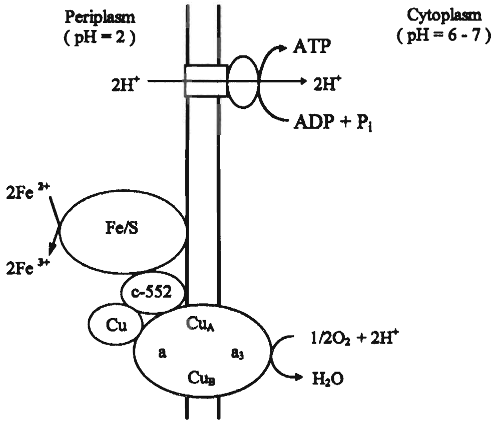

Fig. 2. A schematic presentation of the electron transport system coupled to the Fe(II) oxidation by *T. ferrooxidans*. Fe/S, c-552 and Cu are Fe(II)-cytochrome *c* oxidoreductase, soluble cytochrome *c*, and rusticyanin, respectively. a, $a_3$, $Cu_A$, and $Cu_B$ are likely components of a terminal cytochrome *c* oxidase (Yamanaka, Yano, Kai, Tamegai and Fukumori, 1993; Rawlings and Kusano, 1994; Yamanaka and Fukumori, 1995).

the bioleaching system and, based on a sensitivity of bacterial strain to arsenic ions, affect Fe(II) oxidation and the rate of bacterial leaching of arsenopyrite minerals.

This paper summarizes our results concerning inhibition effects of the arsenic ions on Fe(II) oxidation in *T. ferrooxidans*.

## Materials and methods

Culture conditions and a bacterial suspension preparation of *T. ferrooxidans* (CCM 4253) were described earlier (Mandl and Vyškovský, 1994). Inhibition of Fe(II) oxidation by arsenic(III, V) was studied in bacterial suspension ($10^8$ cells/ml, pH 1.7) supplemented with either $NaAsO_2$ or $Na_3AsO_4$; $FeSO_4$ served as a substrate. The rate of Fe(II) oxidation was measured by the rate of oxygen consumption using a Clark-type oxygen electrode. Regression analysis was used for evaluation of the inhibition. Growth of the culture was monitored by Fe(III) formation using ultraviolet absorption spectrometry (Mandl and Nováková, 1993).

## Results and discussion

All classical kinetic approaches resulted in a non-competitive type of inhibition of Fe(II) oxidation by both the arsenic ions (Mandl, Hrbáč and Dočekalová, 1996). $K_i$ were 45±11 mM and 143±19 mM for As(III) and As(V), respectively (95 % confidence intervals). These results correspond to the conditions without preincubation of cells with arsenic ions and, based on the defined kinetics of enzyme inhibition, a specific initial enzyme inhibition can be assumed.

It is probable that the initial inhibitory effect of arsenic ions is connected with a periplasmic space at the stage of Fe(II)-cytochrome *c* oxidoreductase - the primary acceptor for electrons from Fe(II) (Fig. 2). In contrast to As(V), inhibitory effect of As(III) was not constant in time. After preincubation of cells with arsenic, the defined inhibition character was gradually changed to a form no longer corresponding to any defined type of inhibition only in the case of As(III) (Mandl, Hrbáč and Dočekalová, 1996). This is illustrated in Fig. 3B after 16 h of preincubation.

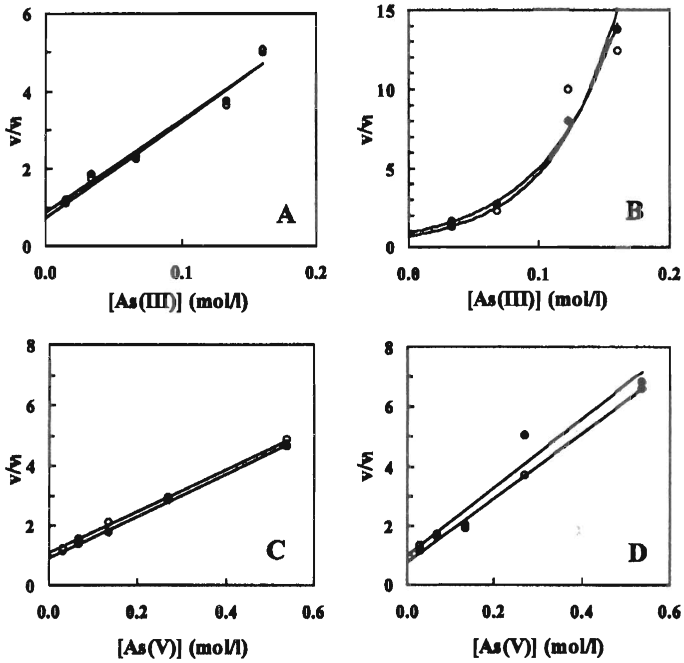

Fig. 3. Dependence of $v/v_i$ on arsenic concentration. $v/v_i = 1+[As]/K_i$, v and $v_i$ are Fe(II) oxidation rates in the absence and in the presence of As(III) (A, B) or As(V) (C, D), respectively, without preincubation (A, C) and after a 16-h preincubation (B, D) of bacteria with arsenic. Fe(II) concentration was 0.36 (o) and 1.79 (•) mM.

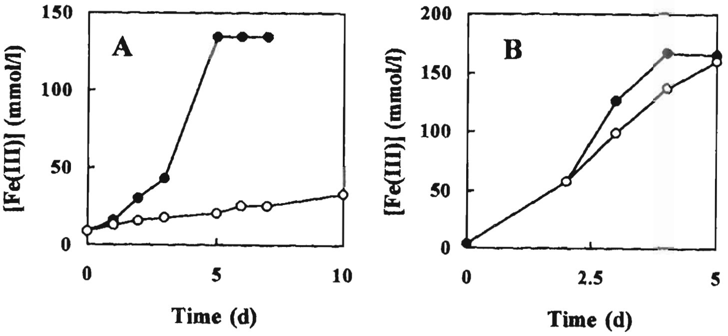

Fig. 4. Submerged growth of *T. ferrooxidans* on Fe(II) at a constant pH 1.5 in the presence (o) and in the absence (•) of 3.3 mM As(III), respectively. As(III) was added at the beginning of cultivation (A) and 2nd day of the growth (B).

The nonlinearity of the kinetic pattern may indicate a toxic effect extending to other components of Fe(II) oxidation system in the membrane or cytoplasm (see Fig. 2) due to As(III) interaction (with SH groups) in the membrane and its gradual penetration into the cells. In contrast to more complex inhibitory effect of As(III), the inhibition type of As(V) remained unchanged during the preincubation period (Fig. 3C, D). The decrease of $K_i$ for As(V) to 98 mM was not significant ($P > 0.01$).

In contrast to As(V), growth of cells was more sensitive to As(III) probably due to the possibility of further inhibitions of biosynthetic pathways. However, the observed preincubation changes may be also included in the increase of inhibitory effect on the growth. The growth of culture at pH 1.5 was strongly inhibited at 3.3 mM As(III) during the lag time (Fig. 4A) at which the unmultiplicating cells were exposed to As(III) for a longer period. The same As(III) concentration affected the active growth only slightly (Fig. 4B). It would correspond to a case when the multiplication rate of cells is higher than the rate of inhibitory changes occurred due to the gradual penetration of As(III) into the cells.

A combination of the sensitivity of the bacterial strain to As(III) and the spontaneous conversion of As(III) to less toxic As(V) influences the rate of arsenopyrite biooxidation. In the case that both the characteristics appear, the negative effect of arsenic on bioleaching process can be significantly decreased (Mandl, Hrbáč and Dočekalová, 1996).

*Acknowledgements.* This work was supported by grant No. 511/94/0487 from the Grant Agency of the Czech Republic.

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# Bacterial leaching of waste materials at the "Tatra" joint stock company, Kopřivnice

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### Abstract

This paper deals with application of bacteria *Thiobacillus ferrooxidans* onto two samples of wastes: grinding sludge and coal cinder and slag, produced by the Tatra Kopřivnice. From the results of bacterial leaching performed with pure cultures of *Thiobacillus ferrooxidans* and lasting one month there follows, that this kind of bacteria needs a long time of adapting onto the used waste samples. As, Ag, Pb and Ni were extracted from grinding sludge and, on the other hand, from coal cinder and slag Mn, Zn were observed. The improvement of these results can be achieved by applying of adapted cultures or by longer duration of leaching.

**Key words:** bacterial leaching, *Thiobacillus ferrooxidans*, grinding sludge, coal cinder and slag

### Bakteriálne lúhovanie odpadových materiálov v akciovej spoločnosti Tatra Kopřivnice

Práca sa zaoberá aplikáciou baktérií *Thiobacillus ferrooxidans* na vzorkách dvoch odpadových materiálov (brusný kal a škvara a troska z uhlia), ktoré produkuje a. s. Tatra Kopřivnice. Z výsledkov bakteriálneho lúhovania, ktoré trvalo jeden mesiac a bolo realizované s čistou kultúrou *Thiobacillus ferrooxidans* vyplynulo, že tento druh baktérií sa pomerne dlho adaptuje na použité odpadové vzorky. Z jednotlivých sledovaných ťažkých kovov sa z brusného kalu najlepšie vylúhujú As, Ag, Pb a Ni, naproti tomu zo škváry a trosky z uhlia sa najlepšie vylúhujú Mn a Zn. Zlepšenie výsledkov by bolo možné dosiahnuť použitím adaptovaných kultúr, alebo predĺžením doby lúhovania.

## The method of bacterial leaching

The bacterial leaching was performed in sterilized Erlenmeyer conical flasks filled with 10 grams of respective waste samples, 180 millilitres of 9K medium without $FeSO_4$, and 20 mililitres of the solution containing bacteria *Thiobacillus ferrooxidans*. The pure cultures of *Thiobacillus ferrooxidans* provided by the Mining Institute of the Slovak Academy of Sciences in Košice were used for the experiments. Acidobasic reaction of the environment was measured by means of the laboratory pH-meter Radelkis (Hungary). All the time during the experiment lasting 28 days, the pH value has been being kept at the optimal level between 1.8 up to 2.0 to eliminate the forming of unwanted mineral jarosite. The temperature during leaching was in the range between 26 up to 30 °C.

Mineralogical and chemical analyses were performed at the Research and Development Institute of Nová Huť steel works, Ostrava. The whole range chemical analysis was done by means of energy-dispersing spectrometre EDAX9900 with the PVQUAN software using the standards. The separate grains analysis was done by the same way, in this case without standards. The analysis of heavy metals, namely Fe, As, Cd, Mn, Cu, Zn, Pb, Ag, Cr, Ni, Ti, Al and Hg was performed at the Central Analytical Laboratory of VŠB-Technical University of Ostrava, using ICP.

## The MPN method

This method, invented by Meynell and Meynell in 1969, was adjusted at DMT Essen, Germany, and applied to special experiments. According to this method, the number of bacteria in 1 mililitre of solution is calculated as so called "most probable number" (MPN) which determines the concentration of $Fe^{2+}$ ions oxidized by bacteria. 27.5 microlitres of mineral suspension is mixed with 250 microlitres of medium in five parallel arrays. Every series is then diluted separately in ten steps in the ratio of 1:10. The dilution is performed on microtitration plates which are subsequently closed and incubated for two weeks in thermostat with the ambient temperature 30 °C. The growth of bacteria to the final dilution is evaluated according to the change of colour caused by the forming $Fe_2(SO_4)_3$. The statistic evaluation based on the standard tables is then performed.

## The characteristics of particular samples and the results of bacterial leaching

The grinding sludge occurs during grinding of workpieces (wheels, shafts, sleeves, etc.) while the workpieces are being cooled by various cooling liquids. The sludge then comes to mud traps, from where it is raised either mechanically or by means of filtre papers to waste containers.

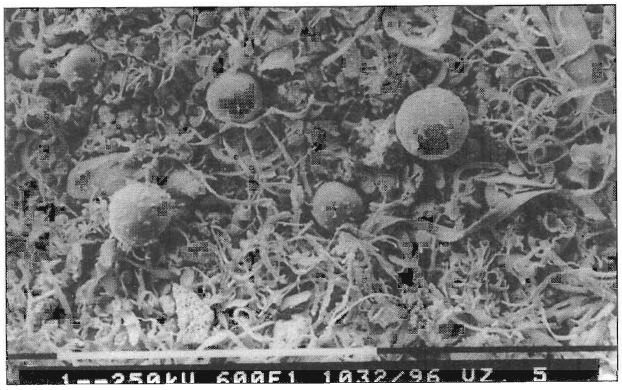

Fig. 1. Appearance of grinding sludge before leaching.

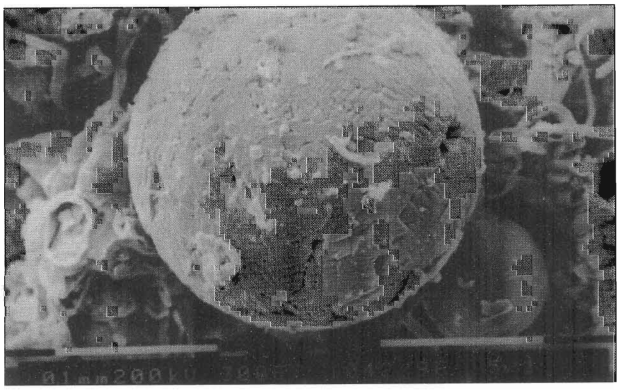

Fig. 2. Detail of iron globule.

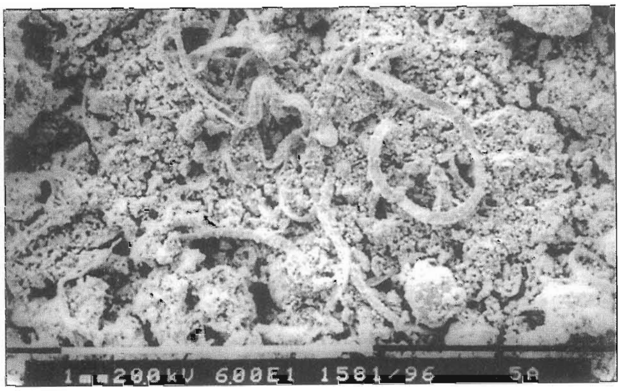

Fig. 3. Appearance of sample after bacterial leaching.

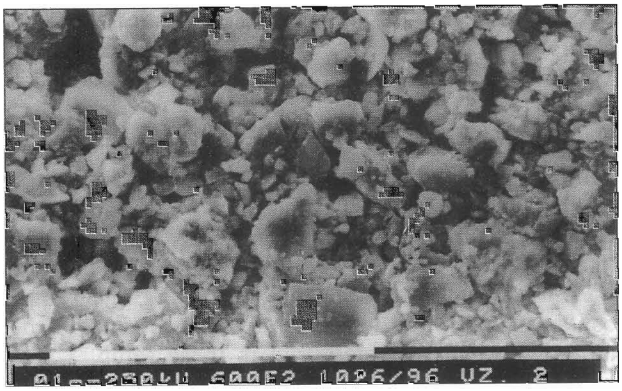

Fig. 4. Appearance of sample before leaching.

According to the used cooling liquid, the grinding sludge is classified as dangerous or normal waste material. In recent years the environmentally friendly liquids tend to be used.

The main component of grinding sludge is iron accompanied by common admixtures, namely Co, Mn and Si. By means of RTG difraction, the iron oxides and silicate phase have been identified in the grinding sludge as well. The sample forms little globules of metal iron before leaching as shown in Fig. 1, while Fig. 2 shows the detail of iron globule. After one month of bacterial leaching the main mineral phases, namely Fe and $Fe_3O_4$, remain in the samples. The morphological character of the sample can be seen in Fig. 3 showing relatively strong deterioration of the former sample.

The results of bacterial leaching presented in Tabs. 1 and 3 suggest that one month of leaching by means of pure bacterial culture is not enough and the improvement of results would require a longer duration of leaching. Out of the tracked heavy metals, the best results of leaching can be seen with As, Pb, Ni and Hg. The dilution of metal iron occurring in the sample can be observed, proved by the growing concentration of bivalent iron in the suspension.

## Coal cinder and slag

Coal from the Dukla Colliery is burned at the Tatra Company in Kopřivnice. Both cinder and slag occur during

Tab. 1
Results of bacterial leaching (in %)

| Element | As | Ag | Cr | Zn | Cd | Pb | Ni | Mn | Cu | Fe | Ti | Al | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Content of element before leaching | 0.0114 | 0.0003 | 1.350 | 0.023 | 0.00008 | 0.0082 | 0.7773 | 0.776 | 0.421 | 79.631 | 0.043 | 0.044 | 0.0005 |
| Content of element after leaching | 0.0016 | 0.0001 | 0.652 | 0.013 | 0.00006 | 0.0013 | 0.1290 | 0.663 | 0.179 | 62.320 | 0.235 | 0.120 | 0.0002 |
| Recovery of element into the leach | 85.96 | 66.66 | 51.70 | 43.48 | 25.00 | 98.41 | 83.40 | 13.45 | 57.48 | 18.89 | - | - | 60.00 |

Tab. 2
Results of bacterial leaching (in %)

| Element | As | Ag | Cr | Zn | Cd | Pb | Ni | Mn | Cu | Fe | Ti | Al | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Content of element before leaching | 0.0089 | 0.00011 | 0.025 | 0.015 | 0.00008 | 0.0030 | 0.0104 | 0.0610 | 0.0102 | 4.519 | 0.0099 | 0.146 | 0.0005 |
| Content of element after leaching | 0.0065 | 0.00030 | 0.012 | 0.004 | 0.00007 | 0.0025 | 0.0060 | 0.0002 | 0.0056 | 3.377 | 0.407 | 6.154 | 0.0002 |
| Recovery of element into the leach | 26.97 |  | 52.00 | 73.33 | 12.50 | 16.67 | 42.31 | 99.67 | 45.10 | 25.27 | - | - | 60.00 |

Tab. 3
Growth of biomass determined by the MPN method and the content of $Fe^{2+}$ ions in the solution

| Duration of leaching | $Fe^{2+}$ (milligrams per litre) | Number of bacteria |
|---|---|---|
| First week | 9,045.0 | $15.0 \times 10^3$ |
| Second week | 15,242.5 | $11.0 \times 10^5$ |
| Third week | 17,085.0 | $17.5 \times 10^6$ |
| Fourth week | 20,225.5 | $35.0 \times 10^9$ |

Tab. 4
Growth of biomass determined by the MPN method and the content of $Fe^{2+}$ ions in the solution

| Duration of leaching | $Fe^{2+}$ (milligrams per litre) | Number of bacteria |
|---|---|---|
| First week | 604.5 | $35.0 \times 10^3$ |
| Second week | 552.8 | $25.0 \times 10^5$ |
| Third week | 435.5 | $90.0 \times 10^8$ |
| Fourth week | 217.7 | $125.0 \times 10^9$ |

burning of this sort of coal but the cinder is a result of lower temperature burning. Both products are stored at the plant site and are used for winter maintenance of roads. The total production of this waste reaches 28,000 tons per year.

From the mineralogical point of view, the sample contains a large portion of carbon and silicates. Other minerals of interest identified in these samples were the grains of pyrite and occasional findings of $BaSO_4$ grains. The appearance of the sample before leaching can be seen in Fig. 4, the grain of $BaSO_4$ is shown in Fig. 5. The appearance of the sample after one month of leaching is shown in Fig. 6. Especially carbon and $SiO_2$ were identified by RTG diffraction after one month of leaching. An interesting grain with the content of Cr was found after leaching as well, as shown in Fig. 7. The results of bacterial leaching as presented in Tabs. 2 and 4 suggest that Zn and Mn are leached to a higher rate, while the content of Ti, Al and Ag grows due to the leaching of soluble mineral phases. Compared to previous case, the *Thiobacillus ferrooxidans* bacteria adapt faster to this sample as illustrated by their higher concentration and also by the decreased content of bivalent iron in the fourth week of leaching. In case of this sample too, the better results could be achieved by longer duration of leaching or by applying of better adapted bacterial cultures.

## Conclusions

The objective of presented research work was to measure and determine the suitability of bacterial leaching by applying it onto two samples of waste materials (grinding sludge and coal cinder and slag) produced by the Tatra Company, Kopřivnice. The results of bacterial leaching proved that these samples are suitable for applying *Thiobacillus ferrooxidans* bacteria,because those bacteria survive in these particular waste materials. However, better results could be achieved by applying adapted bacterial cultures and by longer duration of leaching.

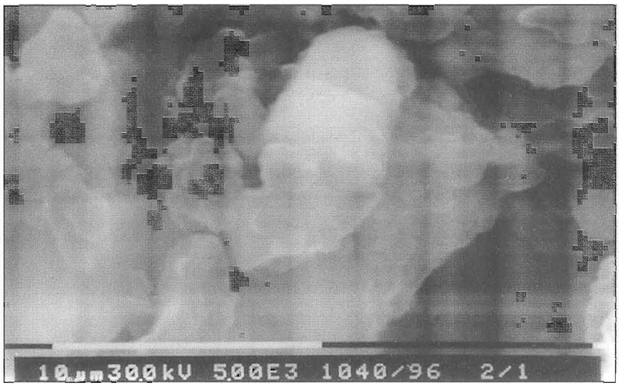

Fig. 5. $BaSO_4$ grain.

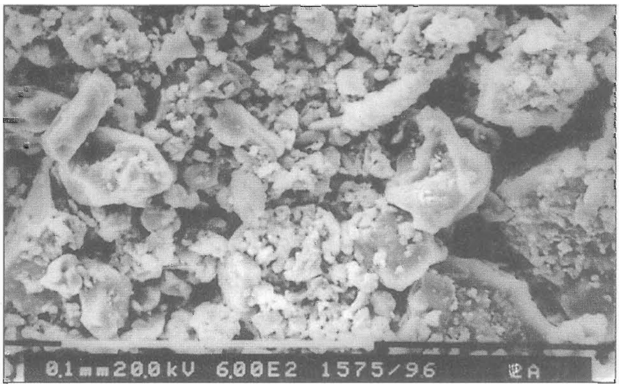

Fig. 6. Appearance of sample after one month leaching.

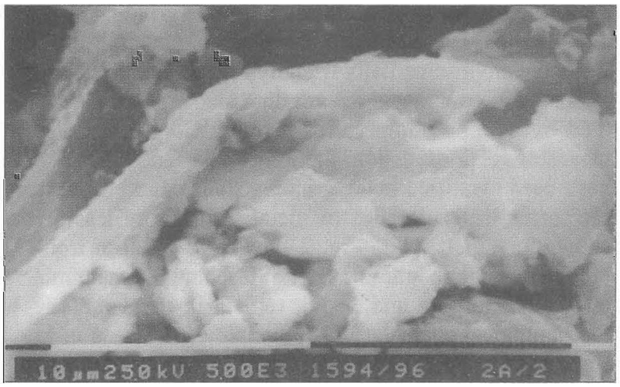

Fig. 7. The grain with higher content of Cr.

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# Inhibition effect of copper, hydrogen ions and increased cell concentration to the kinetics of iron (II) oxidation by *Thiobacillus ferrooxidans*

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## Abstract

The kinetics of Fe(II) to Fe(III) oxidation by *Thiobacillus ferrooxidans* was studied in a wide range of $FeSO_4$ concentrations at various pH and cell concentrations. The effect of cupric ions was also investigated. Michaelis-Menten kinetics equation was used to data processing. The analysis of the maximum reaction rates ($V_{MAX}$) and Michaelis constants ($K_M$) obtained for $Fe^{2+}$ oxidation indicated non-competitive mixed inhibition by $H^+$ ions at pH<1.9; competitive inhibition effect by increased cell concentration ($K_i = 1.16.\ 10^8$ cells. $mL^{-1}$) and non-competitive inhibition by $Cu^{2+}$ ions ($K_i = 14.35$ $g.L^{-1}$).

**Key words:** *Thiobacillus ferrooxidans*, Michaelis-Menten kinetics, copper, inhibition

### Inhibičný vplyv medi, vodíkových iónov a zvýšenej koncentrácie buniek na kinetiku oxidácie Fe(II) baktériami *Thiobacillus ferrooxidans*

Práca bola zameraná na štúdium kinetiky oxidácie Fe(II) na Fe(III) baktériami *Thiobacillus ferrooxidans* v širokom intervale koncentrácií $FeSO_4$, pri rôznych hodnotách pH a rôznej koncentrácii bakteriálnych buniek. Vplyv meďnatých iónov bol taktiež sledovaný. Pre spracovanie údajov bola použitá Michaelis-Mentenovej kinetická rovnica. Z rozboru maximálnych rýchlostí ($V_M$) a Michaelisových konštánt ($K_M$) získaných pri oxidácii $Fe^{2+}$ bola zistená nekompetitívna zmiešaná inhibícia $H^+$ iónmi v oblasti pH<1,9; kompetitívny inhibičný vplyv samotných buniek ($K_i = 1.16.10^8$ buniek .$mL^{-1}$) a nekompetitívna inhibícia iónmi $Cu^{2+}$ ($K_i = 14,35$ $g.L^{-1}$).

## Introduction

The chemolithotrophic bacterium *Thiobacillus ferrooxidans* (Temple and Colmer, 1951) oxidizes Fe(II) sulphate to Fe(III) sulphate in aerobic acid conditions following eq. 1

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O \qquad (1)$$

Ferric ion is a powerful oxidant. It is responsible for release of heavy metals in acid mine drainage waters. The oxidizing property makes the ferric iron one of the most useful reagents in hydrometallurgy, e. g. for dissolution of various minerals, coal desulphurization, etc.

The current model for the iron-oxidizing system in *Thiobacillus ferrooxidans* suggests electron carriers associated with the cell envelope (Bodo and Lundgren, 1974). It assumes the oxidation of ferrous iron at the outer membrane and the reduction of $O_2$ inside the cell. Ingledew (1986) proposed that ferrous iron reduces membrane-bound ferric iron. Electrons are transferred to rusticyanin and subsequently to cytochrome c. Rusticyanin is a 16.5-kDa type I copper protein which is remarkably stable at acidic pH (0.2) and which is though to be the principal component in the iron respiratory electron transport chain of *Thiobacillus ferrooxidans* (Djebli et al., 1992).

This paper presents the inhibitory effect of $H^+$ and $Cu^{2+}$ ions concentration to the kinetics of ferrous iron oxidation by *Thiobacillus ferrooxidans*. Inhibition by increasing concentration of cells is also presented.

## Materials and methods

### *Bacterial strains, cultivation and suspension*

*Thiobacillus ferrooxidans*, laboratory strain [CCM 3973] and three mine isolates, T. f(pe), T. f(mo) and T. f (ho) were used in experiments. Microorganisms were cultivated in standard 9K liquid medium (Silverman and Lundgren, 1959) at 30 °C in 500 mL spherical flasks on a rotary shaker at 180 rpm. Bacterial cells were harvested towards the end of the log phase capturing them on a membrane filter. To remove the rest culture medium from cells they were first washed three times with 0.1 M hydrochloric acid and then with distilled water. Finally the cells were resuspended from the filter to distilled water. The cell concentration in suspension was determined turbidimetrically at 450 nm.

### *Ferrous iron oxidation measurements*

The rate of $Fe^{2+}$ oxidation was monitored by measuring the oxygen uptake rate according to Eq. 1 at 30 ± 0.1 °C. The standard reaction mixture in a volume of 20 mL was

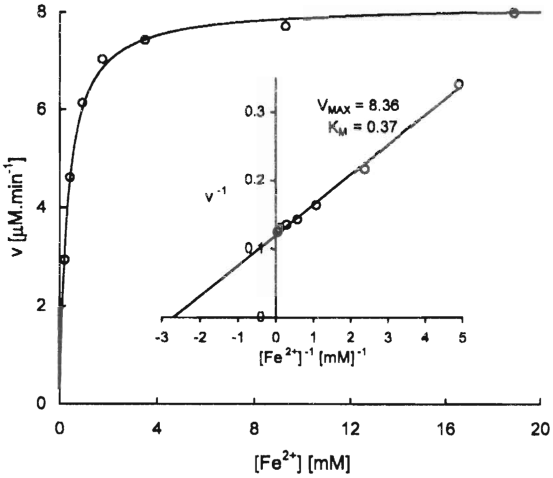

Fig. 1. Effect of $FeSO_4$ concentration on the Fe oxidizing activity (v) by *Thiobacillus ferrooxidans.* The insert is a double-reciprocal (Lineweaver and Burk, 1934) plot obtained after transformation of the Michaelis-Menten equation to linear form: $1/v = K_M/V_{MAX} .1/S + 1/V_{MAX}$.

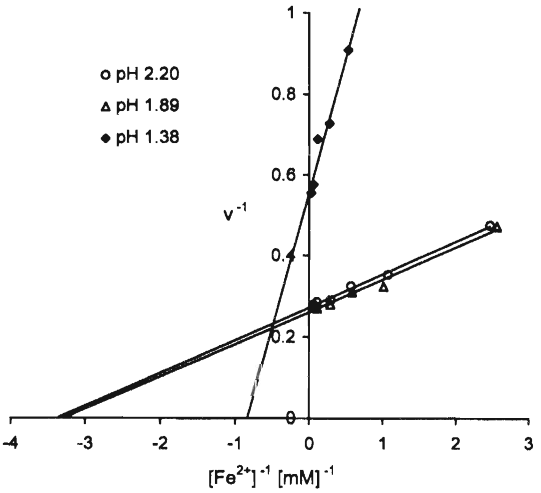

Fig. 3. Lineweaver-Burk plots (1/v vs. 1/ $Fe^{2+}$) of Fe oxidation rates at different pH. pH 2.2: $V_{MAX} = 3.65 \pm 0.04$, $K_M = 0.28 \pm 0.02$ pH; 1.89: $V_{MAX} = 3.76 \pm 0.05$, $K_M = 0.27 \pm 0.02$; pH 1.38: $V_{MAX} = 2.15 \pm 0.01$, $K_M = 1.1 \pm 0.02$. The position of the lines indicate non-competitive mixed inhibition type.

added in a water jacketed glass cell equipped with Clark oxygen sensor and magnetic stirrer. Care was taken in order to prevent any entrapped air bubbles. The measurement cell was sealed with a capillary bored bung to maintain atmospheric pressure within the cell.

The reaction was monitored immediately after appropriate $Fe^{2+}$ solution was added to the cell suspension. The initial linear rate of $O_2$ consumption was taken as the reaction rate (v).

In order to minimize the initial non-equilibrium state caused by thermal compensation of the reaction mixture, solutions were separately tempered before measurement.

$FeSO_4$ concentrations in samples were determined by titration with $K_2Cr_2O_7$.

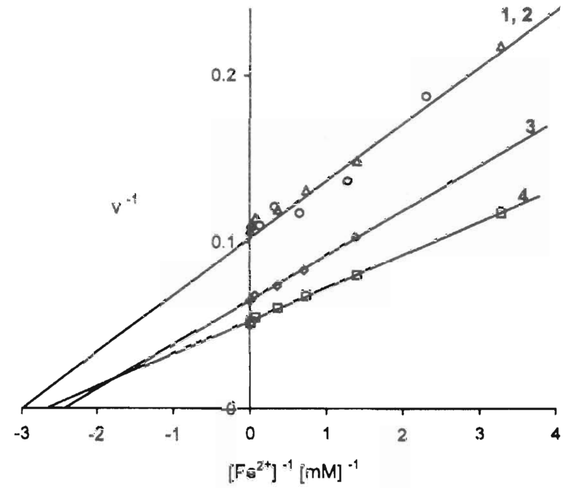

Fig. 2. Lineweaver-Burk plots of kinetics data obtained for various strains of *Thiobacillus ferrooxidans* at pH 1.9. Specific activities $V_{sp}$ ($\mu M.min^{-1}$) are calculated to the cell concentration of $5.10^7$ $mL^{-1}$ 1 - T. f. [CCM-3973] $K_M = 0.33$, $V_{sp} = 9.8$; 2 - T. f.(pe) $K_M = 0.31$, $V_{sp} = 19.3$; 3 - T. f.(mo) $K_M = 0.4$, $V_{sp} = 15.3$ ; 4 - T. f.(ho) $K_M = 0.37$, $V_{sp} = 18.9$.

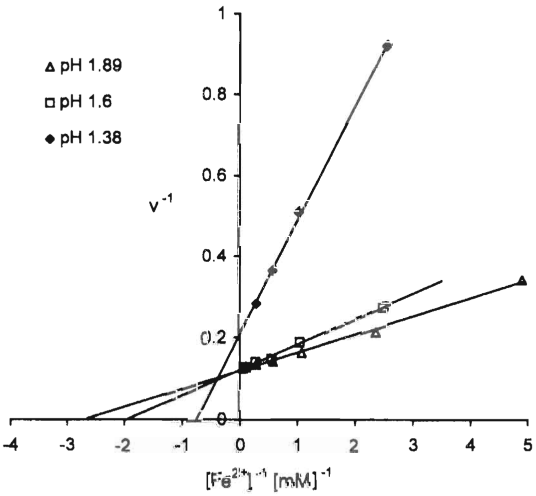

Fig. 4. Lineweaver-Burk plots (1/v vs. 1/ $Fe^{2+}$) of Fe oxidation rates at different pH. pH 1.89: $V_{MAX} = 8.14 \pm 0.10$, $K_M = 0.33 \pm 0.02$; pH 1.6: $V_{MAX} = 8.14 \pm 0.13$, $K_M = 0.49 \pm 0.04$; pH 1.38: $V_{MAX} = 5.44 \pm 0.01$, $K_M = 1.6 \pm 0.17$. The position of lines indicate non-competitive mixed inhibition type.

## Results and discussion

The rate of $FeSO_4$ oxidation measured as $O_2$ consumption ($\mu M.min^{-1}$) at a fixed concentration of cells increased with increasing concentration of $FeSO_4$, Fig. 1, following hyperbolic saturation type kinetics Eq. 2.

$$v = \frac{V_{MAX}.[S]}{K_M + [S]} \tag{2}$$

The double-reciprocal (Lineweaver and Burk, 1934) plots obtained after transformation of the Michaelis-Menten equation become linear $1/v = K_M/V_{MAX} .1/S + 1/V_{MAX}$.

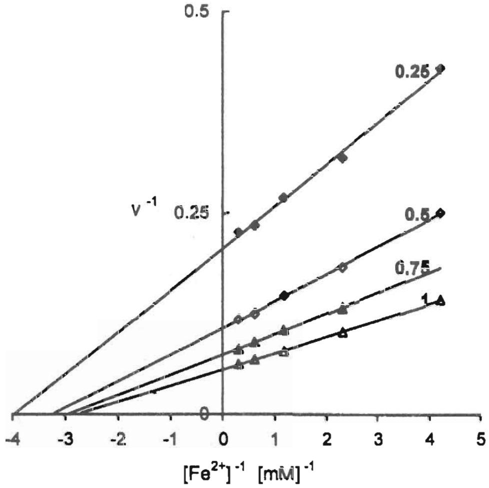

Fig. 5. Effect of $FeSO_4$ concentration on the Fe oxidizing activity of various concentrations of cells T. f. [CCM 3973]. The amounts of cells used were 0.25; 0.5; 0.75; and 1 x $10^8$ .mL$^{-1}$.

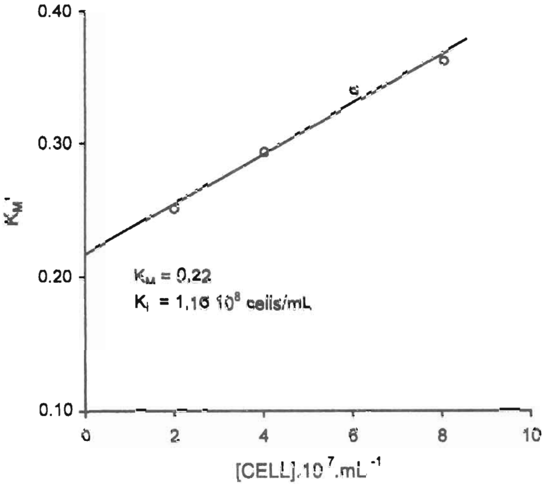

Fig. 6. Plot of the apparent $K_M$\` vs. inhibitor (i. e. cell) concentration ($K_M$\` = $K_M$ + [I].$K_M$/$K_i$). Obtained inhibition constant ($K_i$) value is in number of cells per mL.

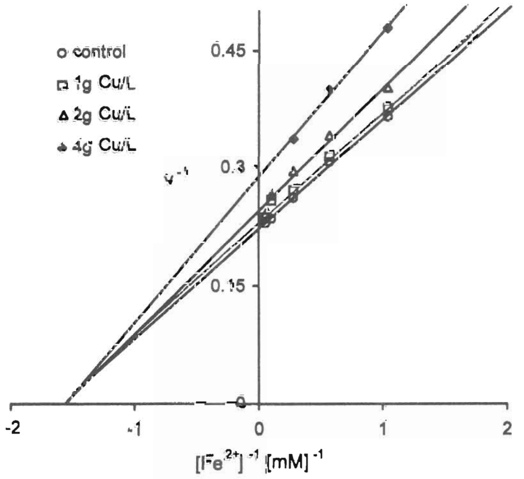

Fig. 7. Non-competitive inhibition of $Fe^{2+}$ oxidation rate at different concentrations of $Cu^{2+}$ ions ($K_i$ = 14.35 g.L$^{-1}$).

Apparent Michaelis constants ($K_M$) for $FeSO_4$ oxidation by cell suspensions of *Thiobacillus ferrooxidans* are reported to lie in a wide range (0.1 - 9.4 mM) (Tuovinen and Kelly, 1974; Bodo and Lundgren, 1974; Steiner and Lazaroff, 1974; Kelly and Jones, 1983; Suzuki et al., 1989). Obtained results can vary due to different experimental conditions and specific strain differences. Fig. 2 shows effect of $Fe^{2+}$ concentration on the $Fe^{2+}$ oxidizing activity of various strains of *Thiobacillus ferrooxidans* under equal conditions.

## Effect of $H^+$ ions

With respect to pH, *Thiobacillus ferrooxidans* is a strict acidophile (Apel and Dugan, 1978). It grows on iron in the pH range 1-4.5 (Jones and Kelly, 1983). Today it is generally agreed that optimal growth and iron oxidation occurs at approx. pH 2.0. There are no reports of growth of *Thiobacillus ferrooxidans* beyond pH 7.0 (Leduc and Ferroni, 1993)

To eliminate the decrease of $H^+$ activity with increasing $FeSO_4$ concentration, samples were adjusted to equal pH under potententiometric control.

Fig. 3 and 4 present results of $Fe^{2+}$ oxidizing activity obtained at different pH of medium. In the pH range of 2.2 to 1.9 ($V_{MAX}$ = 3.65, $K_M$ = 0.28 at pH 2.2; $V_{MAX}$ = 3.76, $K_M$ = 0.27 at pH 1.89) no significant differences in $Fe^{2+}$ oxidizing kinetics were obtained. Higher $H^+$ concentrations (activities) affected both $K_M$ and $V_{MAX}$ kinetics parameters ($V_{MAX}$ = 2.15, $K_M$ = 1.1 at pH 1.38) following non-competitive mixed inhibition type.

## *Effect of increasing concentrations of cells*

The double-reciprocal (1/v vs. 1/Fe conc.) plots (Fig. 5) showed a family of lines which intersected on the x axis at different points, i. e. the $K_M$ values for $FeSO_4$ increased with increasing cell concentrations. The maximum specific reaction rates $V_M$, calculated from individual lines become similar, following typical competitive inhibition. If each cell acts as a competitive inhibitor of another cell (E+I ↔ EI instead of E+S ↔ ES), the rate equation (2) becomes:

$$v = \frac{V_{MAX} \cdot S}{K_M \cdot (1 + ([I] / K_i)) + [S]} \qquad (3)$$

The expression of the apparent Michaelis constant $K_M$\` is a linear function of inhibitor ($K_M$\`= $K_M$ + [I].$K_M$/$K_i$) Fig 6. shows plot of the apparent $K_M$\` vs. inhibitor (i. e. cell) concentration to obtain the inhibition constant ($K_i$) value in number of cells per mL.

## *Effect of cupric ions*

The apparent maximum reaction rates $V_M$\` for $Fe^{2+}$ oxidation decreased with increasing $Cu^{2+}$ concentration without affecting $K_M$ values (Fig. 7) indicating purely non-competitive inhibition.

For the non-competitive inhibition the rate equation (2) becomes

$$v = \frac{(V_{MAX}/(1 + [I]/K_i)).[S]}{K_M + [S]} \tag{4}$$

It is important to note that cupric ion acts as a catalyst of the abiotic oxidation of ferrous iron in the sulphate medium (Mathews and Robins, 1972). This fact can explain the disagreement of the kinetics data obtained for bacterial $FeSO_4$ oxidation at higher $Fe^{2+}$ and $Cu^{2+}$ concentrations with standard Michaelis-Menten kinetics.

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# The study of electrokinetics of *Thiobacillus ferrooxidans* by electrophoretic light scattering

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## Abstract

No significant strain-specific differences have been found in the shape and position of the pH-dependent electrophoretic mobility curve obtained for various strains of *Thiobacillus ferrooxidans* under equal conditions of growth, suggesting similarities in their surface charge development.

**Key words:** electrophoretic light scattering, Zeta potential, electrokinetics, *Thiobacillus ferrooxidans*

### Štúdium elektrokinetiky baktérií *Thiobacillus ferrooxidans* elektroforetickým rozptylom svetla

Pri našom výskume neboli pozorované významné rozdiely v tvare a polohe kriviek závislosti elektroforetickej pohyblivosti od pH získaných pre rôzne kmene *Thiobacillus ferrooxidans* za rovnakých podmienok rastu, čo poukazuje na podobný mechanizmus tvorby povrchového náboja.

## Introduction

The chemolithoautotrophic acidophilic bacterium *Thiobacillus ferrooxidans* has long been associated with ore bioleaching and coal desulphurization. However physicochemical properties of the cell surface, that are generally expected to play a crucial role in microbial adhesion to solid substrate, have not been studied in a systematic way. More specifically, the surface/interface properties of the *Thiobacillus ferrooxidans* cell wall, notably the surface charge and hydrophobicity, are considered to affect the initiatory stage of microbial adhesion. This reversible stage precedes the irreversible final formation of a biofilm related to the microbial metabolic activity (Škvarla, 1993). But there are only few reports on the surface charge and hydrophobicity of *Thiobacillus ferrooxidans* (Misra et al., 1996; Solari et al., 1992; Chakrabarti and Banerjee, 1991). At the same time, most of researchers, although admitting the importance of the microbial adhesion step whether as the part of a long-term process (e. g. bioleaching of pyrite; Konishi et al., 1990, 1993) or as the only short-term process without the metabolic step (e. g. surface biomodification of pyrite prior to flotation or oil agglomeration; Attia et al., 1993; Kempton et al., 1980), concentrate preferably on the "technological effect" without having studied the fundamental colloidal factors of the microbial cell attachment of *Thiobacillus ferrooxidans*. In this context, it is the aim of this study to evaluate the surface charge development of *Thiobacillus ferrooxidans* in more details by measuring the electrophoretic mobility of a range of its various strains with the electrophoretic light scattering technique.

## Materials and methods

### *Bacterial strains - isolation, cultivation and suspension*

Six strains of *Thiobacillus ferrooxidans* isolated from acid water taken at Czech, Slovak and Bulgarian mines Tf (mo), Tf (kh), Tf (pe), Tf [CCM 3973], Tf (ro) and Tf (bg) were studied. All the strains were cultivated aerobically at 30 °C in the 9K liquid medium (Silverman and Lundgren, 1959) of the following composition: $(NH_4)_2SO_4$ 3 g/l, KCl 0.1 g/l, $K_2HPO_4$ 0.5 g/l, $MgSO_4.7H_2O$ 0.5 g/l, $Ca(NO_3)_2$ 0.01 g/l, $FeSO_4.7H_2O$ 44.2 g/l, adjusted with 5M $H_2SO_4$ to pH 1.6. Freshly grown bacterial cells were harvested always at the early stationary phase, capturing them on a membrane filter. To remove the rest culture medium from cells they were first washed three times with 0.1 M hydrochloric acid and then with distilled water. Further, the cells were transferred from the filter to distilled water where the cell concentration was determined turbidimetrically at 450 nm. Finally, to separate the cells from distilled water they were centrifuged at 4000 rpm for 15 minutes and the residual cell pellets were resuspended in various aqueous solutions of moderate ionic strength having pH varied from 3 to 6:

A. sodium acetate-acetic acid buffer solution ($CH_3COONa$-$CH_3COOH$, $1.5x10^{-3}$ M);
B. hydrochloric acid solution (HCl);
C. sulfuric acid solution ($H_2SO_4$);
D. sulphuric acid-potassium sulphate solution ($H_2SO_4$-$K_2SO_4$) with a constant ionic strength ($I = 1.5x10^{-3}$ M).

The 9K culture medium itself or concentrated buffers with $I$ of the order of $10^{-1}$ M were not used as the suspension medium due to their high ionic strength resulting in low values of the cell surface charge (and electrophoretic mobility) as well as in high values of the electric conductivity of the cell suspensions providing nonresolvable ELS spectra; see the next text. Both these effects cause the interpretation of the results to be difficult or impossible.

### *ELS measurements*

The electrophoretic mobility of the *Thiobacillus ferrooxidans* strains, suspended in the solutions was measured immediately with the Zeta Plus apparatus (Brookhaven Instruments Corp.). In this instrument the Doppler shift in the frequency of light scattered by electrophoresing colloidal particles (microbial cells) at the angle of 15° is measured. The Doppler shift is proportional to the electrophoretic mobility of the cells. Besides many advantages of this electrophoretic light scattering (ELS) technique (e. g. all cells in the suspension are detected simultaneously, providing a complete Doppler shift or electrophoretic mobility spectrum), it also suffers from some disadvantages; notably, the ELS signal is not resolvable when measuring cell suspensions with a ionic strength that gives the electric conductivity in excess of about 1 mS/cm, characteristic of pH < 3 or > 11. That is why the ELS measurements were constrained to pH > 3, just the pH at which by a mere coincidence the isoelectric state of most of the strains of *Thiobacillus ferrooxidans* was identified. Each value of the electrophoretic mobility is the modal value of the respective electrophoretic mobility spectrum and represents an average of at least three runs (with the precision of ca. $0.1x10^{-8}$ $m^2s^{-1}V^{-1}$).

## Results and discussion

### *Fundamental findings*

Since there are few ELS measurements of microbial cells in the scientific literature, some facts should be pointed out concerning the ELS spectra provided by *Thiobacillus ferrooxidans*. Above all, regular bell-shaped monomodal ELS spectra have been found, resembling those obtained for ideally uniform colloidal microspheres, so that the cells are true scatterers of the detected light and the measured electrophoretic mobility reflects their actual surface charge. The electrophoretic mobility has been observed to be invariable throughout the whole applied cell concentration range ($10^7$ to $10^8$ cells.ml$^{-1}$).

### *Influence of the suspension medium*

Fig. 1 shows the variation of the electrophoretic mobility of *Thiobacillus ferrooxidans* Tf [CCM-3973] with pH in the solution denoted as A (sodium acetate-acetic acid buffer), B (hydrochloric acid) and C (sulphuric acid). For comparison two separate sets of data are depicted for the solution A and C and three separate sets of data for the solution B. It can be seen that the profiles of the pH-dependent electrophoretic mobility curves do not differ from each other markedly, having a common isoelectric point (IEP) at pH 3. The resemblance in the electrophoretic mobility curves means that the ELS measurements are reliable and any of the anions of the solutions ($CH_3COO^-$, $Cl^-$, $SO_4^{2-}$) are not specifically adsorbed. $H^+$ is the major surface charge determining ion, as expected. The only exception is the curve obtained for the solution B where appreciably lower values of the electrophoretic mobility have been measured over the whole pH range. In this case, however, cells were suspended in the solution for a much longer time.

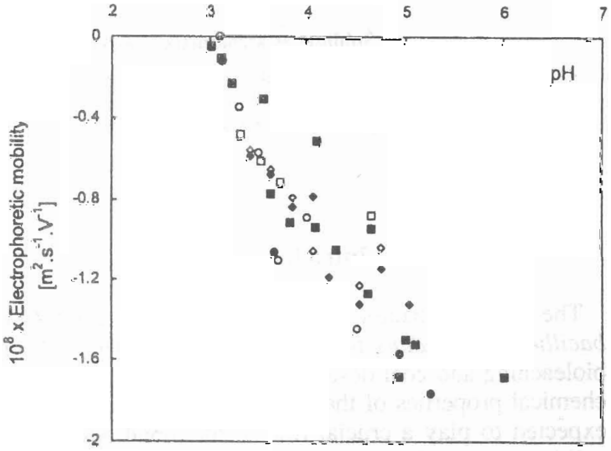

Fig. 1. Variation of the electrophoretic mobility of *Thiobacillus ferrooxidans* Tf [CCM-3973] with pH in three various solutions: A ◆, ◇ - $CH_3COONa$-$CH_3COOH$ ($1.5x10^{-3}$ M); B ■, □, □ - HCl; C ●, ○ - $H_2SO_4$.

### *General mobility-vs-pH curve*

Fig. 2 shows the variation of the electrophoretic mobility of the six *Thiobacillus ferrooxidans* strains with pH in the solution denoted as D at the constant ionic strength $I = 1.5x10^{-3}$ M. When comparing profiles of the electrophoretic mobility-vs-pH curves, one can see that, with the exception of two strains Tf (mo) and Tf (bg), there are no substantial strain specific differences, suggesting similarities in the surface charge development of the cells of these strains.

Generally each profile consists of two parts: the first-horizontal plateau part with invariable mobilities, and the second inclined part intersecting the pH axis at the IEP. This general tendency is better observable by superimposing all the curves (Fig. 3). Fig. 3 reveals the general profile of the mobility vs pH curve for *Thiobacillus ferrooxidans*, having the plateau with the mobility -1.0

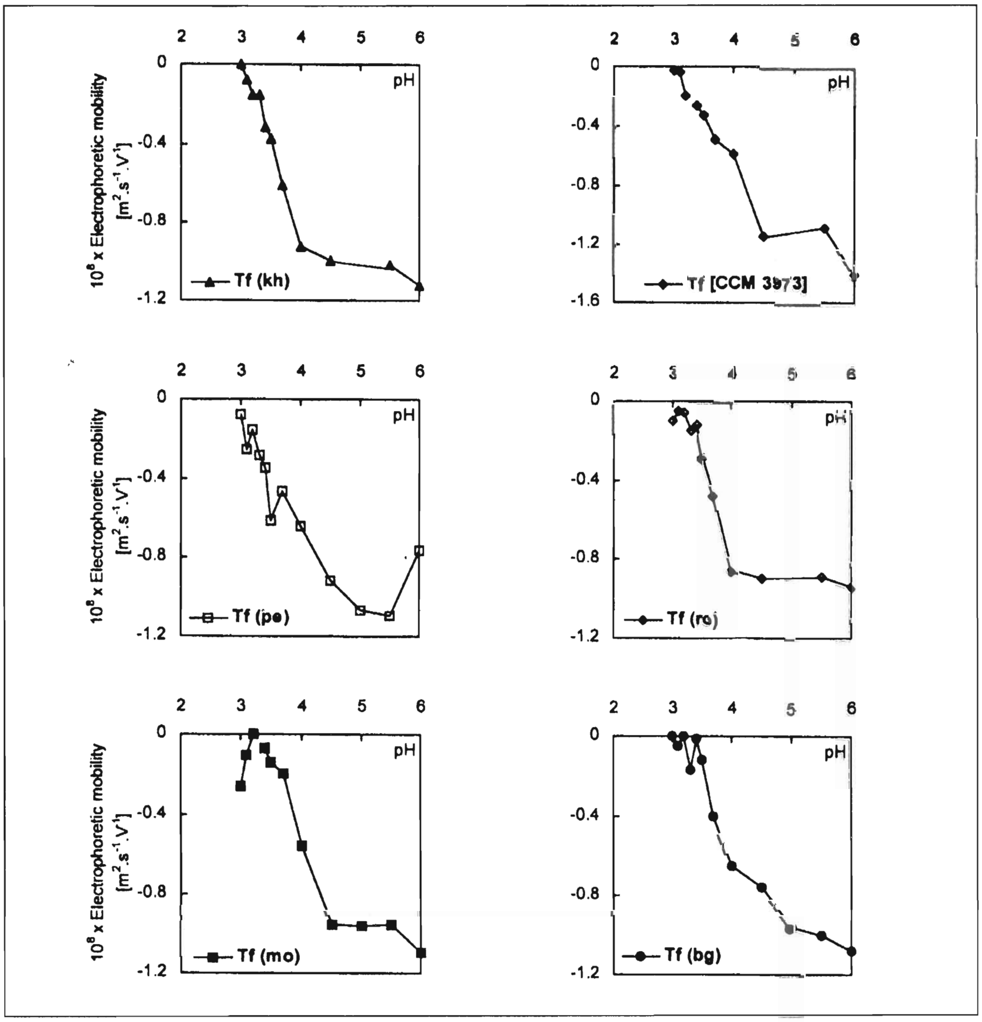

Fig. 2. Variation of the electrophoretic mobility of six strains of *Thiobacillus ferrooxidans* with pH in the $H_2SO_4$-$K_2SO_4$ solution (D) at the constant ionic strength $I = 1.5x10^{-3}$ M.

to $-1.1x10^{-8}$ $m^2s^{-1}V^{-1}$, the breaking point at pH 4.5 and $pH_{IEP}$ 3. Surprisingly, it is similar to the analogical profile (dashed line in Fig. 3) for *Thiobacillus ferrooxidans* (grown in the MSB9 basal medium at pH 2.5 with pills of elementary sulphur as the sole energy source and suspended in the MSHCl medium with the constant ionic strength $I = 5x10^{-3}$ M (published by Solari et al., 1992). The Tf (mo) and Tf (bg) strains are specific by a shifted position of IEP ($pH_{IEP}$ 3.5) and increasing negative mobilities with further decreasing pH.

### *Surface charge development characterization*

It is well known that thiobacilli possess the multilayered architecture of the cell envelope in general similar to, if not identical with, that of other gram-negative bacteria (Shively et al., 1970; Ledue and Ferroni, 1994; Remsen and Lundgren, 1966). The outermost part of the cell wall, that carries the surface charge of gram-negative bacteria, is represented by a highly organized outer membrane structure with an asymmetrical bilayer of phospholipids (PL, the inner leaflet) and lipopolysaccharides (LPS, the outer leaflet). In LPS a polysaccharide chain is covalently attached, through an oligosaccharide "core", to a glycolipid (lipid A) moiety. The bilayer thus has a hydrophobic core due to PL and saturated fatty acids of the lipid A moiety of LPS and an extremely hydrophilic outer surface provided by tightly packed LPS polysaccharide chains. Together with the latter, proteins (P) are also exposed at the surface of the outer membrane (Hancock, 1991). LPS from *Thiobacillus ferrooxidans* has core/lipid A composed of aminosugars as glucosamine and 2,3-diamino-2,3--dideoxyglucose (DAG) (Yokota et al., 1987); the main neutral sugar in the LPS is rhamnose, glucose, 3-O-methyl rhamnose (acofriose) and L, D-heptose in addition to 3-deoxy-D-mannooctulosonic acid (KDO) and 3-hydroxy-tetradecanoic acid is the only major fatty acid. The sugars in LPS of iron-oxidizing bacteria are heptose, glucose, galactose, mannose and KDO (Wang et al., 1970). In general it is supposed that the

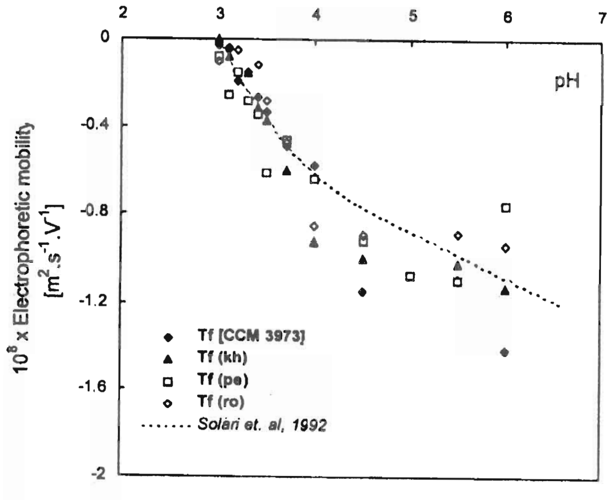

Fig. 3. Superimposition of Fig. 2 with the exception of Tf (mo) and Tf (bg). The dashed line is taken from Solari et al., 1992.

net surface charge of *Thiobacillus ferrooxidans* is determined by the interplay between negative charges created by deprotonated phosphate groups (constituents of LPS and PL) and carboxyl groups (in aminoacids of P) and positive charges due to protonated amino-groups (in aminoacids of P, PL, etc.). However, considering the simple profile of the mobility-vs-pH curves (typical of one anionic group) obtained for all strains studied, it seems that the weakly acidic carboxyl groups play the most important role in the surface charge development of the *Thiobacillus ferrooxidans* cells.

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# Electrochemical study of inorganic and bacterial pyrite oxidation mechanism

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## Abstract

A pyrite electrode was used to study the pyrite oxidation mechanism in the presence of $O_2$, $Fe^{3+}$ and bacteria *Thiobacillus ferooxidans*. According to the electrochemical data, pyrite oxidation in the presence of bacteria corresponded to 14-15 exchanged electrons while in the presence of oxygen the number of exchanged electrons was 2–3. The use of pyrite electrode proved so called direct bacterial attack to pyrite

### Elektrochemické štúdium mechanizmu abiotickej a bakteriálnej oxidácie pyritu

Mechanizmus oxidácie pyritu v prítomnosti kyslíka, $Fe^{3+}$ a baktérií *Thiobacillus ferrooxidans* sa študoval pomocou pyritovej elektródy. Na základe získaných elektrochemických dát prebieha biooxidácia pyritu s výmenou 14 - 15 elektrónov. Bez baktérií sa pri oxidačnej reakcii vymieňajú len 2 - 3 elektróny. Použitie pyritovej elektródy preukázalo tzv. priamy bakteriálny atak na pyrit.

## Introduction

Oxidation of common sulphide minerals is a process of considerable technical importance. It is essential for understanding of chemical and biochemical weathering of sulphide minerals and sulphide ore deposits in nature as well as at several stages in the winning of metals from sulphide ores, e. g. oxidation during mining, storage and transport, concentration by froth flotation and metal extraction by a variety of leaching techniques. This may be also a serious environmental problem because the formation of acid mine waters, acid sulphate soils and distribution of dissolved heavy metals and sulphate in natural waters and aquatic environment. Recently, the interest in the spontaneous oxidation and their electrochemical behaviour increased as a result of problems which occur at corrosion of metals in contact with sulphides (sulphide inclusion in steel and other metals) and in connection with the use of sulphides (e. g. pyrite) in cells producing electromotive force.

Pyrite $FeS_2$ is the most common sulphide which is formed under a variety of conditions, both hypogene and supergene and can be find in nearly all intrusive, metamorphic a sedimentary rocks. Natural spontaneous oxidation of pyrite is a main source of the strong acidification and increased content of sulphates waters and ground waters.

Despite the extensive study in the last two decades there is still great uncertainty in mechanisms of pyrite oxidation, its direct products and influence of bacteria on this process. Oxidation of pyrite (e. g. by oxygen dissolved in water or by action of $Fe^{3+}$ ions) varies between two limit reactions according to minimum and maximum oxidation states of products:

$$FeS_2 \rightarrow Fe^{2+} + 2\ S^0 + 2\ e^- \qquad (1)$$
$$FeS_2 + 8\ H_2O \rightarrow Fe^{3+} + 2\ SO_4^{2-} + 16\ H^+ + 15\ e^- \qquad (2)$$

Because of good electrical conductivity of pyrite (semiconductor) there can be used electrochemical technique to direct study of these reaction mechanisms and influence various reacting agents including bacteria.

### *Principles*

The real oxidation state of pyrite oxidation products varies between limits of both reactions (1) and (2). The number of electrons released from pyrite due to the action of outer oxidation agents is influenced by the agent and can be between 2 and 15. These electrons are directly consumed by oxidant on the pyrite-solution interface
$$\text{agent(ox)} + e^- \rightarrow \text{agent(red)}$$
e. g.

$$O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O \qquad (3)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$
$$\text{bacteria(ox)} + e^- \rightarrow \text{bacteria(red)} \qquad (5)$$

In the case of establishing the equilibrium potential on pyrite-solution interface, its value is given by activity of

dissolved species according to equilibrium reaction, e. g.
$FeS_2 + 8\,H_2O \longleftrightarrow Fe^{3+} + 2\,SO_4^{2-} + 16\,H^+ + 15\,e^-$ (2a)
and Nernst equation e. g.

$$E = E^0 + RT/nF \ln \{[Fe^{3+}]\,[SO_4^{2-}]^2\,[H^+]^{16}\} / \{[FeS_2]\,[H_2O]^8\} \quad (6)$$

where E is potential, $E_0$ is standard electrochemical potential of reaction (2a), R is gas constant, T is temperature, F is Faraday constant, n is number of exchanged electrons in reaction and symbols in [ ] are activities of reacting species. With approximation for diluted solutions equation (6) changes to

$$E = E^0 + RT/nF \ln \{[Fe^{3+}]\,[SO_4^{2-}]^2\,[H^+]^{16}\} \qquad (6a)$$

The net result of this reaction does not change overall state of system because the same amount of pyrite which is oxidized by the forward reaction is at equilibrium, created by the backward reaction.

In the presence of an oxidant, the situation is dramatically changed. The oxidant can consume electrons released by oxidative reaction of pyrite (e. g. (2) or (6)). The potential of pyrite is then established on value when the rate of pyrite oxidation reaction equals the rate of oxidant reduction (more precisely when the amount of released electrons is exactly consumed by oxidant per unit of time). In this case the rate of pyrite oxidation depends on its potential: the higher pyrite potential the higher its oxidation rate. Under these conditions of steady-state, on pyrite-solution interface the anodic current (release of electrons by oxidative reaction of pyrite) and cathodic current (consumption of electrons by an oxidant) are directly compensated on the pyrite surface. The currents connected with each reaction equals

$$j_{cat} = j_{anod} = j_0, \qquad (7)$$

where $j_0$ is so called exchange current and is according to the Faraday law directly proportional to the rate of pyrite oxidation

$$N = Q / (nF) = j_0 t / (nF) \qquad (8)$$
$$dN/dt = j_0 / (nF) \qquad (9)$$

where Q is amount of charge passed across pyrite-solution interface, N is number of moles depending on the stoichiometric coefficients in reaction – with negative sign for oxidized pyrite and with positive sign for products, and dN / dt is rate of pyrite oxidation. For unit pyrite area the oxidation rate is

$$dN/dt = i0 / (nF) \qquad (9a)$$

where $i_0 = j_0 / A$ is exchange current density ($A$ is oxidized pyrite surface).

The anodic and cathodic currents passing across pyrite-solution interface are dependent on potential of oxidized pyrite. At steady-state the pyrite potential takes value to exactly fulfil equation (7). This rest or steady-state potential is totally different from thermodynamically equilibrium potential. We cannot calculate it from thermodynamical data (as for Nernst equilibrium potential) and the result of the reaction course at this potential is different – finally all pyrite is destroyed.

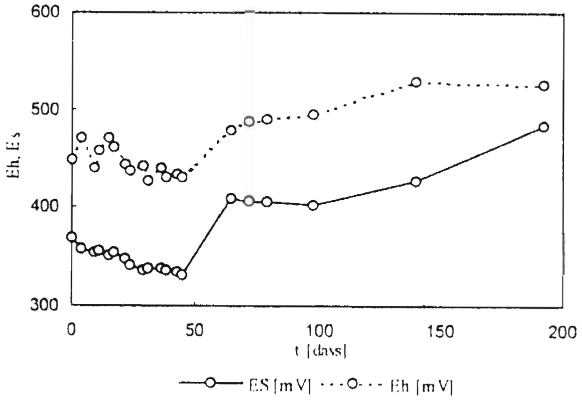

Fig. 1. The rest potential ($E_S$) and redox potential ($E_h$) during pyrite oxidation in water, pH = 1.8.

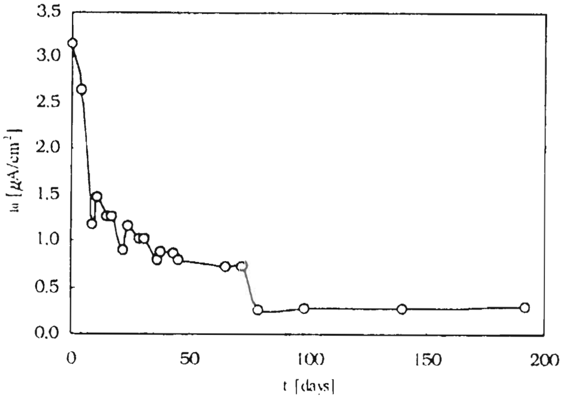

Fig. 2. The exchange current density ($i_o$) during pyrite oxidation in water, pH = 1.8.

The dependence of current passing across pyrite-solution on actual potential of pyrite is result of dependence of anodic and cathodic currents

$$i_{anod} = i_o \{\exp[(E-E_S)/b_a]\} \qquad (10)$$
$$i_{cat} = i_o \{\exp[-(E-E_S)/b_c]\} \qquad (11)$$

and is expressed by the Buttler-Volmer equation

$$i = i_o \{\exp[(E-E_S)/ba] - \exp[-(E-E_S)/b_c]\} \qquad (12)$$

where $i$ is net current density depending (current passing across interface per unit area) on the actual potential $E$, $b_a$ and $b_c$ are so called Tafel's constants for anodic and cathodic reactions (depending on the number of exchanged electrons), respectively, $E_S$ is the rest potential of pyrite at steady-state, $i_o$ is the exchange current density (current density at $E = E_S$). Only $E_S$ and $i = f(E)$ can be measured directly. The exchange current density $i_o$ which is a measure of the oxidation rate (see eqn. 8 and 9) can be obtained numerically

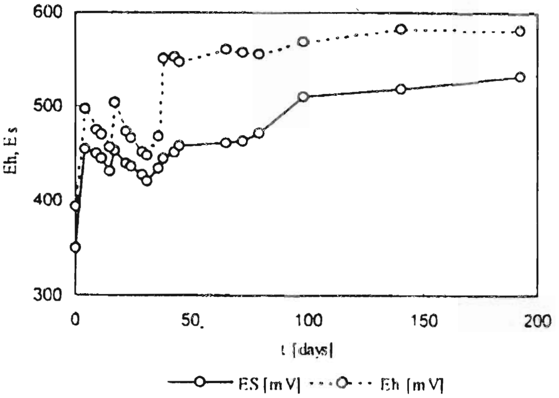

Fig. 3. The rest potential (ES) and redox potential (Eh) during pyrite oxidation in water, pH = 1.8, 10 mg/l $Fe^{3+}$.

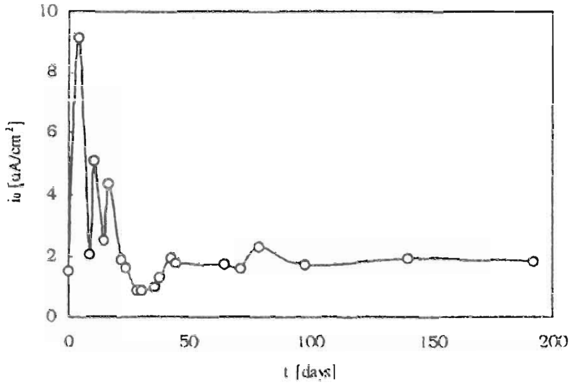

Fig. 4. The exchange current density ($i_o$) during pyrite oxidation in water, pH = 1.8, 10 mg/l $Fe^{3+}$.

from equation (12). The purpose of this paper is to present a new approach in study of pyrite oxidation mechanism.

## Materials and methods

**Bacteria.** A culture of *Thiobacillus ferrooxidans* (CCM4253) and a bacterial suspension preparation were described earlier (Mandl and Vyškovský, 1994).

**Oxidants.** Seven samples of oxidation solutions were tested: *Thiobacillus ferrooxidans* in $H_2O$, pH 1.8 ($10^8$ cells/ml), cultivated on $Fe^{2+}$, sulphur and thiosulphate media with corresponding controls - water, pH 1.8 (adjusted by sulphuric acid) and 10 and 100 mg/l $Fe^{3+}$ without bacteria.

**Pyrite electrode.** Electrodes were made from natural pyrite (Hnúšťa talk deposit, Slovak Republic) similarly as described for arsenopyrite (Zeman et al., 1995). Crystals of approximately 1 cm in diameter were sealed in epoxy resin, cut to discs 2.5 cm in diameter, and 2 mm thick. Discs were polished on both sides and mounted with silicon sealant to special glass holders. The electrical connection between the inner surface of the electrode and polarization device was created by liquid mercury and platinum wire. The outer surface of sulphide was in direct contact with oxidative solution.

**Measuring of $E_S$.** Rest potentials of pyrite electrodes were measured against saturated calomel electrode by pH-mV meter OH-108 (Radelkis, Hungary).

**Polarization curves.** The volume of the electrochemical cell was 50 ml. The pyrite electrode was used as a working electrode, saturated calomel electrode as a reference electrode, and platinum net electrode as a counter electrode. The polarization of the working electrode was carried out using potentiostatic unit of polarographic analyser PA3 (Laboratory Devices, Czech Republic). The linear potential sweep rate was 1 mV/s in both cathodic and anodic directions from the rest potential of working electrode, i. e. to -100 and 100 mV overpotentials (E - ES), respectively.

**Determination of $i_o$.** Equation (12) was fitted to the experimental dependence of exchange current density on the applied potential. Computer assessment of $i_o$ was based on the least-squares non-linear curve-fitting using Gauss-Newton iterative method with Marquardt-Levenberg modification.

**Number of exchanged electrons.** The charge Q passing across pyrite-solution interface over 192 days was determined by integration of experimental dependence $i_o = f(t)$. The number of exchanged electrons can be calculated from modified Faraday equation (8)

$$n = Q / (NF) = j_0 \, t / (NF) \tag{8a}$$

where N is the number of iron moles released into solution during pyrite oxidation. The number of exchanged electrons means number of electrons consumed by oxidant per oxidation one molecule of pyrite.

The content of the total iron in the solution was determined by ICP spectrometry, Fe(III) by ultraviolet absorption spectrophotometery (Mandl and Nováková, 1993).

## Results and discussion

### Control samples

For evaluation of the influence $Fe^{3+}$ ions and bacteria *Thiobacillus ferrooxidans* cultivated in various media on the rate of pyrite oxidation there was performed measurement of pyrite oxidation in pure water at pH = 1.8 (sulphuric acid). The evolution of the pyrite rest potential, redox potential of solution and exchange current density are shown in Figs. 1 and 2, respectively. Both, rest potential and redox potential, after beginning variation increase to the about 500 mV (SCE), the redox potential being higher. The exchange current density during measured period decrease and after the about seventy-five reaches steady value of 0.25 µA/cm$^2$.

The influence of oxidized iron was studied in media with various concentration $Fe^{3+}$ ions. We can illustrate the pyrite behaviour on the example of solution with 10 mg/l $Fe^{3+}$ (dissolved as $Fe_2(SO_4)_3$). The time evolution of potentials is similar as in control experiments but both potentials are nearly about 100 mV higher (Fig. 3). The $Fe^{3+}$ ions act as an oxidant and this is followed by higher oxidation rates (exchange current density below 2.5 µA/cm$^2$).

The influence of bacteria *Thiobacillus ferrooxidans* cultivated in $Fe^{2+}$ mineral 9K medium and on pyrite oxidation is very similar each other and has the most pronoun-

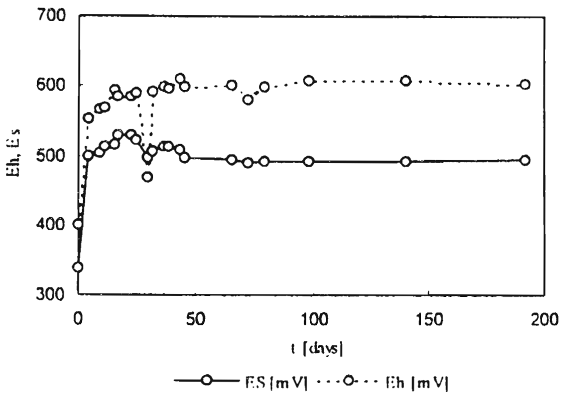

Fig. 5. The rest potential ($E_S$) and redox potential ($Eh$) during pyrite oxidation in presence of bacteria *Thiobacillus ferrooxidans* cultivated in mineral 9K media with $Fe^{2+}$, pH = 1.8.

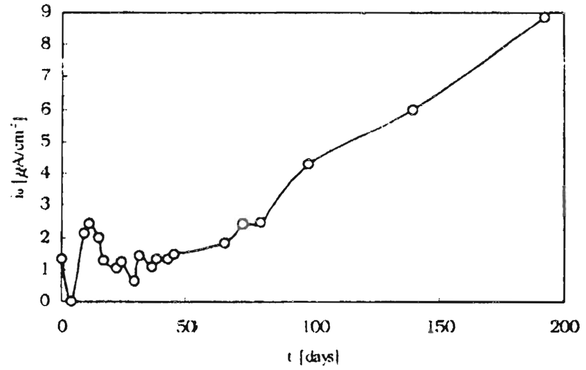

Fig. 6. The exchange current density ($i_o$) during pyrite oxidation in presence of bacteria *Thiobacillus ferrooxidans* cultivated in mineral 9K media with $Fe^{2+}$, pH = 1.8.

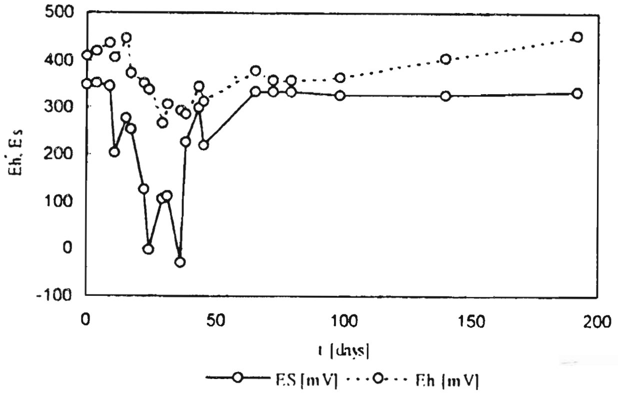

Fig. 7. The rest potential ($E_S$) and redox potential ($Eh$) during pyrite oxidation in presence of bacteria *Thiobacillus ferrooxidans* cultivated on sulphur, pH = 1.8.

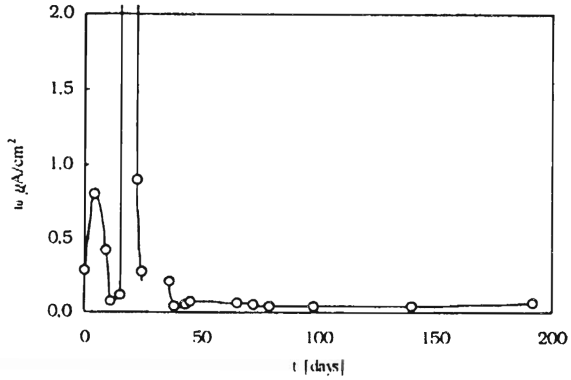

Fig. 6. The exchange current density ($i_o$) during pyrite oxidation in presence of bacteria *Thiobacillus ferrooxidans* cultivated in mineral 9K media with $Fe^{2+}$, pH = 1.8.

ced effect. These oxidizing solutions have the highest redox potentials (about 600 mV) causing the highest rest potentials of pyrite (about 500 mV). The exchange current density after initializing period instantaneously increase reaching about 10 mA/cm² at 200 day.

On the contrary bacteria *Thiobacillus ferrooxidans* cultivated on sulphur media are causing the decrease of pyrite oxidation rate even below rate of pyrite spontaneous oxidation in water with dissolved $O_2$ as oxidizing agent. These bacteria are causing very low redox potential of solution (about 400 mV) and therefore the lowest rest potential of pyrite (about 300 mV).

Number of electrons calculated according Faraday law from amount of iron released during pyrite oxidation and charge passed across pyrite-solution interface varies between 2.5 for pure inorganic oxidation and 13.5 for bacterial oxidation of pyrite. This result was in good agreement with number of electrons preliminary founded from dependence d [Fe] / d$t$ (3.3 and 15.1 electrons, respectively). Detailed results of these experiments will be published later.

## Conclusions

The pyrite oxidation is strongly influenced by presence of bacteria *Thiobacillus ferrooxidans.* Bacteria cultivated on mineral $Fe^{2+}$ 9K medium increase the oxidation rate up to 40 times based on exchange current density and up to 10 times based on the amount of released iron compare with the pure inorganic oxidation after 200 days. The $Fe^{3+}$ ions also increase the rate of pyrite oxidation but much lower then bacteria. The same bacteria cultivated on sulphur on the contrary lowers the oxidation rate. The predominant mechanisms of pyrite inorganic oxidation is

$$FeS_2 \rightarrow Fe^{2+} + 2\,S^0 + 2\,e^-$$

with subsequent oxidation of sulphur to various oxidation states in solution whereas in presence bacteria the main way is

$$FeS_2 + 8\,H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ + 14\,e^-$$

or

$$FeS_2 + 8\,H_2O \rightarrow Fe^{3+} + 2\,SO_4^{2-} + 16\,H^+ + 15\,e^-.$$

*Acknowledgements.* This work was supported by grant No. 511/94/0487 from the Grant Agency of the Czech Republic.

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# Ion exchange as a conditioning practice of the cyanided poor leach

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*(Received July 23, 1996)*

### Abstract

Environmental protection concerns, related to the use of cyanide in the leaching systems, require new trends in precious metal extraction practices.

In this sence recycling of water into the cyanidation stages imposes special attention. The poor leach obtained during gold and silver precipitation contains considerable cyan complexes of copper and zinc (the accompanying minerals of precious metals in their ores), consequently the leaches should not be recycled without prior conditioning.

This paper contains a case study on the laboratory conditioning of quality parameters of the cyanided poor leach resulted from the Săsar plant of Baia Mare, by means of the strongly basic, PUROLITE A850, anionite type ion exchanger.

The review of the experimental data has outlined that ion exchange is a viable alternative to retain the Cu and Zn complexes from the cyanided poor leach.

**Key words:** PUROLITE A850, ion exchange, precious metals, cyanide leach recycling

### Iónová výmena ako možná prax pri kyanidovom lúhovaní

Vysoké ekologické riziká pri použití kyanidového lúhovania si vyžadujú vyvíjať nové postupy extrakcie vzácnych kovov. Špeciálny dôraz sa kladie na proces recyklácie vody v jednotlivých kyanidizačných stupňoch. Výluhy získané počas zrážania zlata a striebra obsahujú kyanokomplexné zlúčeniny medi a zinku (sprievodné minerály rúd vzácnych kovov). Z toho vyplýva, že výluh nie je možné recyklovať bez predchádzajúcej úpravy.

Táto práca obsahuje výsledky laboratórneho štúdia čistenia kyanidových výluhov zo závodu Săsar Baia Mare použitím silne bázického PUROLITU A850, aniónového typu iónového meniča.

Z experimentálnych výsledkov vyplýva, že iónová výmena je vhodnou alternatívou odstraňovania Cu a Zn komplexov z kyanidových výluhov.

## Introduction

Dissolution of gold from its ores in cyanide solutions results in a poor leach including significant amounts of metallic cyanide complexes, such as Cu, Zn, Fe, Co, Hg, Ni.

The most common commercial practice for gold extraction from the pregnant leach liquor is precipitation with zinc dust. The process is adequate to precious metal extraction (gold and silver) but the dissolved Cu, Zn, Fe, Ni, Co remain in solution.

Once the concentration of copper ion increased in the cyanide solution, gold dissolution amenability has dropped. Currently this problem is being solved by discharging nearly a quarter of the barren solution, involving the increase of operation costs and severe pollution hazards, particularly with regard to the cyanide losses.

Ion exchangers are considered to be an alternative to the removal of impurities from the cyanide leach. Conditioning by ion exchange of the quality parameters of poor leach enables its recycling into the flowsheet.

## Experimental testworks with ion exchanges

The experimental works aimed to find efficient procedures that could retain the cyanide complex contained in the poor leach resulted from the cyanidation in view of its recycling into the flowsheet.

This case study has tested the poor leach obtained from the Săsar cyanidation plant of Baia Mare, having the following chemical composition: $CN_{total}$ = 2100 mg/l, $CN^-$ = 260 mg/l, Cu = 210 mg/l, Zn = 320 mg/l and $SO_4^{2-}$ = 615 mg/l. The leach was clear and free of precipitate or suspension at pH = 10.5.

The experimental testworks have been conducted on 81 resin in cylindrical column applying dynamical ion exchange on a fixed ion exchanger bed and descending circulation of the feed.

The experiments were carried out using the PUROLITE A850 type ion exchanger, a strong alkaline anionit (retains the anions of weak acids) with macroporous polyacrylic structure of $Cl^-$ form, slightly noxious towards organic compounds and silica.

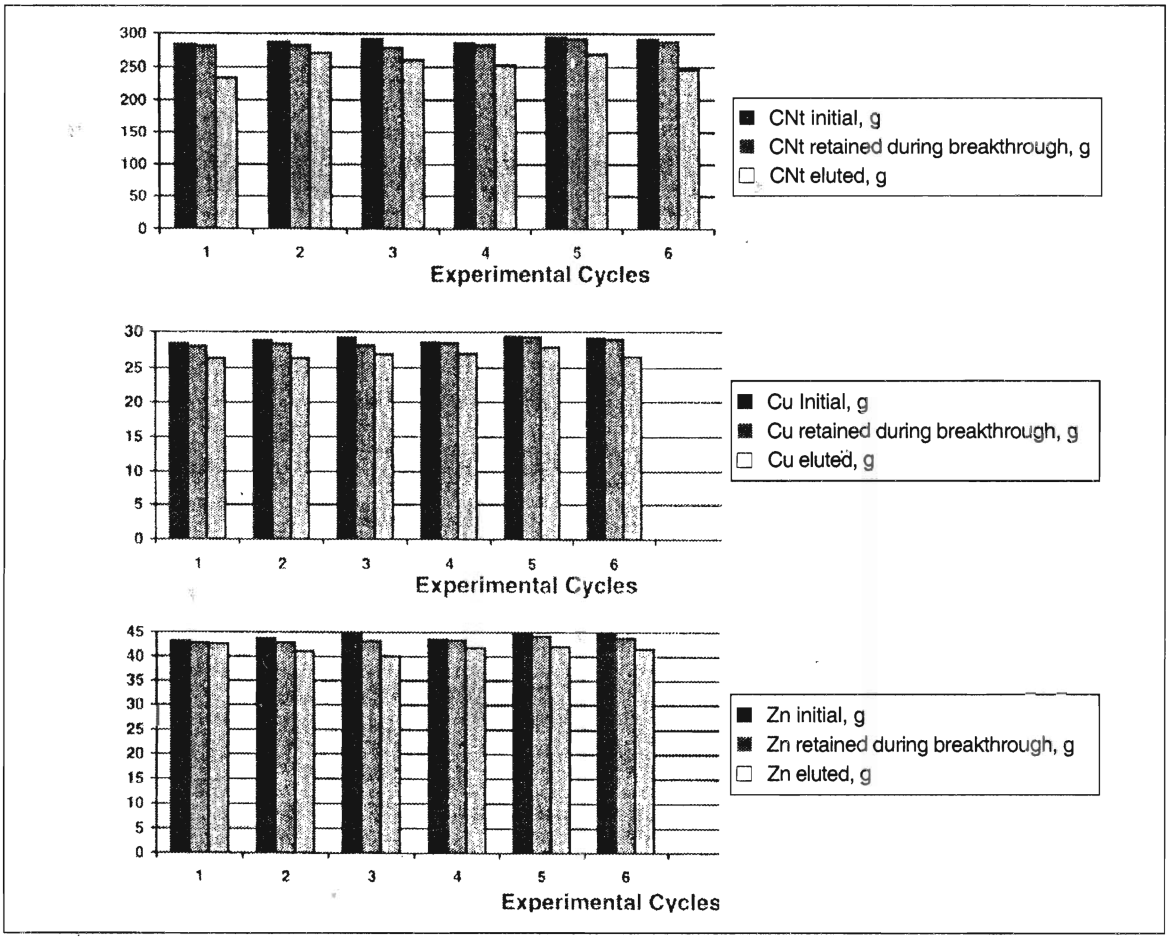


Fig. 1. The experimental results of six sorption cycles.

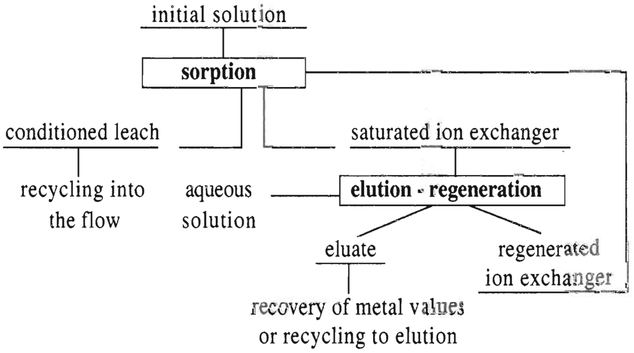
The matrix subjected to laboratory tests has been prepared to estimate the feasibility of this resin in removing heavy metal cyanide complexes from the cyanided poor leach. The tests attempt to answer the following problems:

- loading capacity of the resin with complex cyanide ions of copper and zinc;
- kinetics of sorption;
- kinetics of elution;
- efficiency of elution - regeneration;
- cost of reagents used in the process;
- meeting of labour security and enviromental protection requirements with the applied reagents (at pH <9 HCN is release).

The flowsheet includes three stages:

1. sorption (loading) - in descending flow at 80 l/h feeding rate, established by preliminary tests;
2. elution and regeneration - with 15 % NaCl and 2 % NaOH solution at 18.5 l/h rate simultaneously rendering regeneration of resin and its bringing into active form;
3. stripping and aeration of the resin. It has been proceeded in countercurrent flow as to achieve efficient stripping and aeration;

Following the next scheme:



## Experimental results

Six sorption cycles were employed until effective loading of Cu and Zn values has been achieved while the $CN_{total}$ concentration of the effluent became equivalent to approx. 2 % of the initial concentration of the leach that is further to six elution cycles of the retained complex anions.

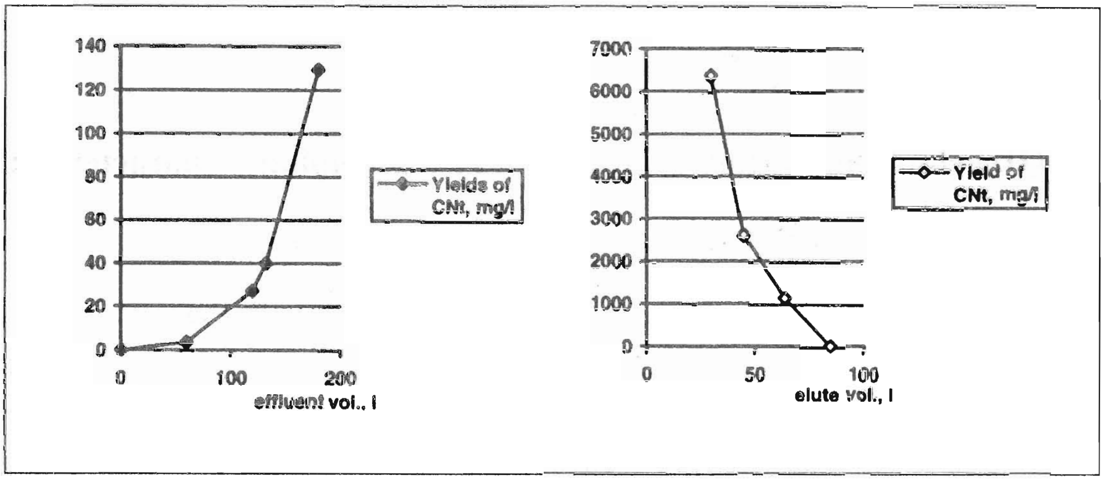


Fig. 2. The sorption and elution curves of $CN_{total}$ for one of the experimental cycles.

The results of the above mentioned experiments are presented in the charts below (Fig. 1).

The charts show the $CN_{total}$ and initial Cu and Zn retained until effective loading and eluted Cu and Zn according to the performed experimental cycles. One may observe that at constant flowrate and constant specific loading, the retained $CN_{total}$, Cu, Zn amounts are roughly constant during effective loading.

The sorption yields are ranging between 95 - 99 % and those of elution between 86 - 96 %

The charts herein show (Fig. 2) the sorption and elution curves of $CN_{total}$ for one of the experimental cycles ($CN_{total}$ level versus volume of effluent and eluate).

The performed experiments indicate that during the six sorption-elution cycles the ion exchange process is likely to be reproduced versus the monitored parameters. The elution process resultes in eluates enriched in $CN_{total}$ (5500 mg/l) and containing on average 650 mg/l of Cu, 900 mg/l of Zn. These could be recovered by precipitation or electrowinning, or the eluate can be recycled into the subsequent elution stages.

## Conclusions

- the strongly basic PUROLITE A850 anionit resin is suitable as cyan complex retainer (Cu, Zn) enabling recycling of the poor leach into the cyanidation flowsheet;
- the recovery yields are high for CNtotal and Cu, Zn either (95 - 99 %);
- the elution - resin regeneration process has achieved its performances.

The retaining capacity of the resin has not decreased during the six integrated cycles.

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# As(III) elimination from solutions and As-precipitates characteristic

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*(Received August, 9, 1996)*

### Abstract

The study of the As(III) removal from aqueous solution by thiourea, sodium sulphide, ammonium sulphide, calcium oxide, ferric sulphate and ferric chloride has been carried out to establish the optimum parameters for the removing of arsenic. The initial As(III) concentration was 100 mg/l. The variables investigated were: the pH value of precipitation (2, 4, 6, 8, 10), the molar ratio of X:As (2, 4, 6), where X = Ca, S or Fe, respectively. Experiments were worked out at room temperature during one hour. The stabilities of the As(III) precipitates are discussed.

**Key words:** trivalent arsenic, precipitation, stability

### Eliminácia $As^{3+}$ z roztokov a charakterizácia zrazenín s obsahom arzénu

Študovali sme elimináciu $As^{3+}$ z roztokov použitím tiomočoviny, $Na_2S$, $(NH_4)_2S$, CaO, $FeSO_4$ a $FeCl_3$ ako precipitačných činidiel. Cieľom bolo optimalizovať parametre eliminácie arzénu z roztoku. Počiatočná koncentrácia $As^{3+}$ v roztoku bola 100 mg/l. Počas pokusov sme sledovali pH tvorby zrazeniny (2, 4, 6, 8, 10) a molárny pomer X:As (X = Ca, S, Fe). Experimenty sa realizovali pri laboratórnej teplote a dĺžka ich trvania bola 1 hod.

## Introduction

Arsenic as one of the toxic elements is almost always present in the process streams of pyrometallurgical or hydrometallurgical production of nonferrous metals from sulphide ores and concentrates. Its behaviour in metal extraction processes is the subject of interest of many research workers and also metal producers mainly from the point of view of environmental protection. The problem of the removal of arsenic is also connected with fact that, whereas the production of arsenic is increasing due to the depletion of high-grade raw materials and processing of ores with higher impurity content, the demand is decreasing. Then the excess arsenic must be eliminated from process streams and converted to the form suitable for safe disposal. Arsenic containing waste can be in solid, liquid or gaseous phases, but the most significant amount of arsenic is usually found in wastewaters. The maximum allowed concentrations of arsenic in waters of cca 50 μg per litre indicate necessity of effective purification of waters to be discharged into the environment.

The most of arsenic in the solid or liquid wastes is in trivalent state. It is generally accepted that arsenic can be removed in environmentally safe way when present in the pentavalent form, mainly as arsenates. Therefore the first step in arsenic removing is usually its oxidation. Studying the arsenic removal from various solutions, we have investigated possibilities of direct precipitation of trivalent arsenic without prior oxidation.

## Arsenic removal by precipitation

Out of the possible methods for arsenic removal from water solutions, the chemical precipitation ranks among the most effective and simple at the same time. This method is based upon the limited solubility of some arsenic compounds, which must not exceed 1 mg/l of arsenic. One of the oldest and the most frequently employed methods is arsenic precipitation as the calcium arsenate. Extremely low solubility of the arsenite sulphite $As_2S_3$ stimulated study of the possibilities of arsenic content reduction in the solutions by precipitation with agents like $H_2S$, $Na_2S$ or $(NH_4)_2S$. The method which has drawn great attention at present is the removal of arsenic from the water solutions by precipitation with ferric ions. The efficiency of arsenic removal by this method and formed precipitates properties are reported to be significantly dependent on the conditions of reaction.

In our study we intended to verify the possibilities of application of the individual agents to As(III) as well as to determine optimal molar ratio and pH value of precipitation for each agent.

## Material and methods

Solution with initial concentration 100 mg/l As was prepared by dissolution of $As_2O_3$ in distilled water where NaOH was added to enhance the dissolution. As the precipitation agents 0.3M solutions of $Fe_2(SO_3)_4.9H_2O$,

Tab. 1
The efficiencies of As(III) removal by various agents

| Precipitation agent | Molar ratio | As(III) removal efficiency (in %) | | | | |
|---|---|---|---|---|---|---|
| | | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
| $Fe_2(SO_4)_3.9H_2O$ | 2:1 | 0 | 63.2 | 85.0 | 93.74 | 85.9 |
| | 4:1 | 0 | 80.02 | 96.9 | 97.31 | 96.91 |
| | 6:1 | 9.3 | 87.0 | 96.8 | 98.5 | 98.0 |
| $FeCl_3.6H_2O$ | 2:1 | 10.9 | 0 | 82.4 | 87.9 | 0 |
| | 4:1 | 0 | 0 | 92.85 | 98.02 | 76.9 |
| | 6:1 | 3.2 | 0 | 93.4 | >99.4 | 97.25 |
| $Na_2S.9H_2O$ | 2:1 | 58.1 | 12.0 | 4.1 | 3.04 | 0 |
| | 4:1 | 98.3 | 13.3 | 10 | 0 | 0 |
| | 6:1 | 98.51 | 3.18 | 7.08 | 0 | 4.12 |
| $(NH_4)_2S_X$ | 2:1 | 11.32 | 3.7 | 6.1 | 5.82 | 0 |
| | 4:1 | 21.03 | 5.47 | 7.96 | 8.88 | 0 |
| | 6:1 | 29.99 | 9.75 | 0 | 0 | 0 |
| $(NH_2)_2CS$ | 2:1 | 31.66 | 14.15 | 40.3 | 26.3 | 17.5 |
| | 4:1 | 42.43 | 28.0 | 38.0 | 33.0 | 36.0 |
| | 6:1 | 32.68 | 33.0 | 40.0 | 26.0 | 33.0 |
| CaO | 2:1 | 26.02 | 17.29 | 39.69 | 15.68 | 22.3 |
| | 4:1 | 13.82 | 10.71 | 9.9 | 11.09 | 10.49 |
| | 6:1 | 0 | 37.39 | 13.56 | 25.08 | 5.03 |

$FeCl_3.6H_2O$, $Na_2S.9H_2O$ and thiourea, 0.025M solution of CaO and 13 % solution of $(NH_4)_2SX$ were used. The amount of the precipitation agent was calculated so that molar ratios of X:As = 2, 4 and 6 were reached.

For pH value control 1M solution of $H_2SO_4$ and 0.1M solution of NaOH were used.

The dependence of arsenic removal efficiency in on the pH value and molar ratio of X:As, where X is Fe, S or Ca have been studied. Precipitation took place at pH 2, 4, 6, 8 and 10 for each molar ratio of X:As. Into the three marked beakers with 100 ml of $As_2O_3$ solution the precipitation agent in proper amounts after the pH adjustment was added. After that followed another pH adjustment to the required value which was maintained during the whole experiment. The speed of the sample agitation was approximately 200 rpm. Experiments were worked out at the room temperature. After 60 minutes samples were filtered and solution was analysed for arsenic content by atomic absorption spectroscopy. Influence of dilution caused by adding the precipitation agent and pH adjustment was corrected by the re-calculation of the analyse results for the real volume of the sample.

## Experimental results

Experimental results of As(III) removal from solutions are shown in the Tab. 1 as arsenic removal efficiencies. The plots of residual concentration dependencies on the Fe, S or Ca to As molar ratio for various pH values of solution are shown on Figs. 1 to 3.

## Results and discussion

1. Suitable precipitation agents for As(III) removal out of studied are: $Fe_2(SO_4)_3$, $FeCl_3$, and $Na_2S$.
2. Molar ratio X:As must be above 4.
3. pH value using:
   a) $Fe_2(SO_4)_3$ must be within range of 6 - 10
   b) $FeCl_3$ must be within range of 8 - 10
   c) $Na_2S$ must be equal to 2.
4. Under these conditions residual concentration of arsenic in solution was from 0.6 to 3.2 mg/l, which means that over 97 % of As(III) could be removed without prior oxidation.
5. The As(III) removal from solution by $(NH_4)_2S_X$, thiourea and CaO under our experimental conditions was not sufficient.

The results of our experiments with As(III) removal from solution by chemical precipitation indicated that there are possibilities to separate trivalent arsenic from the liquid phase to the satisfactory extent. The remaining problem of obtained solid precipitates is their stability.

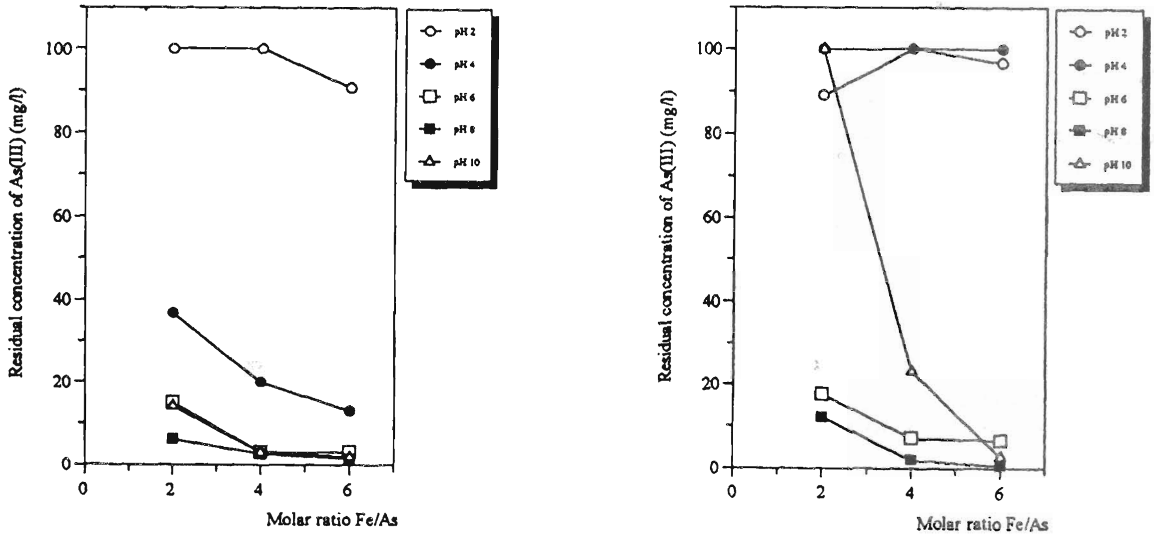

Fig. 1. Dependencies of residual As concentration in solution on the molar ratio using a) $Fe_2(SO_4)_3$, b) $FeCl_3$.

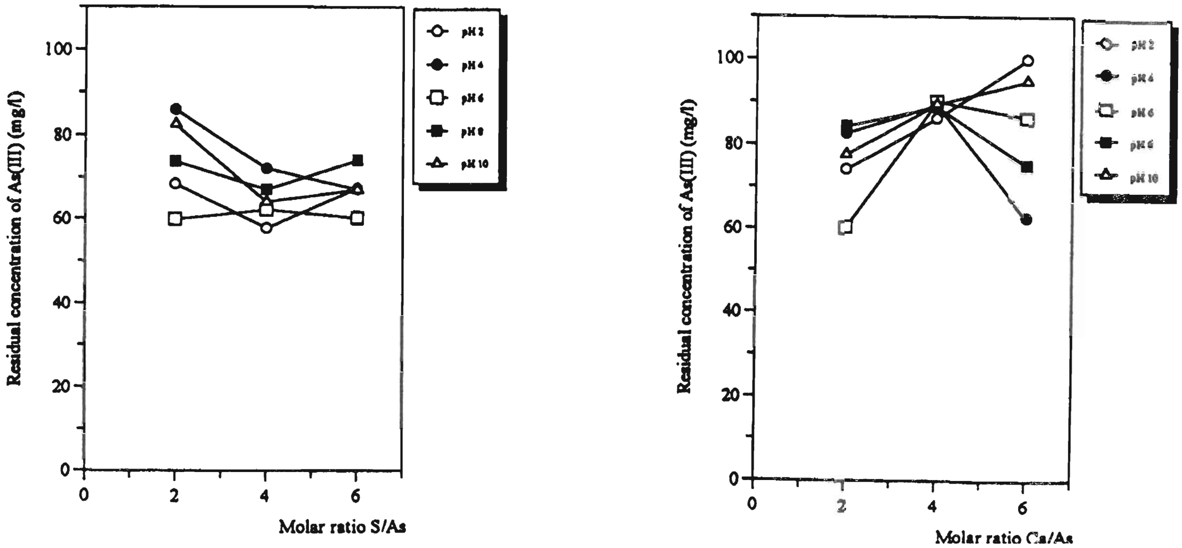

Fig. 2. Dependencies of residual As concentration in solution on the molar ratio using a) $Na_2S$, b) $(NH_4)_2S_X$.

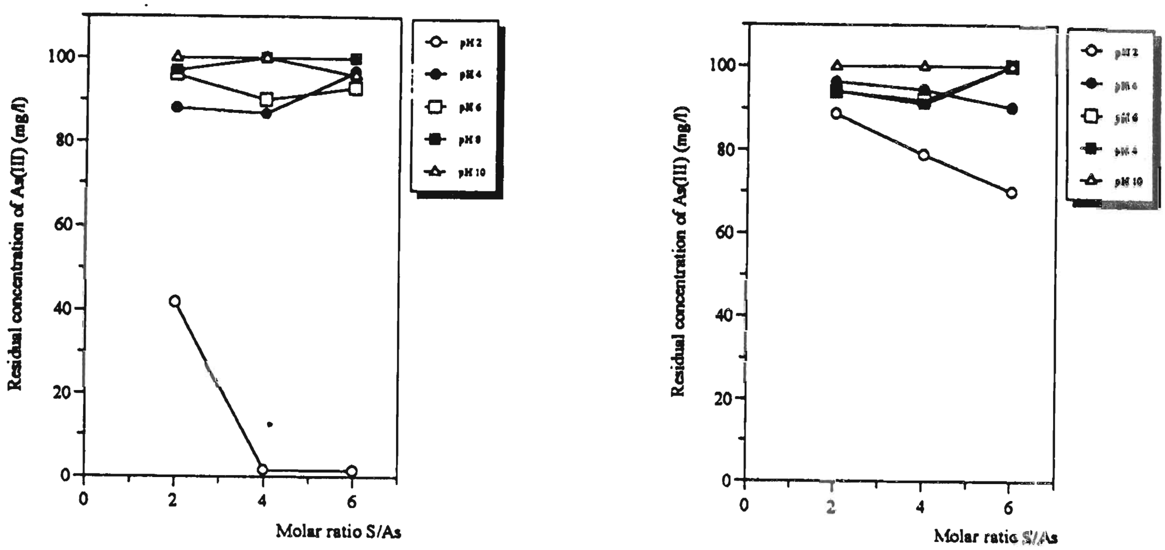

Fig. 3. Dependencies of residual As concentration in solution on the molar ratio using a) thiourea, b) CaO.

The compound $As_2S_3$ (mineral orpiment) is precipitated from arsenic containing solutions to reduce the arsenic concentration in solutions. Although orpiment is regarded as sufficiently insoluble; solubility approximately $6.10^{-4}$ mg/l As seems to be generally accepted, Robins (1988) have determined the solubility of $As_2S_3$ as being 28,5 mg/l As in the pH range 1 - 4. It is known that in case of pentavalent arsenic precipitation by ferric ions the high molar ratio Fe to As is crucial for low solubility of final product (Krause and Ettel, 1989). Harris and Monette (1989) reported that the addition of small amount of metals like Cu, Zn and Cd in co-precipitated ferric arsenates enhances their stability in pH range 4 - 10 (Harris and Monette, 1989). With respect to this, further study of non-stoichiometric ferric arsenites solubility may help to fined the way of their environmental stability improvement.

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# Liquid extraction of lanthanum and samarium from acidic solutions by bis(2-ethylhexyl) phosphoric acid

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### Abstract

The extraction of lanthanum, samarium, and hydrogen ions from aqueous $HNO_3$ solutions by bis(2-ethylhexyl) phosphoric acid solution in benzene has been studied. The distribution ratio dependence on the pH of the aqueous phase and concentration of extractant in the organic phase was investigated. The stoichiometric coefficients of the overall extraction reaction were determined as slopes of the logarithmic dependence of the distribution coefficients on the pH and the extractant concentration.

**Key words:** extraction, equilibrium constant, rare earth

### Kvapalinová extrakcia lantánu a samária z kyslých roztokov účinkom kyseliny bis(2-etylhexyl) fosforečnej

Práca sa zaoberá výsledkami extrakcie lantánu a samária z roztokov $HNO_3$ zriedených benzénovým roztokom kyseliny bis(2-etylhexyl) fosforečnej. Uvádzame výsledky štúdia vplyvu pH vodnej fázy a koncentrácie kyseliny bis(2-etylhexyl) fosforečnej v benzénovej vrstve na hodnotu rozdeľovacieho koeficientu. Celkové stechiometrické koeficienty extrakcie sa určili ako smernice logaritmickej závislosti rozdeľovacieho koeficientu na pH a koncentrácií kyseliny bis(2-etylhexyl) fosforečnej.

## Introduction

Bis(2-ethylhexyl) phosphoric acid (DEHPA) is an efficient extraction and separating agent for rare earth metal ions from acidic aqueous solutions. Several investigations were devoted to the mechanism of extraction during past 20 years (Sato, 1975; Michelson and Schutz, 1971; Lundqvist and Svartesson, 1983; Sato and Ueda, 1973; Torres and Choppin, 1984; Mikhailichenko, Pimenova and Kotlyarov, 1969; Mikhailichenko and Pimenova, 1969; Sato, 1989). They have shown that on extracting Eu and Am from aqueous solution of humic acid the organic phase contains $LnA_3(HA)_3$ where HA is DEHPA and $A^-$ is the corresponding anion (Torres and Choppin, 1984). Authors of papers (Mikhailichenko, Pimenova and Kotlyarov, 1969; Mikhailichenko and Pimenova, 1969) studied the extraction of rare earth metals from aqueous solutions containing $HNO_3$ by DEHPA. It was shown (Mikhailichenko and Pimenova, 1969) that the distribution ratio and the mechanism of extraction depended on the concentration of $HNO_3$ in the aqueous solution.

## Experimental procedures

Organic phase consisting of DEHPA of 99.8 % purity was prepared by the Research Institute of Chemical Technology in Bratislava. DEHPA was diluted with benzene of anal. grade purity. The aqueous solution concentration was between $5.10^{-3}$ - 10 mol.dm$^{-3}$. The nitrates of La and Sm were prepared by dissolving the respective oxide of anal. grade purity (Ventron) in the nitric acid solution. Their final concentration in the aqueous solution was $1.10^{-3}$ - $5.10^{-3}$ mol. dm$^{-3}$. Extraction experiments were carried out at room temperature, approximately 22 °C. The mass ratio of the organic and aqueous phases was 1:1. Both phases were in contact for 5 min by vigorous shaking of the flasks which were then left for 30 min in order to disengage the two phases.

The aqueous phase before and after extraction was analyzed either by spectrophotometric method with additions of ArzenazoIII or by emission spectrometry with excitation in DCP plasma according to the Marinkovitch method. The pH of the solution was determined by pH-meter (Radelkis) OP 265/1.

## Results and discusion

The effects of concentration of the bis(2-ethylhexyl) phosphoric acid and of pH of the aqueous solution on the distribution ratio of La and Sm were studied at constant temperature and constant initial concentration of $Ln(NO_3)_3$ in aqueous solution.

Fig. 1 shows the variation of the logarithm of the distribution ratio $D_{H+}$ with equilibrium pH of the aqueous

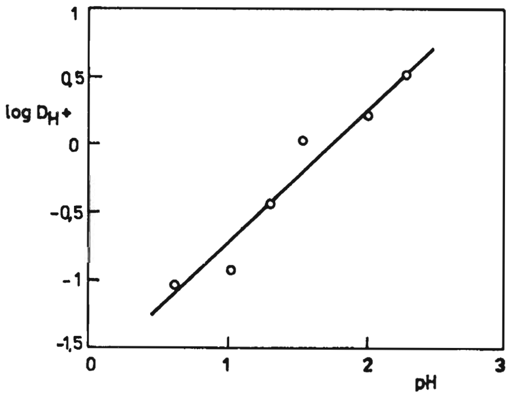

Fig. 1. Variation of logDH+ with pH at equilibrium of the aqueous solution; c(DEHPA) = $1.5.10^{-1}$ mol.dm$^{-3}$.

phase at constant temperature and constant concentration of DEHPA,c(DEHPA) = 0.15 mol.dm$^{-3}$ in the organic phase. The equation calculated by the linear regression from the experimentally determined values of $D_{H+}$ is of the following form

$$\log D_{H+} = -1.86 + 0.98 \text{ pH} \qquad (1)$$

The slope of the line $\delta(\log D_{H+})/\delta(\log \text{pH})$ is equal to the stoichiometric coefficient $n$ and this in eqn (1) is 0.98 which rounded gives the value $n = 1$. Solvent extraction under these experimental conditions takes place in accordance with the following reaction

$$(HA)_2 = HA^-_2 + H^+ \qquad (A)$$

Supposing that the chemical reaction

$$Ln^{3+} + 3\ NO_3^- + m\ HA = Ln(NO_3)_3A_n(HA)_{m-n} + n\ H^+ \qquad (B)$$

of extraction of $Ln^{3+}$ reaches its equilibrium state, we can express the equilibrium constant based on equilibrium concentrations

$$K_e = D_{Ln} \frac{[H^+]^n}{[HA]^m} \qquad (2)$$

As the equilibrium constant remains constant at fixed temperature we obtain by its derivation, taking the logarithm and using the formulae pH = -log [H$^+$] the corresponding stoichiometric coefficient of the reaction (B)

$$\left|\frac{\delta(\log D_{Ln})}{\delta(pH)}\right|_{[HA]} = n \qquad (3)$$

$$\left|\frac{\delta(\log D_{Ln})}{\delta(\log\ [HA])}\right|_{pH} = m \qquad (4)$$

Therefore the slope of lines which represent the variation of $\log D_{Ln}$ with pH (Fig. 2) at constant concentration of the bis(2-ethylhexyl) phosphoric acid gives actually the stoichiometric coefficient $n$ whereas the slope of the line that represents the variation of log $D_{Ln}$ with concentration of the bis(2-ethylhexyl) phosphoric acid at constant pH of the aqueous phase (Fig. 3) corresponds to the stoichiometric coefficient $m$.

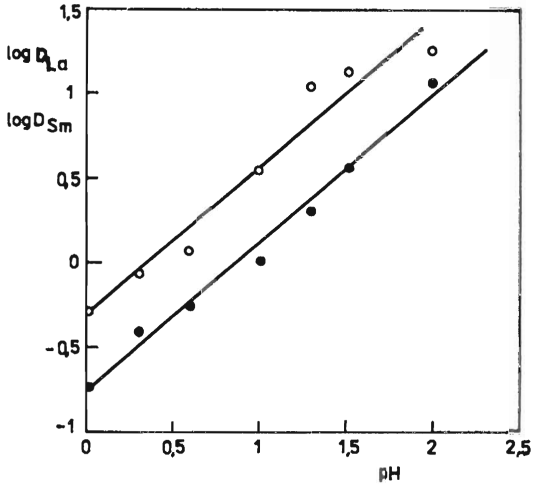

Fig. 2. Variation of $\log D_{La}$ and $\log D_{Sm}$ with pH. Initial concentration of lanthanoids: c(Ln(NO$_3$)$_3$) = $5.10^{-3}$ mol.dm$^{-3}$, c(DEHPA) = $1.5.10^{-1}$ mol.dm$^{-3}$ ● $\log D_{La}$, ○ $\log D_{Sm}$

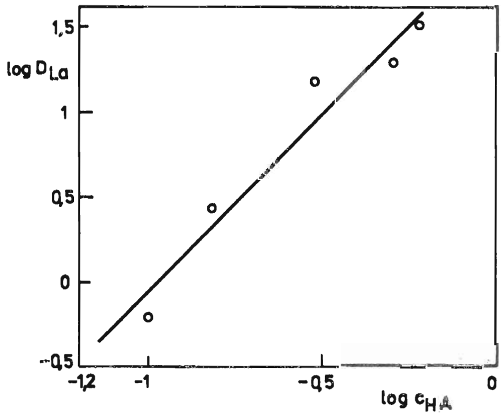

Fig. 3. Variation of $\log D_{La}$ with logc(HA). Initial concentrations: c(La(NO$_3$)$_3$) = $5.5.10^{-3}$ mol.dm$^{-3}$, c(HNO$_3$) = 0.5 mol.dm$^{-3}$.

Fig. 2 shows the experimentally determined distribution ratios of lanthanum and samarium between aqueous and organic phase as log D vs. pH at constant concentration of the bis(2-ethylhexyl) phosphoric acid in the organic phase, $c$(DEHPA) = 0.15 mol.dm$^{-3}$ and at constant initial concentration of lanthanum and samarium in the aqueous phase $5.10^{-3}$ mol.dm$^{-3}$. The linear regression method was applied to calculate the coefficient of the equations describing the variation of $D_{La}$ and $D_{Sm}$ with the pH of the solution

$$\log D_{La} = -0.75 + 0.86\ \mathrm{pH} \qquad (5)$$
$$\log D_{Sm} = -0.31 + 0.87\ \mathrm{pH} \qquad (6)$$

It follows from Fig. 2 and eqns (5) and (6) that the slopes of the two lines are the same. Their rounding to the nearest integer gives the stoichiometric coefficient $n = 1$ in the reaction (B).

When determining the stoichiometric coefficient $m$ only lanthanum ion was used for experiments. It has been assumed that other lanthanoids in solvent extraction process behave similarly.

Fig. 3 shows the experimentally determined values of the distribution coefficients of lanthanum in $\log D_{La}$ - $\log\{c(HA)\}$ coordinates. The linear function calculated by the linear regression method is: $\log D_{La} = 2.03 + 2\log\{c(HA)\}$ coordinates. The linear function calculated by the linear regression method is: $\log D_{La} = 2.03 + 2\log\{c(HA)\}$. The slope of the line is

$$\frac{\delta(\log D_{La})}{\delta(\log\{c(HA\})} = 2$$

which means that the stoichiometric coefficient $m$ equals 2. The obtained stoichiometric coefficients enable to write the chemical reaction in which the associate is being formed

$$Ln^{3+} + 2NO_3^- + 2\ HA = Ln(NO_3)_2AHA + H^+ \qquad (C)$$

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# Review of the lanthanide extraction chemistry

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### Abstract

The separation factors of the lanthanides can be improved by three ways:

1. Modification of the organic phase in the systems with the adduct formation like: $LnL_3B$, $LnL_3B_2$, $LnL_33HL$, $LnL_32HLB$, $LnL_3HL2B$. The improvement in the separation factors (especially in the case of the heavy lanthanides) results from steric effects.

2. Modification of the aqueous phase, when the stability constants of the lanthanide complexonates increase in the lanthanide series and at the same time extraction constants decrease with the atomic number.

3. Selection of the system with different kinetics of the extraction for the particular groups of the lanthanides. In this case crown ethers seem to be very promising extractant showing generally but not universally slower extraction kinetics for the heavier lanthanides.

Two facts are interesting from theoretical viewpoint:

a) The adduct formation constants of mixed species (for example $LnL_3B_2$) can increase or decrease in the lanthanide series, which fact is not necessarily correlated with the steric hindrance. The change of the residual Lewis acidity during chelation of the lanthanides with formation $LnL_3$ species plays the dominant role in the ability to form the adducts $LnL_3B$ and their stability trend in the lanthanide family. In this point it is worth of mention the suggestions of Carugo and Castelani (Carugo et al., 1992; Carugo et al., 1993) who emphasized that the contribution from covalency to bonding in lanthanide complexes increases in the lanthanide series, which manifests as ability of heavier lanthanides in catalyzing the reactions of organic synthesis. Therefore more covalency in heavy lanthanide complexes means less residual Lewis acidity necessary for adducts formation.

b) Hard acids as lanthanoids can accommodate ligands with soft donors: N, S. This accommodation is possible only with the lanthanide chelates and therefore softness of the lanthanides is probably the function of chelation.

### Zrnutie poznatkov z oblasti chémie extrakcie lantanoidov

Hodnoty separačných faktorov (SF) lantanoidov možno vylepšiť tromi spôsobmi:

1. Modifikáciou organickej fázy v prípade tvorenia aduktov, napr. $LnL_3B$, $LnL_3B_2$, $LnL_32HLB$, $LnL_33HL$, $LnL_32HLB$. Priaznivé hodnoty SF vyplývajú zo sférických efektov (najmä v prípade ťažkých lantanoidov).

2. Modifikáciou vodnej fázy, a to tak, aby v rade lantanoidov došlo k zvýšeniu konštant stability komplexotvorných činidiel a poklesu rozdeľovacích koeficientov s rastúcim atómovým číslom.

3. Výberom systému s rozdielnou kinetikou extrakcie pre rôzne skupiny lantanoidov. Korunové étery vykazujú pre niektoré ťažšie lantanoidy väčšie hodnoty rýchlostných konštánt extrakcie.

Z teoretického hľadiska sú zaujímavé nasledujúce fakty:

a) Konštanty tvorby aduktov zmiešaného typu (napr. $LnL_3B_2$) môžu v rade lantanoidov ľubovoľne narastať aj klesať. Z toho vyplýva, že ich hodnoty nezávisia iba od sterických podmienok. Zmena dodatkovej Lewisovskej kyslosti pri chelatácií lantanoidov za tvorby $LnL_3$ má kľúčový vplyv na tvorbu a stabilitu aduktov typu $LnL_3B$. V tejto súvislosti je treba spomenúť ideu Caruga a Castelaniho (Carugo, 1992; Tsay, 1993). Podľa nich sa v sérií lantanoidov postupne zvyšuje kovalentný charakter väzby v komplexoch. To zároveň vysvetľuje schopnosť ťažších lantanoidov katalyzovať organické reakcie. Vyšší príspevok kovalencie znamená nižšiu dodatkovú Lewisovskú kyslosť potrebnú na vytvorenie aduktu pri ťažších lantanoidoch s väčšou atómovou (relatívnou) hmotnosťou.

b) Tvrdé Lewisove kyseliny ako lantanoidy môžu vyhovovať ligandom s mäkkými donormi: N a S. Je to možné len s chelátmi lantanoidov, a preto mäkkosť lantanoidov je pravdepodobne funkciou chelatácie.

## Introduction

Extraction still plays the dominant role in the lanthanide/actinide separation (Nash, 1993), where problem appears during reprocessing of nuclear fuel or radioactive wastes and in the production of the pure lanthanide elements. For this reason searching of the extraction systems with the high separation factors of the lanthanides or lanthanides/actinides is attractive problem.

Since last excellent review of the lanthanide extraction presented in Gmelin Encyclopedia (Gmelin, 1983), several papers concerning different extraction systems of the lanthanides were published and only the most prominent and key positions will be described in this review.

According to the idea introduced by Marcus (Marcus et al., 1969) there are essential three types of systems in the solvent extraction of the lanthanides: solvation, ion pairs and chelate formation. In fact, there are many intermediate types of systems and we will apply the idea presented in Gmelin Encyclopedia (Gmelin, 1983).

## Extraction through solvation

In solvent extraction water in the first coordination sphere of the metal it is replaced by molecules of extractant. Solvated cation associates with the counter ion and is transferred to the organic phase in the form of neutral salt. The most known from this group of extractants is tri-n-butyl phosphate (Koch, 1987), still used in the industry for the separation of the lanthanides. The most interesting last achievements in the chemistry of TBP are oscillating reactions (Gyorgi et al., 1992; Afonin et al., 1993; Smirnow et al., 1994) found for system Ce,Eu$(NO_3)_3$ - *malonic* acid, potassium bromate - TBP. In nonequillibrium state the distribution coefficients of Ce and Eu are changing periodically, passing through minima and maxima and following the analogical changes of oxidation/reduction potential of CeIV/CeIII system.

### *Phosphine oxides, esters of phosphonic acids*

Among the phosphine oxides the most known is tri-n-octyl phosphine oxide used in the system with lanthanide nitrates (Raiss et al., 1994; Mann et al., 1992) or thiocyanates (Khopkar et al., 1972). The separation factors of the lanthanides are low and the system has no reference to the application in the industrial scale.

Carbamoylalkylphosphineoxides and carbamoylalkylphosphonates, solvating extractants, are very effective in the separation of the lanthanides from actinides (Raiss et al., 1994)). High loading of organic phase, even during presence of the high concentrated acid in the aqueous phase, classifies these extractants as very convenient in usage. The solubility of the salts in the organic phase is determined rather by the third phase formation, not by the composition of the formed species. Kolarik (Kolarik et al., 1988) studied the solubility of Nd$(NO_3)_3$ in CPMO (n-Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide). There is interesting, that it depends on the structure of the organic phase solvents, decreasing with the rise of molecular mass of the solvent and with branching of the octyl group of phosphine oxide. Solubility increases evidently for higher homologues of TBP and with the temperature increase.

Nakamura and Miyake (Nakamura et al., 1994) found from their NMR (Nuclear Magnetic Resonance) studies, that the number of CPMO molecules coordinated to Eu(III) and Gd(III) ions in Ln$(NO_3)_3$-CPMO complex is 3 and 2, respectively, in deuterated chloroform, in the presence of excess CPMO.

Phosphonic esters extract lanthanides similarly to TBP. The distribution ratios increase with the atomic number for high acidic media in the whole lanthanide series and start to decrease beginning from the middle lanthanides for lower concentrations of acid in the aqueous phase (Euxin et al., 1982). In this kind of extractant (di(ethylhexyl)isopropylphosphonate) DIOPP is the typical example. Interesting is, that both free energy changes and water content in the organic phase show the double-double effect (Fidelis, 1972) in the dependence vs atomic number of the lanthanide.

Ketophosphonates $[R,C(O)CH_2P(O)(OR)_2]$ act as extractants due to donor power of carbonyl and phosphoryl group or may show acidic character due to enolic tautomerism. Among these compounds the most known is dibutylphenacylphosphonate studied by Ceccaroli (Ceccaroli, 1982). In high acidic media the distribution coefficients of the lanthanides are independent on acidity of solution, which results from neutral extraction. In low acidic media the third power of logD vs lg[H ] dependence was found, which results from acidic character of extraction.

## Extraction by compound formation nonchelating extractants

### *Sulphonic acids*

The extraction of lanthanides by dinonylnaphtalenesulphonic acid has been reviewed by Markovits and Choppin (Markovits et al., 1973). In hydrocarbon diluents it forms inverted micelles or oligo-molecular aggregates. The extent of aggregation depends on the type of diluent. The first power dependence of D on concentration of HDNNS has been observed in some cases, but not universally. According to Danesi (Danesi, 1980) the monomerized form of HDNNS at the interface of toluene solution of the extractant and the aqueous $HClO_4$ containing the trace concentration of lanthanides plays the leading role in the estabilishment of extraction.

### *Carboxylic acids*

Carboxylic acids interact with the lanthanides through exchange of protons. Preston and Preez found (Preez et al., 1992; Preston et al., 1991; Preston et al., 1994) that in the case of sterically hindered carboxylic acids the

$pH_{0.5}$ decreases in the lanthanide series and yttrium behaves similarly to the middle lanthanides. The monomeric complexes $LnA_3(HA)_3$ appear in the organic phase except for Lu, which forms $LuA_3(HA)_2$ complex. For sterically nonhindered acids the values $pH_{0.5}$ decrease to Tb and then start to increase again due to steric obstruction in reaction of the lanthanides with dimerized molecules of carboxylic acids; Y behaves similarly to the light lanthanides. The dimeric complexes $(LnA_3(HA)_2)_2$ appear in the organic phase .

Danilov and Korpusov (Danilov et al., 1992) found that in extraction by 2-ethylhexanecarboxylic acid yttrium takes place in the region Ce-Eu for nitrates; in Ce-Pm for chlorides and in Ce-Pr for sulphates.

### *Phosphoric acids*

Among the organophosphorous acids the most known is (di(2- ethylhexyl)phosphoric acid) HDEHP. The most interesting is the extraction of lanthanides from tartrates or citrates (Crouse et al., 1989) in the presence of contaminants like Cr, Fe or Al. These metals form probably complexes with tartrates or citrates commonly with lanthanides, which are nonextractable and dissociate very slowly. The kinetics of extraction is different for the individual lanthanides. For example iron depresses extraction of Eu and Nd more than Ce, chromium depresses extraction of Ce more than Eu.

Sato (1989) compared the 2-ethylhexyl phosphonic acid with HDEHP in the extraction of the lanthanides and found that separation factors are very similar in both cases. The periodicity in the extraction behavior of lanthanides manifested as double-double effect.

Raieh and El-Dessouky (Raieh et al., 1985) found, that extraction of the lanthanides by HDEHP was synergistically enhanced by the presence of HDNNS (dinonylnaphtalenedisulphonic acid). The ratio 1:1:1 of $Ln3+:(HA)_2:(HDNNS)_m$ in synergistic species was found. The distribution ratio of the lanthanides were found to decrease in the lanthanide series.

Bhattacharyya and Gauguly (Bhattacharyya et al., 1986) found, that the mean separation factor of the lanthanides in the system with HDEHP is improved from 2.53 to 2.85 when glycine as complexon is present in the aqueous phase.

Sladek studied the extraction of the lanthanides in the system with HDEHP with application of 1,1,2,2-tetrachlorodifluoroethane as solvent, which enables converting of the metal chelates formed to the solid phase (Sladek, 1992).

Kopuniec (Kopunec et al., 1989; Kopunec et al., 1993; Kopunec et al., 1991) studied the transport of tervalent rare earths: Sc, Y, Ce, Eu, Gd, Tm, Yb from nitrate medium through flat-sheet supported liquid membrane containing HDEHP in n-dodecane, supported on a nucleoporous filter. The influence of aqueous phase acidity, metal and carrier concentrations were checked. The satisfactory separation of binary mixtures: Ce-Tm, Ce-Yb, Ce-Sc was achieved.

Preston and du Preez (Preston et al., 1988) compared the extraction behaviour of the lanthanides in the systems with organophosphoric, phosphonic and phosphinic acids 2-ethylhexylseries and found the improved separation between lanthanum and cerium offered by the phosphonic and phosphinic acids as compared with that offered by the phosphoric acid.

Komota (Komota et al., 1988) studied the kinetics of the lanthanide extraction by dodecylphosphoric acid and found, that the rate determining step changes from reaction control to mass control at high pHs and at high extractant concentration. The separation of Eu from Gd can be improved through the kinetic way.

Nakamura and Akiba (Nakamura et al., 1989) studied the use of flat-sheet membrane impregnated with diisododecylphosphoric acid in the extraction of the lanthanides. The addition of 1-octanol to membrane improves the stripping process and therefore the Eu can be transported from feed solution of 0.1M HNO3 into the product solution of 5M $HNO_3$.

### *Phosphonic, phosphinic acids*

Kubota and co-workers (Kubota et al., 1993) found significant improvement of the separation factors: Ho/Y and Er/Y in the system with mono-2-ethylhexyl ester of 2-ethylhexylphosphonic acid after partial complexation of the lanthanides in the aqueous phase by DTPA (diethylenetriaminepentaacetic acid).

Li and Freiser (Li et al., 1986) studied the extraction equilibria for a series of lanthanide ions using chloroform solutions of bis(2,4,4-tripentyl)phosphinic acid (HBTMPP), either alone or combined with adduct forming agent. The extraction species were $Ln(BTMPP)_3(HBTMPP)_3$ and $Ln(BTMPP)_3$ (HBTMPP)(TOPO) in the presence of trioctylphosphine oxide. TOPO increases the extractability and separability of lanthanides. The phenantroline as an adductant is not effective in the pH range used for HBTMPP. The distribution coefficients of the lanthanides in the case of another phosphororganic acid as di-2-ethylhexylphosphoric acid or dioctylphosphoric acid are higher.

The kinetic and extraction equilibria of the lanthanides and HBTMPP in the micellar phase (polyethyleneglycol tert-octylphenylether) were studied by Inaba and co-workers (Inaba et al., 1993). The extraction constants of the lanthanides Kex in the micellar phase are 4-6 orders larger than the values in $CHCl_3$ -$H_2O$. The extraction behavior in the micellar system is similar to the behavior in $CHCl_3$ -$H_2O$ in the presence of ligand such as TOPO, which forms 1:1 adduct with $M(HL_2)_3$. Two series of lanthanide-HBTMPP dimer complexes having ratios 1:2.5 and 1:3 were extracted into the micelles, and for both series the $K_{ex}$ values for the heavy lanthanides are higher than for the light lanthanides. The rate constants for the dissociation reaction of these complexes are larger for the light lanthanides than those for the heavier lanthanides. The former complex 1:2.5 is more reactive than the latter.

The use of the dicyclohexylphosphinic acid in the extraction of the lanthanides led Freiser and Cecconie (Cecconie et al., 1989) to the conclusion, that the selectivity of DCHPA is lower when comparing with another phosphinic acids, which results probably from the steric hindrance in chelate formation invoked by cyclohexyl substituents.

## Extraction by compound formation chelating extractants

### *ß-diketones*

Acetylacetone (HAcAc) is the simplest compound from the ß-diketones. Albinsson and co-workers (Albinsson et al., 1989) studied the extraction of the lanthanides by Hacac using AKUFVE method. They found, that stability constants of the lanthanide acetylacetonato together with the partition constants of the neutral complex Ln(acac)$_3$ increase in the series.

Among the other ß-diketones dodecylbenzoyltrifluoroacetone (LIX 51), benzoylisooctanoylmethane (LIX 54) and dibenzoylmethane (DBM) were studied in respect to lanthanides (Nakamura et al., 1989). It was found that in all three cases the extraction behaviour of the lanthanides showed the tetrad effect. The mean separation factors are: 1.71, 1.95 and 2.23 in the whole lanthanide family for LIX 51, LIX 54 and DBM, respectively .

Shigematsu and co-workers (Shigematsu et al., 1967) studied the extraction of the lanthanides by benzoyltrifluoroacetylacetone Hbtfacac either alone or with addition of adductants such as: n-hexyl alcohol, TBP, or TOPO. They found, that the stability constants of chelates increase with the atomic number, whereas the overall stability constants of adducts decrease with atomic number. All lanthanides except for Lu form adducts Ln(btfacac)$_3$(A)$_2$

Nakamura and co-workers (Nakamura et al., 1986) studied the extraction of lanthanide La(III), Sm(III), Tb(III) and Lu(III) with three ß-diketones (HA) (hexafluoroacetylacetone (Hhfa), pivaloyltrifluoroacetone (Hpta) and benzoylacetone Hba) in the presence of a bidendate ligand (S)-1,10 phenantroline. The general composition of the adducts formed was Ln(A)$_3$S. Ln(A)$_3$(S)$_2$ was also found for La-Hhfa, La-Hpta and Sm-Hhfa. The adduct formation constants increase with the atomic number for Hhfa and Hpta, ß-diketones forming less stable chelates with lanthanides than Hba and HAcAc. The adduct formation constants decrease with the atomic number for Hba and Hacac.

Hasegawa and coworkers (Hasegawa et al., 1990) studied the synergistical extraction of the lanthanides by the mixture of (theoylotrifluoroacetylacetone) Htta and derivatives of benzoic and phenylacetic acids. They found, that ability of the lanthanides to form adducts Ln(tta)$_3$(A)$_2$ decreases with the atomic number.

This fact they explained by the diminishion of residual Lewis acidity for successive lanthanides forming stronger complexes with chelates. Furthermore they concluded that phenylacetic, phenyllactic and methoxyacetic acids act as bidendate ligands.

Nakamura and Suzuki (Nakamura et al., 1993) found synergistic enhancement of the lanthanide extraction in the system with 4,4,4-trifluoro-1-(2-triethyl)-1,3-butanedione in the presence of 10-phenantroline (phen) or 2,9-dimethyl-1,10 phenantroline.

The formation constants of Ln(tta)$_3$phen adducts increase in the lanthanide series, whereas those for Ln(tta)$_3$dphen decrease with the atomic number.

Satake, Tsukahara and Suzuki (Satake et al., 1993) used ethylenediamine (en), diethylenetriamine (dien) and triethylenetetramine (trien) as synergistic adductants in the extraction of Ln by Htta. The adduct formation constants increase with the atomic number of the lanthanide for Ln(tta)$_3$ en species and decrease for Ln(tta)$_3$dien and Ln(tta)$_3$trien species.

Le and co-workers (Le et al., 1993) investigated the extraction of the lanthanides by 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and TOPO. The formation constants of Ln(PBI)$_3$(TOPO)$_2$ species follow the order: La<Pr>Eu>Ho>Yb.

Suzuki, Satake and Tsukahara (Suzuki et al., 1993) reported about the extraction of the lanthanides by Htta and terpyridine(tpy). The species Ln(tta)$_3$(tpy) were found in the organic phase and their formation constants decrease with the atomic number of the lanthanides and were compared with those for other heterocyclic amines.

Satake and co-workers (Satake et al., 1993) studied the synergistic extraction of the lanthanides by the mixture of Htta and phosphoryl type uncharged bidendate ligands, such as: tetraphenyldiphosphine dioxide (tpdpo) or bis(diphenyl-phosphinyl)methane (bdppm). The species Ln(tta)$_3$S (n=1 or 2) for tpdpo and n=1 for bdppm were found. For each lanthanide the adduct formation constant ßs for bdppm is larger than the ß$_{s,1}$ and ß$_{s,2}$ for tpdpo and ß$_s$ values for both ligands decrease with atomic number of lanthanide.

### *Phenol derivatives*

Li, Qu and Freiser (Li et al., 1987) studied the extraction of La, Pr, Eu and Yb by 2-(3,5-dibromo-2-pirydylazo)-5-diethyl aminophenol alone or combined with TOPO. In the first case LnL$_3$ species were found in the organic phase, while in the second case adducts Ln(OH)L$_2$(TOPO)$_2$ were recognized. System displays good selectivity for the lighter lanthanides and was compared with different extractants .

Karalova and Lawronowicz (Karalova et al., 1994) studied the extraction of Am and lanthanides by the sulphur derivatives of alkylphenol in the presence of different complexing agents in the aqueous phase. They found, that the elements were extracted by the disulphide of thirdbutyl phenol and its polymeric derivative oktofor 10S in conditions where different hydroxocomplexes are formed in the aqueous phase.

Alkylpyrocatechol extractants are used in the separation of the actinides from lanthanides. The separation factor

Eu/Am $\beta_{Eu/Am}=70$ was found in nonequilibrium extraction (Karalova et al., 1982) for system 4-(O,O dioctylethyl)-pyrocatechol/NaOH/DTPA or DTPHA (diethylenetriamine-N,N,N,N,N-pentamethylenephosphonic acid). The high separation factor results from the differences in the rates of complexons reaction with metals in the aqueous phase.

### *Pyrazolones*

Acylpyrazolones has been extensively studied in the extraction of the lanthanides. Also divalent and trivalent metals are extracted from acidic media because of the strong acidity of acylpyrazolones. Freiser and co-workers studied the extraction of the lanthanides by 1-phenyl-3-methyl-4- trifluoro- acetyl-5-pyrazolone (Freiser, 1988) in the presence of different adductants such as: tri-n-octylphosphine oxide (TOPO), n-octyl-(phenyl)-N,N-diisobutyl-carbamoylmethyl phosphine oxide (CPMO), methylenebis(diphenylphosphine oxide (MBDPO). Lanthanides were extracted as Ln(PMTFP)$_3$(TOPO)$_2$ and Ln(PMTFP)$_3$(CPMO), respectively. In the extraction with MBDPO the extracted species are Ln(PMTFP)$_3$ (MBDPO)$_2$ in the absence of perchlorates and Ln(PMTFP)$_2$(ClO$_4$)(MBDPO)$_2$ in the presence of perchlorates. The extraction constants in the case of MBDPO were the highest. It was noticed, that adduct formation constants decrease in the lanthanide family. From practical viewpoint it was very important, that separation factors of the lanthanides were evidently improved, especially for Ho/Yb pair, when comparing the system with pyrazolone alone and with adductants: TOPO and MBDPO.

Dukov and Genov (Dukov et al., 1986) studied the extraction of selected lanthanides by 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) and Aliquat 336 (QCl). The species LnP$_4^-$ Q$^+$ were found in the organic phase. With tri-n-octylamine as adductant the species LnP$_4^-$ TOAH$^+$ were recognized in the organic phase.

Nekimen and co-workers (Nekimen et al., 1992) studied the extraction of the lanthanides by synergistical mixture of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-thione and TOPO. They found that composition of synergistic complexes changes across the lanthanide series with the decrease of HBMPPT and increase of number of TOPO molecules. The separation factors of the lanthanides are poor but taking into account the previous results with Am, this system seems to be convenient for the separation of the actinides from lanthanides. There is interesting, that yttrium places near La in respect to the values of distribution coefficient.

Quyen Thi Hahn Le and co-workers (Le et al., 1993) found that the selectivity in the extraction of the lanthanides by the ß-diketones and pyrazolones depends on O-O distance. This distance may be controlled either by ring-structure geometry or by the steric effect between 3-methyl group and bulky 4-acyl substituents in acylpyrazolones. In former case they compared 2-trifluoroacety pentanone, -cyclohexanone and -cycloheptanone. In the latter case they showed behavior of 1-phenyl-3-methyl-4-acetyl, 4-propionyl, 4-isobutyryl, 4-pivaloyl-5-pyrazolone in the extraction of the lanthanides. The separation factor Yb\La increases with the decrease of O-O distance in ß-diketones. The 3-phenyl-4-benzoyl-5-isoxazolone was also included in this comparison.

### *Oximes*

Apart from the application in the separation of d-electron elements described by Szymanowski (Szymanowski, 1990), oximes can be successfully used in the separation of the lanthanides.

Abbruzzese and Piga (Abbruzzese et al., 1992) compared two commercial extractants: SME 529 (an alkylhydroxyoxime) and Kelex 100 (an alkyl hydroxyquinoline). In the case of Kelex 100 the separation factor ßLa/Ce=200. Hydroxyoxime extracts lanthanum through formation of species LaR$_2$OH, whereas Kelex 100 through the species LnR$_3$. The case of cerium is the same for both extractants with the formation of LnR$_3$. The higher selectivity of La/Ce for Kelex 100 was explained as the consequence of the easy release of proton from Kelex molecule.

According to Abruzesse, Fornari, Masida and Urbanski (Abruzesse and Fornari et al., 1992) extraction of Ce and La by Lix 70 (2-hydroxy-3-chloro-5-nonylobenzophenone oxime) was found to depend on pH and on extractant concentration, but not dependent on metal or chloride concentration. Both lanthanides were found to be extracted as 1:3 metal:reagent complexes.

### *Quinolines*

Freiser (Freiser, 1988) studied the extraction behavior of lanthanides in the system with hydroxyquinoline and bipyridine as well as phenantroline. The species LnQ$_3$.HQ.DNBP were found in the organic phase for Yb, Ho, Eu, Pr and LaQ$_3$ for La. In the case of phenantroline the complexes LnQ$_3$.2HQ.phen were recognized. The bipyridine was supposed to be bidendate and phenantroline monodendate. The separation factors of the heavy lanthanides were distinctly improved in synergistic system when comparing them with nonsynergistic system. The extraction constants involving the dinonylbipyridine are intermediate in value to those corresponding to the di- and tri-self adducts and are lower than those involving phen. Difference between phen and bpy is responded to the steric hindrance of nonyl-groups on DNBP and represents the probable cause of the poorer lanthanide extractability. Phenantroline gives higher extraction constants, since in general phen complexes are stronger than those with 2,2-bipyridine.

The extraction behavior of lanthanides with hydroxyquinoline were also studied by Pustelnik and Czakis-Sulikowska (Pustelnik et al., 1991). They found the presence of synergic complexes with methanol Lnox$_3$2CH$_3$OH in the organic phase. Nonlinear change of the extraction constants with the atomic number of the lanthanides they explained by double-double effect.

Recently Saitoh and co-workers and at the same time Ionue (Inoue, 1991) found that different hydroxylamines can be used in the extraction of the lanthanides. From the slope dependencies (Saitoh et al., 1994) they found that lanthanide are extracted as $LnL_3.2HL$ compounds. The separation factors for the heavy lanthanides for some phenylhydroxylamines are comparable with HDEHP. The comparison of phenylhydroxylamines having primary, secondary and tertiary substituents near the carbonyl group led to the conclusions, that the separation factor of the lanthanides is correlated with the inductive effect (Taft Constant) of the substituents. The lower is the value of the Taft constant, the strongest is the binding strength between the carbonyl oxygen and the lanthanides (III) and at the same time the better is the separation factor of the lanthanides.

### *Amides*

Jarvis and co-workers (Jarvis et al., 1993; Jarvis et al., 1994) used N,N,N,N- octabutylimidodiphosphotetramide (HA) for the extraction of the lanthanides. It was found, that extractant should act as a neutral in the lower pH range and at higher acid concentration. Within the pH range possibly loses its imidic proton and acts as a monoanionic bidendate extractant. The following species were found in the toluene solution of HA during extraction of Nd: ($Nd.3NO_3.3HA$), ($Nd.2NO_3.A.2HA$), ($Nd.2NO_3.A.HA$), ($Nd.NO_3.2A.2HA$), ($Nd.NO_3.A.OH$), (Nd.A.2OH) depending on the equilibrium pH of the aqueous phase.

### *Crown ethers*

Crown ethers extract lanthanides either alone or with synergistic agents. The values of the distribution coefficients and their trend in the lanthanides series depends on the different factors, the most important are: cavity size of the crown ether and the kind of counter ion (Frazier et al., 1993).

The distribution coefficients of the lanthanides in 18-crown-6 decrease in response to the fitness of ions in the cavity size of the crown ether. The separation factors are better than in case of HDEHP for some pairs of the lanthanides. Light lanthanides form 1:1 complexes, whereas the heavy- 1:2 complexes Ln(CR)n(TCA)3 with n=1 or 2 (TCA-trichloroacetic acid).

Khalifa and co-workers (Khalifa et al., 1988) studied the extraction of the selected lanthanides by 12C4 and 15C5 from perchlorate media. They found that the distribution coefficients of the lanthanides in the case of 15C5 are higher than in case 12C4, which they explained by the cavity size of the former compound. The selectivity in the former case was also better. They found, that separation factors Yb\Eu and Tm\Eu were higher than 50. Slope analysis indicated the existence of $Ln(OH)_2^+ClO_4^-(CE)_2$ complexes, however this data were not compatible with the results of Tsay/70/, which found only one mole of CE participating in the extraction of the lanthanides from picrate-nitrate media.

The role of lanthanide hydration on the extraction process is evident, especially when water is replaced be heavy water (Inoue et al., 1993; Nakagawa et al, 1991). By comparison with the extraction of alkali and alkaline earths metals it is clear, that lanthanides retain some water in the complex transferred to the organic phase during extraction. The deuterated water is bound with first coordination sphere of the lanthanide ions through the hydrogen bonds. Therefore the distribution coefficients of the lanthanides dramatically change when changing water media for heavy water media, which fact is not observed during extraction of alkaline and alkaline earths loosing their first coordination sphere water during extraction.

Szczepaniak and co-workers (Szczepaniak et al., 1992) reported about the extraction of the lanthanides by 1,4,7,10,13,16-hexaazacyclooctadecane (HA18C6) in the presence of erythrosine. The following stoichiometry of extracted ion associate is proposed: $Ln(OH)HA18C6^{2+}$-erythrosine $A^{2-}$. In strongly alkaline solutions significant differences in ion extraction efficiency of particular lanthanides were observed. The Pr, Nd, Sm, Eu, Gd(III) may be separated from Y, Er, Tm, Yb, Lu(III). The kinetics of the extraction of the middle lanthanides is much slower than the heavy lanthanides and yttrium. The results of the authors are very important from the analytical viewpoint allowing to determine spectrophotometrically the middle lanthanides without the disturbance from the heavy ones.

Ensor and Pruett (Ensor et al., 1988) reported about the enhancement of the extraction of the selected actinides and lanthanides by the thenoilotrifluoroacetylacetone in the presence of linear and cyclic polyethers. They found the pronounced increase of the distribution coefficients of the actinides especially in the case of polyethers containing the nitrogen atom, such as: (1,13-bis-quinolyl)-1,4,7,10,13-pentaoxatridecane and 5,6,14,15-dibenzo-4,7,13,16,21,24-hexaoxa-1,10 diazabicyclo[8,8,8] hexacosane. The polyethers with rigid structure bind lanthanides more strongly than polyethers with linear, flexible structure. In all kinds of polyethers the slight selectivity actinides toward lanthanides was obtained. Comparison with cyclic polyether K22DD having rigid structure with linear polyether K5 led to the conclusion that the stronger bond of N atoms with lanthanides is formed in this former case.

Chang and co-workers (Manchanda et al., 1986; Chang et al., 1989) analyzed the extraction of selected lanthanides by Htta in the presence of crown ethers: 1,7-diaza-4,10,13-trioxacyclopentadecane-N,N-diacetic acid (DAPDA) and 1,10-diaza-4,10,13-trioxacyclooctadecane-N,N-diacetic acid (DACDA). For the light lanthanides the ternary complexes Ln(L)tta are transferred to organic phase, for Lu and Yb only binary complexes $Ln(tta)_3$ were found in the organic phase. The kinetics of the heavy lanthanides extraction is governed by the slow dissociation of ternary complex Ln(L)tta in the aqueous phase. The extraction constants of the lanthanides increase with the atomic number and their difference for Lu/Yb pair is improved for DAPDA and DACDA when comparing with Htta alone. The change of the pH alters the order of the lanthanides extractabilities if EDDA (ethylenediaminediacetic acid) is present in the aqueous phase. According to the authors the observed trend in the ternary complex extraction constants could be attributed to:

1) variation in the stability of primary complex of macrocyclic ionophore

2) increasing ionic potential and steric hindrance of the resulting ternary complex with the increase of atomic number

3) increasing partition coefficient of ternary complex with the atomic number.

The separation factor Yb/Lu is significantly improved in ternary system when comparing with binary system with Htta alone. It results from stronger complexation of Yb by polyethers in aqueous phase. For the pair Nd/La the separation factor decreases in ternary system, which results from similar distribution constants of Ln(DAPDA/CAPDA)tta complexes for Nd and La. A break near Nd(III) in the curve obtained in the presence of EDDA (ethylenediaminediacetic acid) and lack of regular increase in distribution ratio could be explained on the basis of the increase of $\beta_2$ second stability constant of lanthanide-EDDA complex. Different behavior of lanthanides for different pHs, especially for DACDA, result from different nature of species in the organic phase and change of conditional stability constants.

Mathur and Khopkar (Mathur et al., 1987; Mathur et al., 1988) studied the extraction of Am, Cm, Cf and Eu by mixture of 1-phenyl-3-methyl-4-trifluoroacetylpyrazolone-5 (HPMTFP) and a crown ether dicyclohexano-18-crown-6 (DCH18C6) or monobenzo-15-crown-5 (B15C5). They concluded from the slope data, that in the absence of crown ethers sulf-adducts $Ln(PMTFP)_3.(HPMTFP)$ are formed, whereas in the presence of crown ethers complexes $M(PMTFP)_3.(DCH18C6)$ and $M(PMTFP)_3.2(B15C5)$ are formed.

If the bis-adduct is formed, the sandwich type complex moiety probably exist, because the second stepwise formation constants logK are much higher than the first stepwise formation constants $\log\beta_1$ of the crown-ether-adductants- lanthanide complex. Another explanation for unusual sequence of stepwise stability constants is that the replacement pyrazolone molecules by crown ether in self-adducts, which leads to an apparent smaller $\beta_1$ values.

### *Cyclophanes*

The solvent extraction behavior of lanthanides with cyclophanes of calixarene type were described by Ludwig and co-workers (Ludwig et al., 1993). In the case of p-tert-butylcalix/6/arenehexacarboxylic acid (L1) the lanthanides are extracted through cation exchange mechanism in the form 1:2 metal:ligand complexes. The order of their extractability is Nd, Eu>La>Er>Yb. This order is very similar to the extraction of the lanthanides by crown ethers, where the change in the coordination number of the lanthanides and increase in the hydration energy in the lanthanide series determines the order of the lanthanide extractability. However lanthanide ions are probably coordinated by oxygens of carboxylic groups, not by the oxygen of ether groups. These last probably binds the sodium ions during extraction of the lanthanides from sodium perchlorate media. In this last case the presence of Na depresses the distribution ratio of the lanthanides. The species transferred to organic phase are 1:1 type. The p-tert-butylcalix/4/arene tetracarboxylic acid (L2) with smaller cavity size extracts lanthanides with the results of lower distribution coefficients. In the presence of sodium ions the distribution coefficients increase. The order of extraction is: Eu>Nd>Yb>Er>La. Contrary to L1 both the separation factors of Ln and their distribution ratio increase in the case of third cyclophane (L3) containing four carboxylic groups, but with larger cavity size than L2, the order of extraction is Yb>Er,Eu>Nd>La at pH 3.0. At the pH>3.5 Eu is the best extracted element. The sodium ion is transformed to organic phase according to ion exchange mechanism.

### *Ionic pairs*

Primary, secondary, tertiary amines can be used in the extraction of lanthanides. Except for quaternary ammonium salts, extraction by amines is conducted from acidic media.

Milyukova (Varezhkina et al., 1986; Milyukova et al., 1986; Milyukova et al., 1988) studied the primary amines. The presence of heteropolyanions in the the aqueous phase increases the separation factors of the lanthanides. The distribution coefficients of the lanthanides can be divided on two groups: cerium and europium. Their values depend strongly on the acid, heteropolyanion and extractant concentration. In this last case the dependence has complicated character, which proves results from different association equilibria of amines in the organic phase. In the presence of hydrochloric acid in the aqueous phase separation factors of the lanthanides are much higher than in case of nitric acid concentration. For example the value of $\beta_{La/Nd} = 78.9$ for $HNO_3$ and 977 for HCl. The system is effective also for the separation of the lanthanides from actinides. The tests with sulphuric acid in the aqueous phase were unsuccessful due to the third phase formation in the organic phase.

In the case of tertiary amines their selectivity in the separation of the lanthanides depends mainly on steric factors (Kopyrin et al., 1978; Derewianko et al., 1974; Szwedow et al., 1976). Therefore unsymmetrical methyldialkylammines are the best in respect to the separation factors of the lanthanides. The extraction power of amines can not be correlated directly with the inductive effect of substituents on nitrogen atom. It depends rather on steric effects .

Kovalancik and Galova used benzyldibutylamine (Kowalancik et al., 1992) to the separation La from Sm and Ce from Y. In the first case they found, that introduction of 2-hydroxyethylenediaminetetraacetic acid into the aqueous phase results in the 7-10 fold increase of the La/Sm separation factor. In the second case presence of EDTA in the aqueous phase improves 100-200 times the Ce/Y separation factor. Quaternary ammonium salts extract lanthanides from nitrate, chloride, thiocyanate or sulphate media. The very detailed study from nitrate media was described by Sokolowska and Siekierski (Sokolowska et al., 1983). They found that in case of Adogen 464 (trioctylmethylammonium nitrate) the lanthanides appear in the organic phase as 1:5 complexes ($Ln:NO_3$). Consideration of thermodynamic functions of formation of these complexes of Ln and Y results in conclusion, that stability of these complexes decreases in the lanthanide series and that the contribution from covalency to bonding is the same in the aquo ion and in the 1:5 nitrato complex.

Majdan and Kolarik (Majdan et al., 1993) studied the synergistic system Aliquat 336-TBP in the extraction of lanthanide nitrates. Contrary to Huang and Bautista (Huang et al., 1983) they found several synergistic species in the organic phase and evident worsening of the separation factors of the lanthanides with TBP concentration increase in the synergistic mixture. The synergistic effect was very pronounced only in the case of dodecane as diluent of organic phase. In purely aromatic solvents, like xylene, the effect was very weak.

Sohsah, Krejzler and Siekierski (Sohsah et al., 1990)studied the extraction of the lanthanides by Adogen 464 from chloride media. They concluded about the decrease of the stability of the innersphere chloride lanthanide complexes across the lanthanide series. Apart from that, they found that the equilibrium constants for the transfer of the negatively charged chloro-complexes increase with the lanthanide atomic number.

Extraction of the lanthanides, actinides and yttrium in the thiocyanate media was studied by Borkowski (1991). He found, that yttrium is similar to the light lanthanides in the extraction behaviour and the actinides are similar to the heavy lanthanides. From this fact he concluded, that there is some contribution from covalency in bonding in lanthanide thiocyanate complexes. Furthermore he calculated the stability constants $\beta_1$ and $\beta_2$ of $Ln(SCN)_n^{3-n}$ complexes.

The values of $\beta_1$ are essentially unchanged in the lanthanide series, whereas the $\beta_2$ values decrease with the decrease of lanthanide radius, which is the evidence for outersphere character of thiocyanato complexes of the lanthanides. On the other hand the $\beta_2$ values increase in actinide family, which results from inner sphere character of actinide thiocyanato complexes.

Komasava and Hisada (Komasawa et al., 1987) found, that separation factor Pr/Nd in the system with trioctylmethylammonium nitrate increases from 2 to 9 when DTPA is present in the aqueous phase.

Hirai and Komasava (Hirai et al., 1991) investigated the extraction of lanthanides by tri-n-octylmethylammonium nitrate (TOMAN) and ß-diketone (O-acetyl-m-dodecylaceto- phenone) in the presence of EDTA in the aqueous phase.

The separation factors Tb/Dy and Dy/Ho were improved from 1.57 and 1.84 to 1.05 and 1.15 when comparing the conditions without and with EDTA in aqueous phase.

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# Sorption of heavy metals from waste waters on specific materials

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**Abstract**

Over the last several years, the investigations of the natural zeolites application in the sorption processes have been intensified. Purification of waste waters in order to remove lead, cadmium, copper and other heavy metals, is one significant example of such application. In this paper, the investigations results on characteristics of the natural zeolites from the region of Vranje (Serbia), and chemically activated natural zeolite, are presented. Adsorptive characteristics of zeolite in a liquid medium, depending on granulation and concentrations of lead, zinc, cadmium and cobalt, were examined on laboratorial level. The experiments were peformed with zeolites after determination of their physicochemical characteristics, while the adsorptive characteristics were examined using zeolites of selected granulation.

As the obtained results show, these natural materials can be used to remove heavy metals from waste waters, efficiently and economically.

**Key words:** natural zeolites, waste waters, sorption Cd, Cu, Pb, heavy metals

**Sorpcia ťažkých kovov z odpadových vôd na špecifické materiály**

V posledných rokoch došlo k zintenzívneniu výskumov v oblasti využitia prírodných zeolitov ako sorpčných materiálov. Jednou z významných aplikácií je možnosť ich využitia na odstránenie ťažkých kovov z odpadových vôd. Išlo napr. o Cu, Pb, Cd a iné. V tejto práci prezentujeme výsledky pre prírodné zeolity a chemický aktivované zeolity z oblasti Vranje (Srbsko). V laboratórnych podmienkach sme sledovali adsorpčné charakteristiky zeolitov v kvapalnom médiu v závislosti od ich zrnitostného zloženia a od koncentrácií Pb, Cd, Zn a Co v médiu. Pred adsorpčnými experimentmi boli stanovené fyzikálno-chemické charakteristiky príslušných zeolitov. Podľa nich sa potom zvolila najvhodnejšia disperzita pre adsorpčné experimenty.

Ako vyplýva zo získaných výsledkov, prírodné zeolity sú vhodné na odstránenie ťažkých kovov z odpadových vôd, a to jednak z ekonomického hľadiska, ale aj z hľadiska účinnosti.

## Introduction

The investigations of the natural zeolites applications performed worldwide, including our country, proved their efficiency in the certain fields of industry, in agriculture and in a cattle breeding. A great number of published papers points to a widening application of natural zeolites in water processing. Very good results were achieved with adsorption of the cations from waste waters.

The zeolite applications are particularly well developed in the countries that possess their own deposits of these minerals. Yugoslavia (particularly Serbia) is in the very top of Europe in natural reserves, quality and potential for economical exploitation. Over the last several years, systematic investigations of natural zeolites in Yugoslavia, their processing and application, have been undertaken.

Institute for Technology of Nuclear and Other Raw Materials - Belgrade, have been deeply engaged in investigations connected with utilization of the natural zeolite from Vranjska Banja deposits. The results obtained so far enabled characterization of tuffs, the carriers of the zeolite minerals, from geological, mineralogical and physicochemical aspect, and development of technological processing procedures corresponding to various application fields. The aim of the investigations that are in a due course is to extend the scope of these applications.

Most of the natural zeolites are efficient ion exchangers. For this reason, they are also excellent demineralizers and decontaminators in waste water treatment. They are applied either statically, dynamically or in combination of the two. The ion-exchange system requires use of crystalline material (organic or inorganic), capable of exchanging specific ions in it's crystal structure.

Most of the zeolite minerals have affinity towards ions (exchange, adsorption). For this reason, this work has focused on the effects of the natural zeolites on removal of heavy metals from waste waters.

In this work, the adsorption characteristics of used natural zeolites were investigated, in order to determine the basic parameters necessary for applications of zeolites in purification of water intended for industrial use.

The application of zeolites is based on certain properties of the molecular forces and cation exchange capacity. In comparison with other, synthesized ion-exchangers, only natural zeolites can be economically used for removal of heavy metals from waste waters.

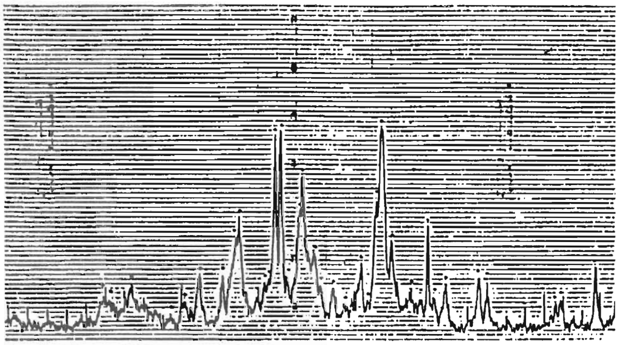

Fig. 1. X-ray diffractogram of investigated zeolite.

Besides, their capacity for separation of molecules on the basis of their size and distribution of electric charge in dehydrated central cavities, enable adsorption of molecules with permanent dipoles.

Most of the natural zeolite deposits were formed by sedimentation and hydration of finegrained volcanic ash, later transformed into microic zeolite crystalline.

Sedimentary zeolite rocks, the zeolite tuffs, usually contain 50-90 % of densely concentrated mineral. The content of pure mineral in the tuff determines the zeolite grade. Its futher use will depend on its physical and chemical properties, determined by its chemical composition and its crystal structure.

Natural zeolites are hydrated alumosilicates of the alkaline and alkaline-earth cations, having infinite three-dimensional crystal structure. The basic unit of the zeolite structure is tetrahedral, with central silicon or aluminium ion, while the corners of this tetrahedral structure are occupied by four oxygen atoms. Each oxygen's atom is common to two tetrahedrons. In this way, all tetrahedrons participate in built up of the tetrahedral structure which is open, with the cavities filled in with water. These cavities are connected by channels and pores, in one, two or three directions.

Although natural zeolites differ in their chemical composition, their idealized chemical formula can be represented in the following way:

$M_{x/n}(Al_xSi_yO_{2(x+y)p}H_2O$

where:

M - denotes one-valent or two-valent cations
n - cation valency
y/x - the range of 1 to 6
p/x - the range of 1 to 4

Application of natural zeolites is based on its physical characteristics: grain size and shape, porosity and hardness, type of exchangeable cation. This exchangeable cation in the zeolite mineral is linked by weak forces into tetrahedral structure, making it relatively easily removed or replaced due to the activity of the stronger cations present in the solution.

In practice, cation exchange capacity occurring in the contact between zeolite and medium is under the influence of numerous factors, such as: pH, temperature, cation competition, type of solvent, present cations, solution concentration and presence of aggregates.

The structure and topography of zeolite mineral determines its selectivity towards individual cations.

## Materials and methods

In Yugoslavia, there are deposits of the various zeolite tuffs grades. In this investigation, zeolite mineral with high content of clinoptilolite was used.

As already mentioned, one of possible applications of natural zeolites is their use in processing of natural waters with raised content of certain ions, or purification of waste waters containing heavy metals. Having this in mind, all experiments were carried out in a liquid medium, with synthetic solutions. The starting parameter use as criterion for selection of the synthetic solutions concentration was the highest legally acceptable concentration of investigated pollutants in waters of the I and II category. All experiments for investigation of the adsorption characteristics were performed with zeolites from the

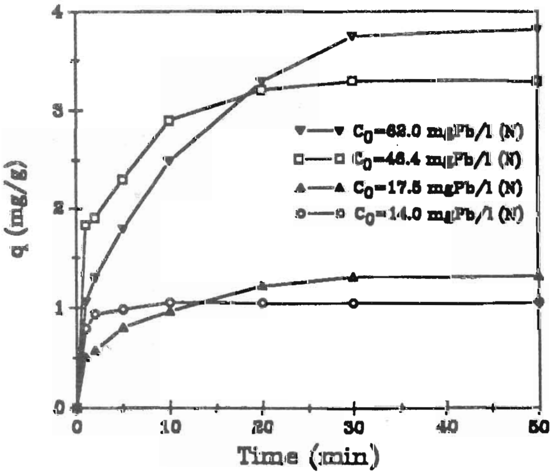

Fig. 2. Adsorption rate of Pb by natural zeolite.

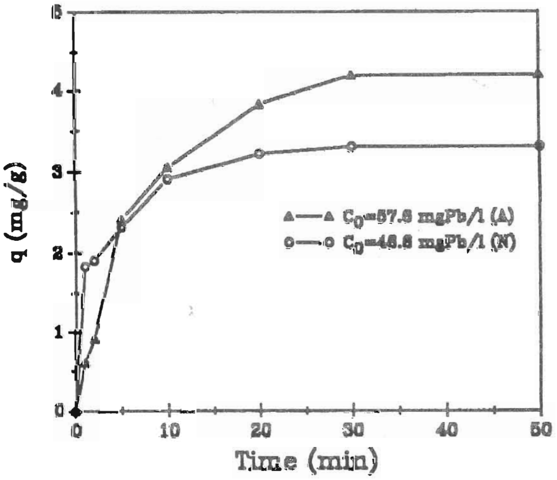

Fig. 3. Adsorption rate of Pb by natural (N) and activated (A) zeolite.

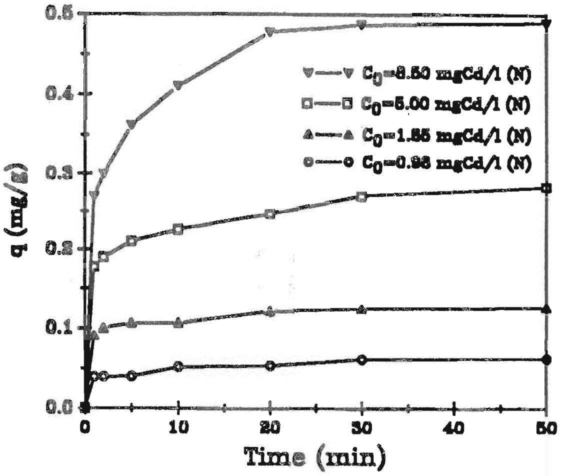

Fig. 4. Adsorption rate of Cd by natural zeolite.

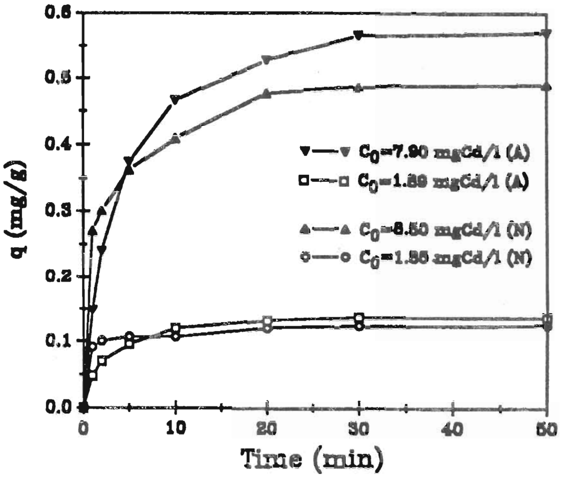

Fig. 5. Adsorption rate of Cd by natural (N) and activated (A) zeolite.

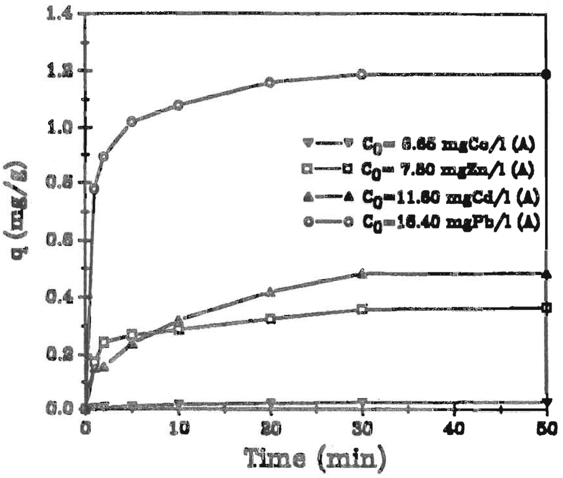

Fig. 6. Adsorption rate of cation from the mixture by activated zeolite.

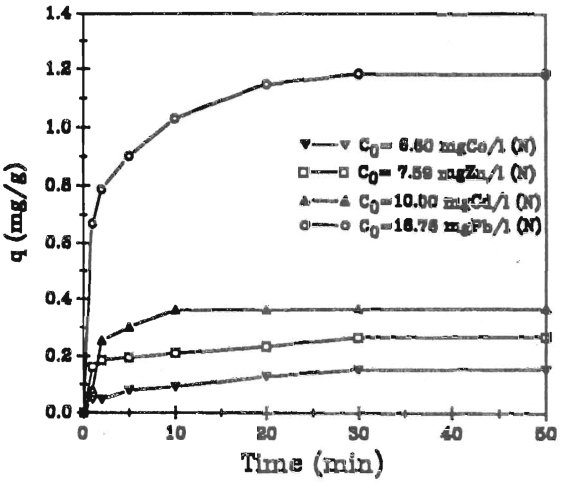

Fig. 7. Adsorption rate of cation from the mixture by natural zeolite.

region of Vranje, containing over 90 % of clinoptilolite, after having determined their physicochemical characteristics.

The chemical formulae of investigated zeolite reads as follows:

(K, Na, 1/2 Ca)$_2$ O.Al$_2$O$_3$.10 SiO$_2$.8 H$_2$O

Chemical composition of the average sample (in wt %): $SiO_2$ 61.96-66.24, $TiO_2$ 0.15-0.22, $Al_2O_3$ 12.46-14.02, $Fe_2O_3$ 1.33-2.05, MnO 0.05, MgO 1.53-1.96, CaO 3.03-4.34, $Na_2O$ 0.70-1.11, $K_2O$ 0.78-1.32, $H_2O$ (100 °C) 4.22-4.72, $H_2O$ (1000 °C) 7.65-9.58.

From the seven available classes of natural zeolites, +2-1 class was selected. This granulation was found to be the most appropriate one to manipulation in the flow-through systems. At the same time, the chemical stability of the zeolite tuff was checked in media of pH value in the range of 1 - 12. It was found out that zeolite was stable in pH region of 4 - 10. By a number of experiments, the optimal time for the cations adsorption was determined. As the experiments showed, adsorption in the investigated system practically ended for 30 mins. After this time, the adsorption degree is relatively low - therefore, for the reason of the experiment rationalization, this time is considered to be necessary for attaining the equilibrium state.

Experimental work involved determination of the adsorbing characteristics and equilibrium parameters. In order to determine the adsorption equilibrium, i. e. to determine the adsorption isotherms by Freundlich, the experiments were performed at defined concentration of pollutants in a liquid medium, selected granulation (+2-1 mm) and defined time, necessary to attain the equilibrium state (30 min). The amount of zeolite was a variable parameter (0.5, 1, 2, 5, 7 and 10 gr). Obtained results were used as a basis for further investigations.

In the second group of experiments, the change of the heavy metals concentration after treating the same amount of solution (150 ml) of the known concentration with equal amounts of natural and activated zeolites, were observed.

After intense stirring in electrovibrator (Heidolph Vibramax 100), the phase separation was performed in the shortest possible time and content of heavy metals in each thus obtained filtrate was determined. To this purpose, a standard AAS method has been used. For the measurings, atomic adsorption spectrometer "Perkin Elmer-703" was used.

## Results and discussion

Obtained results on the adsorption efficiency, presented in diagrams 1 - 6, are expressed as sorbate/sorbant (gram) ratio (ordinate), depending on adsorption time (abscissa). In Fig. 2, adsorption dynamics of lead on natural zeolite, at various initial concentrations, is presented. It can be noticed that for initial concentration influences the adsorption degree, i. e. adsorption is higher when initial concentration is higher. Such a tendency is in accordance with Freundlich adsorption isotherm. In Fig. 3, q = f(t) relation for adsorption of lead on natural and activated zeolite, obtained in two experiments with approximately the same initial concentration, is presented. Although the adsorption characteristics of activated zeolite are a little higher, the improvement achieved by activation is not significant. In Fig. 4, cadmium adsorption dynamics, for various initial concentrations, is presented. Similar to lead, the adsorption degree is higher if the initial concentration is higher. In case of cadmium, activation has influenced the adsorption degree only at the higher concentration, as presented in Fig. 5. Similar behavior is characteristic for adsorption of cobalt and cadmium.

It was also noticed that activation of sorbent (zeolite) changes the mechanism of adsorption to a certain extent. In case of the natural zeolites, the adsorption is fact in the starting phase (5 min), followed by a showed growth of adsorbent quantity, until the equilibrium value. Activated zeolites, however, have somewhat slowed dynamics attaining the equilibrium state. In Figs. 6 and 7, the adsorption dynamics for individual pollutants (from the mixture containing lead, cadmium, zinc and cobalt) on natural and activated zeolite, is presented. It can be noticed that the affinity towards adsorption, in both cases, is in the following sequence: Pb, Cd, Co, whereby the affinity towards lead is particularly well expressed.

Tab. 1
Adsorption capacity of natural and activated zeolite for the mixture of pollutants (initial concentration of each pollutant is 0.01 mol/l)

| | Adsorption (in %) | |
|---|---|---|
| Pollutant | Natural zeolite | Activated zeolite |
| Pb | 94.3 | 96.6 |
| Cd | 48.9 | 55.4 |
| Co | 31.1 | 49.5 |

Adsorption time - 30 min, solution volume - 150 ml, zeolite mass - 2 gr, $C_0$ - 0.01 mol/l

Activation of zeolite only slightly improves the adsorption capacity towards lead, while it is significantly increased for cadmium and cobalt, as shown in Tab. 1.

On the bases of performed investigations, it can be concluded that both natural and activated zeolite have considerable adsorption affinity towards investigated pollutants. Irrespective of the adsorption mechanism - in micropores or at surface, the zeolite can be classified in adsorbers of high adsorption characteristics.

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# Processing of the waste with content of arsenic

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### Abstract

The aim of the work was to find the way of the processing of the waste with great content of arsenic. Producer of this waste is producer of the semiconductor parts from the monocrystalline silicon, dopped with arsenic. The aim was not only the liquidation of the waste, but also the recovery of the arsenic.

**Key words:** semiconductor production, arsenic, waste, recyclig

### Úprava odpadov s obsahom arzénu

Cieľom prezentovanej štúdie bol návrh postupu spracovania odpadov s vysokým obsahom arzénu. Použili sme pritom odpad z výroby polovodičových komponentov z monokryštalického kremíka, kde sa arzén využíva ako dopant. Navrhli sme a overili možnosť detoxikácie cestou izolácie arzénu.

## Introduction

Content of arsenic compounds in any waste is one of the greatest problem at the waste deposition or liquidation. Arsenic in the soluble form is of high toxicity and is deposed in human body. The possibilities od waste deposition with content of arsenic are given in the Order of goverment for the waste No. 513/92 Sb and No. 69/1991 Sb; which classified the waste to groups of risks.

Technical application of arsenic and several its intermetallic compounds is in the production of semiconductor parts. As dopped into monocrystalline silicon, it is the donor of free electrons. GaAs is the semiconductor material, used in the production of fast processors. Arsenic, used for the semiconductor production, must be of the high purity, 4N at least. In Czech Republic the producer of the semiconductor parts from arsenic dopped silicon is the company Terosil a. s. in Rožnov pod Radhoštěm.

Arsenic in gaseous phase blows under level of the melted silicon in the production of silicon single crystals with n-type conductivity by the Czochralski technology. Arsenic solves in the melt, partially occupies the places in the structure of the silicon single crystal and partially evaporates due to the high temperature of silicon melt, which is higher than the arsenic sublimation temperature. Arsenic vapours and volatile SiO are commonly exhausted by the argon from the melting equipment, condense and are trapped in the cloth filter. The filters with venamon $As_2O_3$ are deposed. The "production" of this waste is less than 100 kg per year.

Our task was to find the way of recovery of this arsenic of purity as high as possible. The reason for the waste recovery was not only the economic, but also the lack of the deposit area.

## The possibilities of the arsenic source processing

Pyrometallurgical way of the arsenic production is the heating of the raw material in vacuum. Arsenic sublimes and condenses in the cool parts of device. Other technology is the chloration of raw material, distillation of arsenic chloride and reduction by the hydrogen; this is the way for the production of arsenic with high purity (Terayama, 1989). Pyrometallurgical technologies utilize the volatility of arsenic and its compounds, but the work with arsenic in gaseous state is problematic.

Hydrometallurgical processing of arsenic raw materials utilize the pressure sour or alkalic leaching. The work with arsenic solution is more simple and safety, than the work with arsenic vapours (Bloom, Maysilles and Dolezal).

The most often hydrometallurgical technology is the pressure leaching in sulphuric acid at the following conditions

- pure oxygen, pressure 200 - 225 kPa
- $H_2SO_4$ concentration 20 - 60 g/l
- time 60 - 180 min
- temperature ≥ 185 °C.

Precipitation of the metallic arsenic from the solution is possible by the cementation, pressure precipitation by hydrogen or electrowinning (Dewalens, Heerman and Van Simayes, 1975; Takagi and Yabe, 1956).

## Specification of the waste

The composition of the waste is given in the Tab. 1. The waste is the fine-grain powder, trapped on the clothes filter. Material has about 50 - 60 % of As, in the form of $As_2O_3$.

Tab. 1
Analysis of the waste

| As | Si | Mg | Fe | Hg |
|---|---|---|---|---|
| 46.2 % | 11.2 % | 24.8 % | 0.9 % | 0.75 % |

## Proposal of the waste processing

Due to the high content of silicon (silica resp.) and the wish of waste producer (recovery of the arsenic with high purity) we did propose the following system of waste processing:

1. Multistage contraflow sour leaching of the waste in $H_2SO_4$. The final concentration of arsenic in the filtration cake must not be higher than Order of goverment for the waste No. 513/92 Sb allows.
2. Electrowinning of As with the insoluble anode. Electrowinning allows to obtain metallic As of the high purity and also to recover the $H_2SO_4$ for the next leaching.
3. There would be possible to refine the product for the higher purity, if necessary, by the way of vacuum sublimation.

Tab. 2
Composition of the dried filtration cake

| As | Si | Mg | Fe | Hg | S |
|---|---|---|---|---|---|
| 10.3 % | 33.6 % | 4.9 % | 1.7 % | 0.05 % | 1.56 % |

The first two operations were experimentally verified. There is possible to transfer the arsenic from the waste into solution by the way of pressure sour leaching in the concentrated $H_2SO_4$ at the temperature 200 °C at least; lower temperature is not sufficient. The composition of the filtration cake is given in the Tab. 2.

There is possible to precipitate the metallic arsenic from the solution by the electrowinning. Arsenic electrode potential is +0.25 V and its deposition on cathode is possible. We electrolysed the solution on the laboratory electrolyser with insoluble platinum anode and arsenic deposed on the platinum cathode.

Parameters of electrowinning

| | |
|---|---|
| - voltage | 4 V |
| - cathodic current density | 1 - 3 $A.dm^{-2}$ |
| - temperature | > 60 °C |

Arsenic precipitated in the powder form and partially falls back to the solution.

## Discussion

Mentioned waste in possible to process by the way of pressure leaching in $H_2SO_4$ with following electrowinning to obtain the metallic arsenic. Due to the oral discussion with the technicians from company Terosil a. s. in Rožnov pod Radhoštěm. The final product can be used in the semiconductor production. There is necessary to answer next questions:

a) number of the leaching steps for the final composition of the filtration cake acceptable by the Order of government No. 513/1992.

b) to optimize parameters of electrowinning to improve the current efficiency

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*Mineralia Slovaca, 28 (1996), 427 - 428*

# The Co/Ni separation in Aliquat 336, Aliquat 336+Topo, Aliquat 336+TBP systems from chloride media

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### Abstract

The extraction data concerning the systems: Co, NiCl$_2$-Aliquat 336+TBP, Co, NiCl$_2$-Aliquat 336+TOPO are presented. In the first case the separation factors $\beta_{Co/Ni}$ change in the range 25-260 depending on the composition extractants mixture. The increase of the TBP (tri-n-butyl phosphate concentration) results in worsening of $\beta_{Co/Ni}$. In the second case the values of the separation factors change from 100 to 260 and increase of TOPO concentration results in the improvement of the $\beta_{Co/Ni}$.

**Key words:** extraction, cobalt, nickel, methyltri-n-octylammonium chloridethe Cu and Zn complexes from the cyanided poor leach

### Separácia kobaltu a niklu z chloridového média v Aliquat 336, Aliquat 336+TOPO a Aliquat 336+TBP

Boli zistené extrakčné podmienky pre systémy: Co, NiCl$_2$-Aliquat 336+TBP a Co, NiCl$_2$-Aliquat 336+TOPO. V prvom prípade sa separačný faktor $\beta_{Co/Ni}$ pohyboval v závislosti od zloženia extrakčného média v rozmedzí 25-260. Nárast koncentrácie TBP (tri-n-butylfosfátu) mal za následok zhoršenie hodnoty separačného faktora. V druhom prípade sa hodnoty separačného faktora pohybovali v rozmedzí 100 - 260 a nárast koncentrácie TOPO viedol k zlepšeniu hodnôt separačného pomeru.

## Experimental procedures

*Determination of the distribution coefficients of Co and Ni*

Aqueous phase containing CoCl$_2$, NiCl$_2$ and NaCl (POCH Gliwice, pure for analysis) was equilibrated with organic phase in small glass tubes with stoppers through 15 min. After separation of the phases the concentration of Co and Ni was determined using flame atomic absorption spectrometry technique. In the case of organic phase (Aliquat 336 - methyltri-n-octylammonium chloride, TBP - tri-n-butyl phosphate, TOPO - tri-n-octyl phosphine oxide in xylene, Aldrich, R-grade) Co and Ni were back extracted with water before determination. The distribution coefficients D were calculated as a ratio of metal concentration in organic and aqueous phases.

## Results and discussion

The data for Aliquat 336+TBP are presented in Fig. 1. When summary concentration of extractants (Aliquat 336, TBP) is constant (part A), the increase of Aliquat 336 concentration improves the value of separation factor $\beta_{Co/Ni}$ ($\beta_{Co/Ni} = D_{Co}/D_{Ni}$). Extraction of Co and Ni by pure Aliquat 336 (part B) results in the very high value of $\beta_{Co/Ni}$ (above 200). The increase of Aliquat 336 at constant TBP concentration (part C) improves extractability of both elements and (similarly to part A) and their separation. The values of D for both elements and their separation factor remain essentially constant during increase of TBP at constant Aliquat 336 concentration (part D).

The data for Aliquat 336+TOPO (tri-n-octyl phosphine oxide) are presented in Fig. 2. Similarly to the previous system the four alternatives were investigated: constant summary concentration of extractants (part A), constant TOPO concentration (part B), constant Aliquat 336 concentration (part C), pure Aliquat 336 (part D). In all cases the values of $\beta_{Co/Ni}$ are very high (above 100) and the increase of TOPO concentration in extractants mixture (parts A, C) improves the separation of the elements. Contrary to the system Aliquat 336+TBP the increase of TOPO concentration at constant Aliquat 336 concentration (part C) results in the improvement of D values for both elements, which fact, according to the authors, is the evidence for the formation of synergistic complexes of Co and Ni in the organic phase.

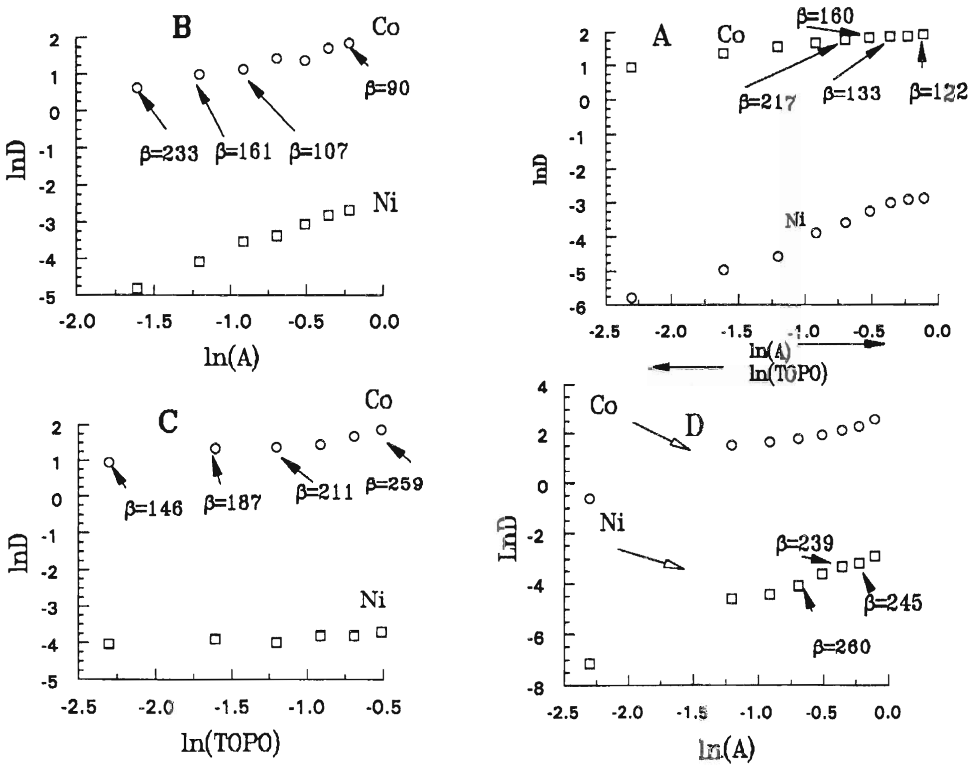

Fig. 1. Distribution coefficients of Co and Ni in Aliquat 336+TBP system ([Co] = [Ni] = 0.1 M in the aqueous phase, t = 17 °C). Part A: organic phase with xylene as solvent, the summary concentration of Aliquat 336 (A) and TBP = 1M, the phase volume ratio V(o)/V(aq) = 1; Part B: organic phase- [A] = 0.1-0.9 M, V(o)/V(aq) = 1; Part C: organic phase- [A] = 0.2-0.8 M, [TBP] = 0.2 M, V(o)/V(aq) = 2; Part D: organic phase- [A] = 0.4 M, [TBP] = 0.1-0.6 M, V(o)/V(aq) = 2.

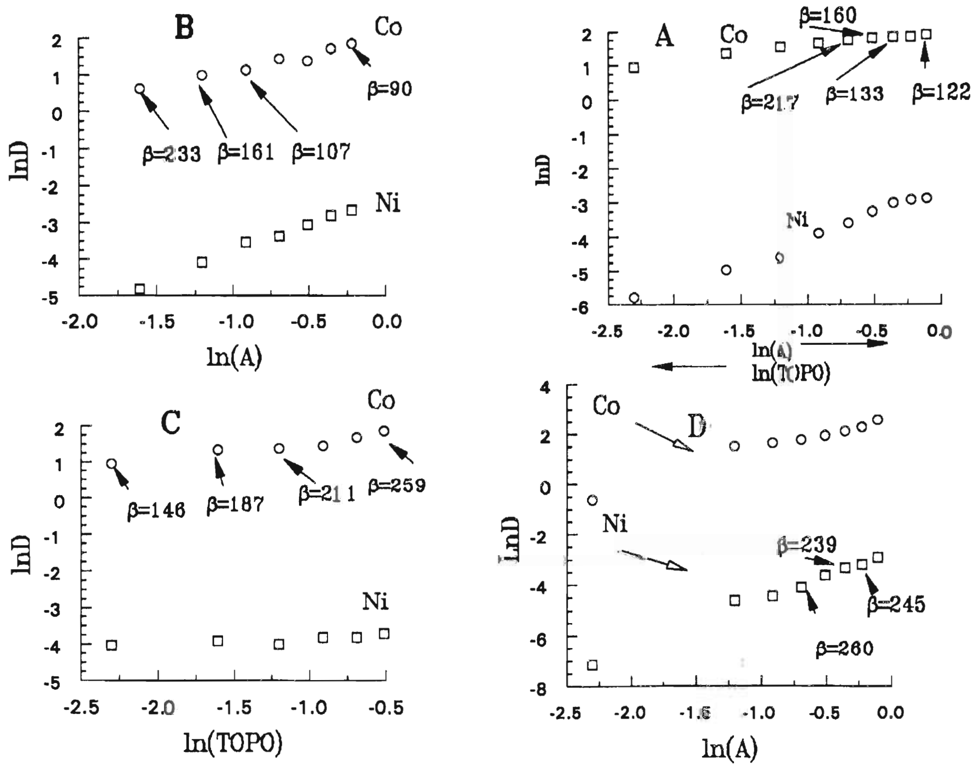

Fig. 2. Distribution coefficients of Co and Ni in Aliquat 336+TOPO system ([Co] = [Ni] = 0.1 M in the aqueous phase, t = 17 °C). Part A: [A] + [TOPO] = 1M (xylene as solvent), V(o)/V(aq) = 1; Part B: [TOPO] = 0.2 M, [A] = 0.2-0.8 M, V(o)/V(aq) = 1; Part C: [TOPO] = 0.1-0.6 M, [A] = 0.4 M, V(o)/V(aq) = 1; Part D: [A] = 0.1-0.9 M, V(o)/V(aq) = 1.

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# Hydrometallurgical extraction of gold from electronic waste

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### Abstract

At the present time pyrometallurgical, hydrometallurgical and combined technologies for processing of precious metals containing wastes are awailable. The main aim is to recover gold and silver. Experimental work was focused to the material balance and recycling of gold from computer scrap.

**Key words:** electronic waste, recycling, gold

### Hydrometalurgická extrakcia zlata z odpadu pochádzajúceho z elektrotechnického priemyslu

V súčasnosti sa v oblasti získavania drahých kovov z odpadov využívajú pyro- a hydrometalurgické technológie, prípadne ich kombinácie. V priemysle je ťažisko ich využitia v získaní Au a Ag. V našich pokusoch sme sa zamerali na materiálovú bilanciu a recykláciu Au spracovaním odpadu z výroby počítačov pri aplikácii hydrometalurgického postupu.

## Introduction

Precious metals, especially silver and gold, are widely used in the industrial branch, due to their specific properties. They are used mainly in the production of the contact parts of electronic devices.

Due to the modernizing of electronical equipment in Czech Republic the volume of electronic scrap increased. The estimation of the electronic scrap mass is inaccurate because the control of its moving is not provided.

The electronic scrap is recovered from the environmental reasons, and due to the increasing of costs for its deposition in the EU countries; the economical reason of recovery is the price of precious metals.

## Material characteristic of the electronic waste

Electronic scrap is formed by the metals, plastics and fireproof oxides. The group of metals includes the Cu, Fe, Ni, Pb, Al and Zn. Precious metals, Au, Ag and Pd, form the surface of connectors, which are parts of integrated circuits, etc. Precious metals are cladded on the iron, nickel, copper or alloy connectors and contacts. The plastic parts are from the C-H-O polymers like polyethylene, polypropylene, etc. Fireproof oxide is mainly the silica from the glass parts of the computers (monitors).

## Selected methods of recovery

There is possible to divide the different technologies of electronic scrap processing like the secondary raw source of precious metals into the several groups. The technologies include the combination of mechanical, pyrometallurgical, hydrometallurgical, electrochemical and biotechnological processes. Selected processes of electronic scrap recovery are given in the table 1.

## Experimental part

### Processed waste

The samples for experiments were obtained from the discarded computers in Kovošrot Ostrava, a. s. The samples were produced in Tesla Banská Bystrica, there were the several motherboards of different types. The construction of the parts with content of gold was

- mechanically divided parts with gold-cladded contacts from copper-cladded plastics,
- self-stated gold-cladded contacts from the brass.

### Material balance

The results of material balance, focussed to the precious metals, which was provided for the both types of motherboards

- the gold-cladded contacts make 3.2 % from the basic mass of motherboard in average, which corresponds with the literature source (Surn, 1991), the following separation for the processing is necessary;
- the average mass of one motherboard is 133.57 g, the total amount is cca 3000 pieces per year (Burkovič, personal information).

Tab. 1
Selected technologies of the electrotechnical waste
(Sum, 1991; Christianová, 1993; Hilliard and Dunning, 1985; Patent, 1985)

| Metal of interest | Process | Main part of technology | Product |
|---|---|---|---|
| Au (98.5 %) | P | Heating in $Cl_2$ at 500 °C | $AuCl_3$ |
| Au (100 %); Ni | H | Leaching in aqua regia | Au |
| Au | H | Leaching in thiourea | Au-complex |
| Cu, Ag, Au | H | Leaching in NaOH | Cu, Ag, Au |
| Ag, Au | P, E | Electrorefining of copper | Au, Ag in anode slime |
| Au (97 %) | B | Biological leaching with $Fe^{3+}$ | Au |
| Au | H | Leaching in $CuCl_2$, NaCl with HBr or HCl, precipitation | Au, solution of met. |

P - pyrometallurgical, B - biological, H - hydrometallurgical, E - electrometallurgical process

### *Processing of the contacts*

The proposed method of gold extraction from the gold-cladded brass contacts was verified by the experiments. The base of the process was the four-steps leaching in the mixture of 5 % sulphuric acid, nitric acid and hydrogen peroxide, with aeration. The contact base materials and metals from tin solder were dissolved and the solid filter cake was formed by the gold foils and powder tin. The final gold separation was done by the leaching in hydrochloric acid. The gold was melted under the flux into the compact form.

The purity of produced gold was 2N6 (given by the AAS), the main impurities were Sn (0,1 %), Cu (0.2 %), Ni (0.057 %). These impurities transfer into the gold from the base materials and from the tin solder. Ni transfers from the alloy AuNi5, which was used for cladding of contacts. This alloy has very low contact resistance and very good corrosion resistance and is used in the hard conditions (Sedláček, 1979).

## Conclusion

This paper deals with the possibilities of the gold recovery from the electrotechnical waste, mainly from the discarded computer unit.

There will be necessary the next experiments for the optimizing of the leaching conditions, like the time and temperature.

The electrotechnical waste has to be processed due to the environmental reasons, because the waste law will start into the full application. This law is similar to the EU countries; for example in Germany is duty to recover the computer scrap.

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# The influence of accompaining elements to gold and silver leaching

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### Abstract

The work was aimed to the study of influence of admixtures on the efficiency of gold and silver extraction and on the consumption of thiourea in the leaching process, as well as the influence of pH and the oxidizing agent to the yield of gold.

The results indicate that there is a need to reduce the concentration of cupric ions in the thiourea solution under the value of 0.2 $g.dm^{-3}$ in order to avoid decrease of yield of gold extraction and degradation of thiourea.

In addition, the results of the experiments showed that zinc ions have no influence on the yield of gold or silver extraction to the solution.

### Vplyv sprievodných alebo vedľajších prvkov na lúženie zlata a striebra

V tejto práci sa určila hraničná koncentrácia meďnatých iónov, do ktorej sa výťažnosť zlata zvyšovala a pri ktorej oxidoredukčné podmienky reprezentované redox potenciálom 210 mV zabezpečovali najvyššiu výťažnosť zlata. Zistili sme, že zinočnaté ióny neovplyvňujú výťažnosť zlata do roztoku. Zvyšovaním množstva meďnatých iónov v roztoku rastie spotreba tiomočoviny. Výsledky experimentov lúhovania koncentrátu ukázali negatívny vplyv meďnatých iónov na výťažnosť striebra. Na základe získaných experimentálnych výsledkov je možné navrhnúť postup pri odstraňovaní meďnatých iónov z kyslého tiomočovinového roztoku.

## Introduction

Leaching of gold and silver from ores and concentrates using acid thiourea solutions represents one of the promising methods, which could replace leaching processes using toxic cyanides. Leaching using thiourea is faster, safer and more selective.

The available literature sources prove that researchers devoted a great deal of their interest mainly to the study of dissolution processes of gold and silver in acid thiourea solutions, and/or their recovery from those solutions, respectively (cementation, adsorption on charcoal, ion exchange, electrolysis). There is only a few literature about study of influence of admixtures to the leaching efficiency of gold and silver, to the consumption of thiourea and/or oxidizing agent. However, the influence of admixtures is very important, especially to the leaching efficiency of gold. In many cases gold is being extracted from ores or concentrates containing other metals, which are soluble in acid solutions of thiourea as well. In these cases the soluble admixture metals remarkably affect the yield of gold extraction to the solution (Torma and Gundiler, 1988; Sandberg and Huiatt, 1986; Chocjanovskij, Molodcova and Ledovskich, 1973). Zinc and copper are the most frequently occurring admixed metals (especially in domestic ores and concentrates), which form complexes with thiourea and are soluble in sulphuric acid as well.

## Experimental part

The experiments in this study are divided into two parts:

I. Study of the influence of concentration of reagents and admixtures to the efficiency of recovery of gold during leaching of electrolytical purity gold in acid thiourea solutions using rotating disc method.

II. Study of the influence of concentration of reagents and admixtures to the efficiency of recovery of gold during leaching of gold-bearing concentrate in acid thiourea solutions.

Based on a literature survey and on experience from previous studies at the Department of Non-ferrous Metals, Faculty of Metallurgy of Technical University, Košice, the following parametres and elements have been recognized as essential and important for the leaching process: pH, concentration of thiourea, concentration of $Fe^{3+}$ ions, concentration of $Zn^{2+}$ and $Cu^{2+}$ ions in the solution.

The experimental conditions for leaching of concentrates from the locality of Hodruša, Slovakia, have been chosen on a basis of a literature survey and experimental results from studies using rotating disc.

## Used materials

For the rotating disc experiments the gold of electrolytical purity (PLATAURUM Ltd.) min. 99.99 % was used.

As real material we used a gold-bearing concentrate from the locality of Hodruša, Slovakia, containing:

Au 0.00645 %, Ag 0.0047 %, Cu 1.47 %, Pb 3.87 %, Zn 5.52 %, Fe 22.36 %, S 30.69 %, Si 11 %, Ca 1.15 %. The mineralogical composition was represented mainly by quartz and pyrite: 30.62 % $SiO_2$, 47 % $FeS_2$, 5 % ZnS, 5.36 % $CuFeS_2$, 5.68 % $Al_2O_3$, 4.5 % PbS, 1.61 % CaO.

Any other chemicals used in experiments were of p. a. purity.

## Results and discussion

### *Influence of copper ions on the recovery of gold*

Various concentrations of $Cu^{2+}$ ions, in range from 0.02 to 2.00 $g.dm^{-3}$, were added to the leaching solution in form of $CuSO_4 . 5H_2O$.

Approximately up to the concentration of 0.18 $g.dm^{-3}$ the added amount of cupric ions remains in the solution and the yield of gold increases from 96 to 97 %. When adding more cupric ions to the solution, namely 0.25 $g.dm^{-3}$, a white precipitate appears, the yield of gold extraction falls to 86 % and the concentration of cupric ions in the solution decreases to 0.094 $g.dm^{-3}$. Further addition of cupric ions causes further decrease of their concentration until addition of 1.25 $g.dm^{-3}$ of $Cu^{2+}$. Exceeding this concentration value the concentration of $Cu^{2+}$ ions in the solution steadily increases and reaches the value of 0.186 $g.dm^{-3}$ of $Cu^{2+}$. Further increase of concentration is reached by further addition of $Cu^{2+}$ ions. After exceeding the level of 2 $g.dm^{-3}$ of added $Cu^{2+}$ ions the concentration of $Cu^{2+}$ ions in the solution increases to 0.5 $g.dm^{-3}$ and the yield of gold extraction falls to 57 %.

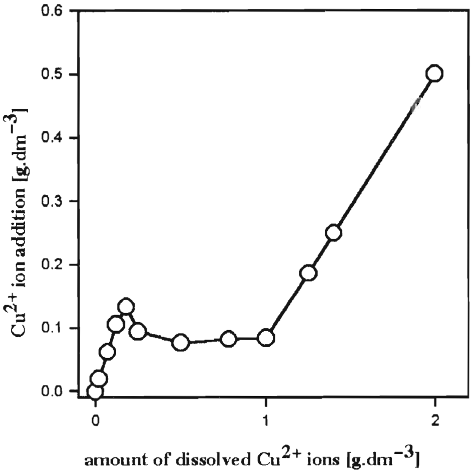

Fig. 1. Dependence of the concentration of dissolved $Cu^{2+}$ ions on the concentration of added $Cu^{2+}$ ions.

As it can be seen from the results, concentration of cupric ions during leaching of gold essentially affects the yield of gold extraction.

The yield of gold extraction moderately increases with the increasing concentration of $Cu^{2+}$ ions up to 0.18 $g.dm^{-3}$ (to 96 - 97 %). Over this concentration of cupric ions it falls down to 87 - 57 %. The $Cu^{2+}$ ions are reduced by thiourea and formamidine disulphide and $Cu^{1+}$ ions are formed (Akretche, Kerdjoudj and Gavach, 1993).

$$Cu^{2+} + 2CS(NH_2)_2 \rightarrow 2Cu^+ + (CS(NH)(NH_2))_2 + 2H^+ \quad (1)$$

The newly formed formamidine disulphide is a so called internal oxidant, which is inevitable for the leaching process and influences extraction of gold. Addition of $Cu^{2+}$ ions to the solution means an increase of concentration of formamidine disulphide and so an increase of the yield of extraction of gold. On the other hand formamidine disulphide irreversibly decomposes and causes an increase of consumption of thiourea.

During the leaching process the influence of cupric ions to the consumption of thiourea was studied, too. According to the results presented on Fig. 3 it is obvious that the consumption of thiourea increases with the increasing amount of copper added to the leaching solution.

From the results of the study of influence of ferric ions to the consumption of thiourea it follows that the concentration of thiourea in the leaching solution decreases with the increasing concentration of $Fe^{3+}$ ions. It indica-

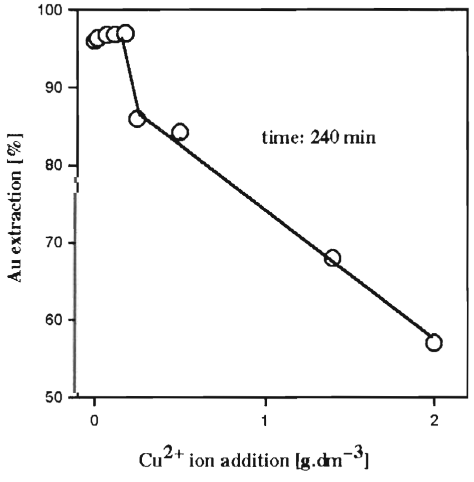

Fig. 2. Dependence of yield of gold extraction on the concentration of added $Cu^{2+}$ ions.

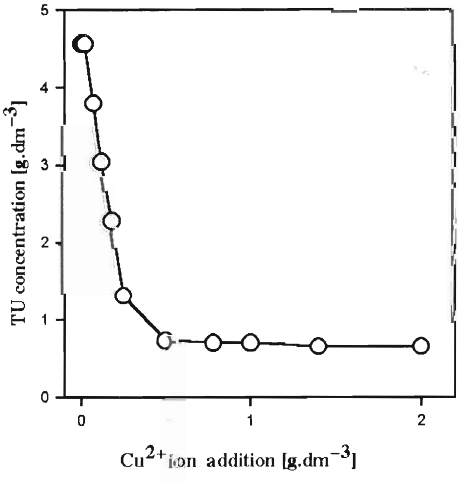

Fig. 3. Dependence of concentration of thiourea on the addition of $Cu^{2+}$ ions.

tes that the increased concentration of ferric ions causes an irreversible decomposition of thiourea.

Due to change of the oxidation number of the oxidizing agent a change in the redox potential occurs, which expresses the number of donated and received electrons.

Similarly, higher addition of cupric ions to the leaching solution causes a change in the course of the redox reactions, the power of the oxidizing agent is increased and is expressed by an increase of the redox potential, see Fig. 4.

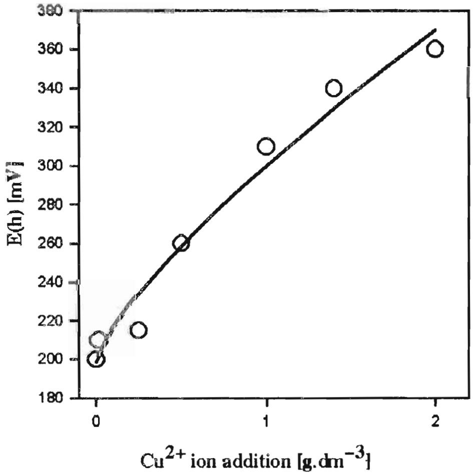

Fig. 4. Dependence of E(h) on amount of added $Cu^{2+}$ ions.

## Influence of $Zn^{2+}$ ions on the recovery of gold

Fig. 5 expresses the dependence of the yield of gold extraction on concentration of zinc ions. As follows from the dependence on Fig. 5, various additions of zinc ions have no influence on gold recovery and the concentration of $Zn^{2+}$ ions in the leaching solution simply increases by the added amount. The redox potential of the particular system had an unchanged value of 200 mV during the whole leaching process.

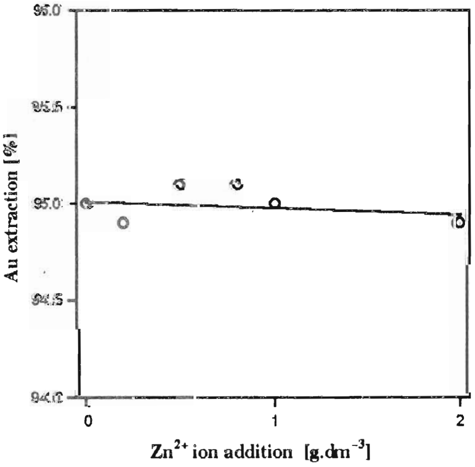

Fig. 5. Influence of zinc ions to gold recovery.

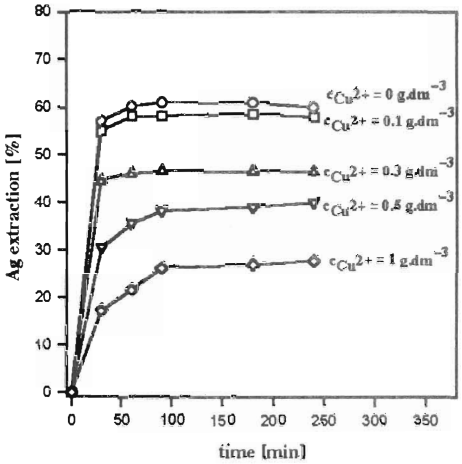

Fig. 6. Dependence of yield of silver extraction on amount of added $Cu^{2+}$ ions.

## Results of experiments from leaching of concentrate

Similarly, as in case of leaching the electrolytical purity gold at rotating disc, also in case of leaching the real concentrate, the copper $Zn^{2+}$ ions over the added concentration level of 0.2 $g.dm^{-3}$ decrease the yield of gold extraction and increase the consumption of thiourea. In case of extraction of silver, as it is shown on Fig. 6, the addition of $Cu^{2+}$ ions to the leaching solutions decreases the yield of silver extraction, while the zinc ions have no influence either to gold or to silver extraction to the solution.

## Discussion and results

According to several publications (Krzewska, Podsiadly and Pajdowski, 1983; Štofko and Štofková, 1993) the oxidizing components do not act as direct oxidants of gold or silver, but at the beginning of the process formamidine disulphide is formed from thiourea and this acts as an internal oxidant. In this stage the oxidation process of thiourea to FDS has to be stopped in order to avoid further irreversible decomposition process.

The amount of $Fe^{3+}$ ions added to the solution is therefore limited and the experiments showed that the highest yield of gold recovery (96 %) was reached at concentration of 5 g. $dm^{-3}$ of $Fe^{3+}$ ions at the stabilized redox potential value of 200 mV. With the increasing concentration of ferric ions in the solution the redox potential is increased (at concentration of 10 $g.dm^{-3}$ of $Fe^{3+}$ ions the value of redox potential settled at 290 mV). This indicates an increased oxidation capabilities of the oxidant, however, at the same time higher concentration of $Fe^{3+}$ ions causes an irreversible decomposition of thiourea. The final consequence is a decrease of the yield of gold extraction to 55 %.

After addition of cupric ions to the acid thiourea leaching solution the following chemical reactions occur: Thiourea is oxidized at the presence of cupric ions and forms formamidine disulphide:

$$2Cu^{2+} + 2TM(2) \rightarrow 2Cu^{+} + FDS + 2H^{+} \qquad (2)$$

at the same time thiourea forms a redox couple with FDS

$$2TM \rightarrow FDS + 2H^+ + 2e^- \qquad (3)$$

both thiourea and formamidine disulphide form complexes with $Cu^+$

$$Cu^+ + TM \rightarrow [Cu(TM)]^+ \qquad (4)$$

$$Cu^+ + FDS \rightarrow [Cu(FDS)]^+ \qquad (5)$$

thiourea forms a complex with $Cu^{2+}$

$$Cu^{2+} + TM \rightarrow [Cu(TM)]^{2+} \qquad (6)$$

the newly formed [Cu(FDS)] is reduced to TU

$$[Cu(FDS)]^+ + e^- \rightarrow Cu^\circ + FDS \qquad (7)$$

$$FDS + 2e^- + 2H^+ \rightarrow 2TM \qquad (8)$$

$$2TM + 2Cu^{2+} \rightarrow 2Cu^+ + FDS + 2H^+ \qquad (9)$$

$$2Cu^+ + 2FDS \rightarrow 2[Cu(FDS)]^+ \qquad (10)$$

As follows from Fig. 1 the curve of the dependence of dissolved $Cu^{2+}$ ions on the added $Cu^{2+}$ ions can be divided to three parts:

In its first part, in the range of 0.02 to 0.18 $g.dm^{-3}$, the redox potential is increased from the initial value of 200 mV to 210 mV, what indicates an increased oxidizing effect to TU, which causes an increase of FDS concentration in the solution. In this concentration interval the yield of gold extraction is increased to 97 % and at the same time the consumption of thiourea is higher than in the solution free of cupric ions.

In the second part of the curve, at addition od $Cu^{2+}$ ions in range of 0.18 to 1.0 $g.dm^{-3}$, the formation of FDS is increased (increase of redox potential to 310 mV), however, at the same time its irreversible decomposition occurs, which decreases the concentration of thiourea in the solution, what leads to the decrease of yield of gold extraction. At the same time and under the existing conditions the concentration of thiourea complex with $Cu^{1+}$ increases (the $Cu^{1+}$ ions are in the solution on latent form until the concentration of $Cu^{2+}$ reaches 0.18 $dm^{-3}$ and after reaching and exceeding this value they precipitate in form of white clot).

In the third part, at the addition of more than 1 $g.dm^{-3}$ $Cu^{2+}$ ions the concentration of $Cu^{2+}$ ions in the solution increases remarkably due to lack of thiourea required for reduction of cupric ions to cuprous ones and for formation of complexes, as documented by reactions (2) - (9).

## Conclusions

- An optimum concentration of $Fe^{3+}$ ions (5 $g.\ dm^{-3}$) there has been found, at which the redox conditions represented by redox potential of 200 mV provided the highest yield of gold extraction (96 %).

- The concentration limit of $Cu^{2+}$ ions (0.2 $g.dm^{-3}$) has been established, under which the yield of gold extraction increases and at which the optimum redox conditions represented by redox potential of 210 mV provided the highest yield of gold extraction (97 %).

- The consumption of thiourea increases with the increasing amount of cupric ions in the solutions.

- The study of influence of zinc ions to the yield of gold extraction provided a conclusion that these ions have no influence on the yield. The amount of $Zn^{2+}$ ions added to the solution lead to proportional increase of concentration of the same ions in the solution.

Zinc ions, on the contrary to cupric ones, have no oxidizing effect and neither take part in redox reactions. They participate only in complex reactions.

- The results of the pH studies of the solution showed that the pH value did not change during the leaching. This means that no pure acid or basic forms are formed in the solution and the pH equilibrium is maintained by electron exchange between redox couples.

The results obtained during experiments with electrolytically pure gold and rotating disc are fully applicable in real systems.

- The results of the experiments showed a need to reduce the concentration of copper in the leaching solution below the value of 0.2 $g.dm^{-3}$ in order to avoid decreasing of yield of gold extraction and irreversible decomposition of thiourea.

- The experiments showed that cupric ions decrease the yield of silver extraction, while zinc ions show no influence on yield of silver extraction to the solution.

The importance of the obtained experimental results on the influence of concentration of dissolved copper on the yield of gold extraction to the thiourea solution is emphasized also by Akretche and co. (Akretche, Kerdjoudj and Gavach, 1993), who studied possibilities of removal of copper from the solution by dialysis. The determination of a copper concentration limit in the solution enables to determine the moment of purification of acid solution of thiourea before its repeated utilization in the process.

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# The treatment of wastes with noble metals content

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### Abstract

The results of anode slime leaching with the main aim to extract gold and silver are presented. Less toxic (in comparison with cyanide solution) solvents were tried. The results of leaching procedures based on thiourea and thiosulphate solvent are showed. The tried procedures are compared.

It is stated that on the basis of experimental study the most perspective seems to be the procedure where thiourea as a leaching agent is used. The economical and environmental point of view has to be taken into consideration.

**Key words:** Leaching, noble metals, gold and silver, selenium, thiourea, thiosulphates, anode slime

### Spracovanie odpadov s obsahom drahých kovov

V práci sú uvedené výsledky lúhovania zlata a striebra z anódových kalov lúhovaním činidlami s nižšou toxicitou ako sú klasicky využívané kyanidy. Na základe experimentálnych výsledkov sa ako najperspektívnejší javí postup tiomočovinového lúhovania, a to tak po stránke technickej, ako aj ekonomickej a environmentálnej.

## Introduction

The extraction of noble metals from different types of wastes, or better to say, from secondary metals sources is the present-day question. It is connected with rising portion of noble metals exploited in technical practice and of course with increasing quantity of different types of wastes.

One from the possible methods of noble metals extraction - especially gold and silver extraction - is a hydrometallurgical one. It is possible to use at present already classical leaching process in cyanide solution, but there exists effort to replace it by less toxic leachants as for example thiourea or $(NH_4)_2S_2O_3$, $(NH_4)_2SO_3$ are.

The classical example of interesting waste from the point of main Cu production, is anode slime. It is typical example when it is better to call it the secondary source because slime may be source of noble metals and also the source of Se, Te, Cu, Ni, Sn, Pb, Sb in depence on primary ore composition or secondary source composition used for copper production.

There are a lot of methods for anode slime processing (Štofko and Štofková, 1991; Imriš et al., 1993; Cooper, 1990; Štofko et al., 1994).

In this work leaching of Au and Ag by means of less toxic leaching agents is shown. The mentioned leaching agents must fulfil conditions: strong complexes formation and thus creation of good conditions for noble metals transfer into solution.

The creation of stable complexes in used solvents may be in the case of gold described as follows:

$$Au + 2CS(NH_2)_2 = Au[CS(NH_2)_2]_2^{+} + e^{-}$$
$$Au + 2\ S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + e^{-}$$
$$Au + 2\ SO_3^{2-} = Au(SO_3)_2^{3-} + e^{-}$$

The system anode slime-solvent is much more complicated. Important is a function of copper ions, which acts as an oxidant in the case of Au and Ag dissolution in thiourea solutions. The increase of $Cu^{+2}$ content over the value ~ 0.18 gdm$^{-3}$, copper ions are beginning to influence the gold and silver dissolution negatively (Harvanov, 1996).

The role of copper ions in gold and silver leaching in thiosulphate solution can be described as follows (Abbruzzese, Fornari, Massidda, Veglio and Ubaldini, 1995).

$$Au + 5\ S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-} + 4\ NH_3 + Cu(S_2O_3)_3^{5-}$$

and as may be seen, it is oxidation of metallic gold to gold ion $Au^{+}$.

## Experimental procedures

In experiments the anode slime from Kovohuty a. s., Krompachy was used. Its composition is in table 1.

The leaching of anode slime with the aim to extract gold and silver is not simple. It needs very strong solvent as for example aqua regia is or preliminary preparation of slime for leaching.

The necessity of strong solvent or preliminary treatment (roasting, oxidative leaching) is possibly to explain by formation of compounds of noble metals with selenium for example or by existence of spherical particles dissolution of which is prevented by in-

Tab. 1
The composition of anode slime (in %)

| Slime | Au | Ag | Se | Cu | Ni |
|---|---|---|---|---|---|
| 1 | 0.0284 | 4.99 | 1.25 | 10.46 | 0.84 |
| 2 | 0.026 | 4.56 | 1.39 | 10.32 | 0.53 |

| Slime | As | Sb | Pb | Sn | Zn |
|---|---|---|---|---|---|
| 1 | 1.99 | 10.82 | 12.04 | 9.33 | 0.54 |
| 2 | 2.46 | 11.65 | 14.80 | 12.86 | - |

Tab. 2
The composition of slime after roasting (in %)

| Prod. | Au | Ag | Se | Cu | Ni |
|---|---|---|---|---|---|
| 3 | 0.027 | 4.68 | 0.85 | 10.44 | 0.34 |
| 5 | 0.028 | 4.77 | 1.08 | 10.94 | 0.37 |
| 13 | - | - | 0.16 | - | - |

| Prod. | As | Sb | Pb | Sn |
|---|---|---|---|---|
| 3 | 2.74 | 11.74 | 14.87 | 13.15 |
| 5 | 2.67 | 11.07 | 15.00 | 13.00 |
| 13 | - | - | - | - |

soluble shell - the problem is discussed by E. N. Petkova in her publication (Petkova, 1994).

Before the leaching of Au in thiourea solution, slime was roasted with the aim to break insoluble compounds and of course to roast off selectively selenium.

The composition of slime after roasting is in table 2.

The showed roasted products (tab. 2) were in the first step leached in $H_2SO_4$ solution at 90 °C. The experimental results are in table 3.

It can be seen in table 3 that the yield of leaching is dependent on the degree of selenium roasting off. It means that selenium forms insoluble compounds together with silver and copper or at least takes part in the forming of already mentioned insoluble shells (Petkova, 1994) which prevents the dissolution of core containing copper, or copper with silver.

The following step was leaching of residue in thiourea solution (tab. 4).

Beside the connection with thiourea content and of course secondary with copper content in sample (Štofko et al., 1994), there is evident connection with efficiency of the previous roasting.

There is another possibility of leaching steps. In the first step without previous roasting, the leaching in $HNO_3$ solution may be applied and then in the second step leaching in thiourea solution may be used. In the first step Se, Cu, and Ag with high yield (tab. 5) can be extracted. The leaching residue is then leached in thiourea solution with the aim to extract gold. The results are in table 6.

In the second part of experiments the possibility of gold and silver leaching in $(NH_4)_2S_2O_3$ and $(NH_4)_2SO_3$ resp. were tried. The results of basic leaching (sample without preparation) are in tab. 7 and 8.

The condition of leaching were chosen on the basis of C. Abbruzzes and others (Abbruzzese, Fornari, Massidda, Veglio and Ubaldini, 1995) literature data. As it can be seen, the yield of noble metals is low and because it can be pressumed that it is the result of insoluble compounds influence, the samples for the future leaching in thiosulphates were prepared by leaching in 30 % solution of $HNO_3$ (results are in tab. 5). The results of such improved leaching are in tab. 9, 10 and 11.

It is evident increase in gold and silver (mostly leached out in previous leaching in $HNO_3$) yield, but of course the optimal conditions need further experimental work.

## Conclusions

From the point of practice at the present stage of experiments it appears to be the most perspective the following procedure of slime processing:

1. *Roasting* - Se extraction (high efficiency of Se roasting off is inevitable condition for high yield of noble metals).
2. *Leaching in $H_2SO_4$ at 90 °C*
- leaching of Ag with high yield and very simple extraction by cementation
- leaching of Cu and Ni with high yield
3. *Leaching in thiourea solution*
- leaching of gold with yield more than 80 % and its winning in electrolytic process

Another tried procedure is:

1. *Leaching in 30 % $HNO_3$ at 65 °C*
- leaching of Ag with yield more than 65 % and possibility to extract it as AgCl
- leaching of Se with yield 95 %
- leaching of Cu with yield near to 100 %
2. *Leaching of rest in thiourea solution*
- leaching of gold with yield more than 80 % and its winning by electrolysis

The disadvantage of this procedure is in introducing of anot-

Tab. 3
The experimental results of leaching in $H_2SO_4$

| | | | Analysis (gdm$^{-3}$) | | | Yield (in %) | | |
|---|---|---|---|---|---|---|---|---|
| Prod. | Sample | L:S | Ag | Cu | Ni | Ag | Cu | Ni |
| 3 | S1 | 3:1 | 12.68 | 39.99 | 0.82 | 64.3 | 91.0 | 57.1 |
| 3 | S11 | 3:1 | 11.12 | 34.31 | 0.86 | 61.2 | 84.6 | 65.0 |
| 5 | S3 | 3:1 | 11.86 | 39.00 | 0.72 | 56.6 | 81.2 | 44.6 |
| 5 | S31 | 3:1 | 9.35 | 30.88 | 0.78 | 49.4 | 71.2 | 53.2 |
| 3 | S51 | 5:1 | 8.28 | 17.46 | 0.38 | 88.5 | 83.6 | 55.6 |
| 5 | S61 | 5:1 | 6.33 | 19.21 | 0.50 | 61.0 | 80.8 | 61.9 |
| 13 | S7 | 5:1 | 8.75 | 19.88 | 0.45 | 96.3 | 95.4 | 63.8 |

Conditions: 100 - 1000 g roasted product solution 300 gdm$^{-3}$ $H_2SO_4$, 90 °C, 180 min.

Tab. 4
The results of thiourea (TU) leaching

| Sample | S:L | Cont. TU ($gdm^{-3}$) | Analysis ($gdm^{-3}$) | | Yield (in %) | |
|---|---|---|---|---|---|---|
| | | | Au | Ag | Au | Ag |
| S14 | 2:1 | - | 0.0747 | 0.0144 | 50.1 | 0.06 |
| S34 | 2:1 | 8.4 | 0.0558 | 0.382 | 38.8 | 1.56 |
| S53 | 5:1 | 18.3 | 0.0246 | 3.198 | 45.6 | 14.2 |
| S63 | 5:1 | 19.8 | 0.036 | 2.24 | 64.3 | 23.5 |
| S73 | 5:1 | 12.9 | 0.057 | 0.151 | 97.7 | 1.5 |
| S74* | 5:1 | 3.8 | 0.052 | 0.112 | 85.4 | 1.1 |

Conditions: solution 30 $gdm^{-3}$ thiourea in 1 % $H_2SO_4$, 25 $gdm^{-3}$ $Fe_2(SO_4)_3.9H_2O$ (~ 5 $gdm^{-3}$ $Fe^{+3}$), 120 min., 25 °C, *20 $gdm^{-3}$ TU

Tab. 5
The leaching in $HNO_3$ solution

| | Au | Ag | Cu | Se |
|---|---|---|---|---|
| Inlet (g) | 0.0568 | 9.98 | 20.92 | 2.50 |
| Analysis ($gdm^{-3}$) | 0 | 6.20 | 19.72 | 2.275 |
| Content (g) | 0 | 6.53 | 20.75 | 2.39 |
| Yield (%) | 0 | 65.4 | 99.2 | 95.6 |

Conditions: 30 % $HNO_3$, 65 °C, 240 min., L:S = 5:1

Tab. 6
The leaching in thiourea (TU) solution

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | Yield (%) | | |
|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Au | Ag | Cu |
| 71 | 30 | 0.054 | 0.021 | 0.256 | 78.6 | 0.16 | 0.98 |
| 72 | 90 | 0.057 | 0.013 | 0.429 | 81.4 | 0.1 | 1.64 |
| 73 | 180 | 0.063 | 0.005 | 0.627 | 89.3 | 0.04 | 2.39 |

Conditions: 15 $gdm^{-3}$ TU in 1 % $H_2SO_4$, 5 $gdm^{-3}Fe^{3+}$, L:S = 4:1, inlet 50 g, 25 °C

Tab. 7
The leaching in solution 4M $Na_2S_2O_3$ + 4M $NH_3$

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Se | Au | Ag | Cu | Se |
| 121 | 30 | 0.0041 | 0.241 | 1.62 | 0.142 | 5.7 | 1.9 | 6.2 | 4.5 |
| 122 | 90 | 0.0044 | 0.171 | 1.29 | 0.204 | 6.4 | 1.4 | 4.9 | 6.5 |
| 123 | 180 | 0.0056 | 0.344 | 1.16 | 0.177 | 11.4 | 3.9 | 6.3 | 8.1 |

Conditions: L:S = 4:1, inlet 50 g, 25 °C

her leaching agent - $HNO_3$ - into the process and problems with processing of such solutions.

Finally was tried the procedure as follows:

1. *Leaching in 30 % $HNO_3$ at 65 °C*

- results are mentioned above

2. *Leaching in thiosulphate solutions.* The results are not yet enough high for practical treatment of anode slimes. After the leaching electrowinning or activated carbon adsorption can be applied.

The direct leaching of slime in thiosulphate solutions does not seem to be perspective because of low yields. Thiosulphate solutions have relatively low stability and they are pretentious in further treatment. It is necessary to optimalize individual conditions.

Tab. 8
The leaching in solution 1.5M $Na_2SO_3$ + 4 $NH_3$

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Se | Au | Ag | Cu | Se |
| 131 | 30 | 0.0137 | 0.86 | 14.6 | 0.035 | 19.3 | 6.9 | 55.8 | 1.1 |
| 132 | 90 | 0.0156 | 1.04 | 13.5 | 0.033 | 22.1 | 8.4 | 51.6 | 1.1 |
| 133 | 180 | 0.0144 | 1.05 | 13.4 | 0.033 | 30.0 | 12.4 | 75.3 | 1.6 |

Conditions: L:S = 4:1, inlet 50 g, 25 °C

Tab. 9
The leaching in solution 2M $Na_2S_2O_3$ + 4M $NH_3$

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Se | Au | Ag | Cu | Se |
| 81 | 30 | 0.0178 | 2.72 | 0.88 | 0.048 | 25.7 | 21.8 | 3.4 | 1.5 |
| 82 | 90 | 0.0150 | 2.24 | 0.95 | 0.045 | 21.4 | 18.0 | 3.6 | 1.4 |
| 83 | 180 | 0.0110 | 2.05 | 0.88 | 0.031 | 18.6 | 19.4 | 4.0 | 1.2 |

Conditions: L:S = 4:1, inlet 50 g, 25 °C

Tab. 10
The leaching in solution 1M $Na_2S_2O_3$ + 4M $NH_3$

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Se | Au | Ag | Cu | Se |
| 91 | 30 | 0.0297 | 3.50 | 0.122 | 0.079 | 42.1 | 28.1 | 0.46 | 2.5 |
| 92 | 90 | 0.0329 | 3.47 | 0.129 | 0.072 | 47.1 | 27.9 | 0.50 | 2.3 |
| 93 | 180 | 0.0239 | 2.51 | 0.123 | 0.046 | 40.0 | 23.7 | 0.55 | 1.7 |

Conditions: L:S = 4:1, inlet 50 g, 25 °C

Tab. 11
The leaching in solution 1.5M $Na_2SO_3$ + 4M $NH_3$

| Sample | Time (min.) | Analysis ($gdm^{-3}$) | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Au | Ag | Cu | Se | Au | Ag | Cu | Se |
| 101 | 30 | 0.043 | 2.07 | 0.97 | 0.119 | 62.8 | 17.0 | 3.8 | 3.8 |
| 102 | 90 | 0.0327 | 1.81 | 0.91 | 0.099 | 47.4 | 14.9 | 3.6 | 3.2 |
| 103 | 180 | 0.0367 | 2.98 | 0.79 | 0.138 | 71.5 | 32.7 | 4.1 | 5.9 |

Conditions: L:S = 4:1, inlet 50 g, 25 °C

Before we choose any from above showed procedures it is necessary to compare them from economical point of view and also from environmental point of view.

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# Analysis of cadmium and lead in natural water using supported liquid membrane technique and atomic absorption spectrometry

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## Abstract

Determination of heavy metals in drinking water or in natural reservoirs is very important due to their toxicity and bioaccumulation processes in tissue of human beings, animals or plants. Concentration of these pollutants is usually very low and they need sample preconcentration and clean-up before determination.

Supported liquid membrane technique was used for clean-up and enrichment of lead and cadmium from water samples.

**Key words:** supported liquid membrane, heavy metals, cadmium, lead, natural water analysis

### Stanovenie kadmia a olova v prírodnej vode za použitia techniky nanesených kvapalných membrán a atómovej absorpčnej spektrometrie

Stanovenie ťažkých kovov v pitnej vode, alebo v prírodných rezervoároch je veľmi dôležité vzhľadom na ich toxicitu a kumuláciu v ľudských, živočíšnych a rastlinných tkanivách. Koncentrácia týchto polutantov je bežne veľmi nízka a vyžadujú nakoncentrovanie a prečisťovanie vzoriek pred ich stanovením. Na obohatenie a prečistenie olova a kadmia zo vzoriek vody bola použitá metóda nanesených kvapalných membrán.

In this method immiscible organic liquid with dissolved carrier were immobilized in teflon microporous filter which separates the donor and the acceptor solution. Sample stream in adequate pH passes hydrophobic liquid membrane and analyzed ion of metal creates with carrier the complex soluble in the membrane liquid. After passing the membrane the complex is broken on the acceptor side and enrichment process is obtained.

Concentration of metals in acceptor solution was measured by means of flame atomic absorption spectrometry (FAAS). Home made the slotted tube atoms trap system was applied to increase the limit of detection. The system was activated by nebulizing of lanthanum chloride solution and absorbance of metals was measured.

The use of supported liquid membrane method for sample preparation permits to analyze heavy metals by FAAS instead of much more expensive and time consuming graphite furnace atomic absorption spectrometry (GFAAS). We were able to analyze very low concentration of heavy metals in river water: 0.3 ppb and 0.05 ppb of lead and cadmium respectively.

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# Hydrometallurgical method of the processing of the slurries from zinc salts production

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### Abstract

In the paper there are demonstrated the results of leaching of residual slurries from the production of zinc salts. In the present state, when the average granularity is 10-15 μm and average content of observed metals is very high, to 37 % Zn, to 12 % Fe, to 6.5 % Pb and to 1.4 % Cu, they cannot be stored on the deposits of the 1st or 2nd class. For these causes it is necessary to process them to the state which enables they economical utilization and at the same time the residual slurries could be stored on the mentioned deposits.

### Hydrometalurgické spracovanie kalov z výroby síranu zinočnatého

V príspevku sú demonštrované výsledky lúhovania zvyškových kalov z výroby zinočnatých solí. V súčasnom stave, keď stredná zrnitosť dosahuje 10 - 15 μm a priemerný obsah sledovaných kovov je veľmi vysoký (do 37 % Zn, do 12 % Fe, do 6,5 % Pb a do 1,4 % Cu) nemôžu sa uskladňovať na skládkach 1. a 2. triedy. Z týchto príčin je potrebné upraviť ich do stavu, ktorý umožňuje ich hospodárske využitie a zároveň zvyškové kaly umožňuje uskladňovať na spomínaných skládkach.

## Introduction

The residual slurries from the hydrometalurgical technologies result in serious problems. The hydrometallurgical slurries in general consist of the matters which cause their problematic storing.

From the point of the present legislation in the sphere of the waste, the slurries of such kind are classified as the special type of waste. There are two ways of the solution for their producers :

- The complete use of the problem causing components forming the waste and in such a manner their content is reduced and the waste can be stored on the common deposits of the 1st or 2nd class.
- The waste has to be stored in its original form on the specially selected deposits.

The project devoted to the processing of the slurries from zinc salts production arised as the result of the above mentioned problems. The results of the flotation processing did not provide the acceptable reduction of the metals content, therefore it was necessary to deal with the possibility of the slurries processing by the leaching.

The variety of factors influence the leaching process, among mentioned should be at least the following ones: grain size, porosity, substance composition and concentration of the solid phase particles, concentration of the leaching agent, hydrodynamic conditions, temperature, pressure and leaching period and so on (Pawlek, 1983).

## Slurry grain size distribution and chemical composition

It was stated, in the course of the rough grain size distribution estimation, that this material consists of highly fine grains. Therefore the grain size distribution estimation was carried out by the photosedimentograph of Japanese firm Sheishin. The drinking water was used as the dispersion environment. The material density was estimated prior the grain size distribution estimation. The density value is $\rho = 2,87\ g.cm^{-3}$ (± $0,04\ g.cm^{-3}$). The samples grain size distribution is represented by the summary curves of the grain size distribution shown in Fig. 1.

The further characteristics expressing the material grain size distribution are as follows:

| Sample | 1 | 2 |
|---|---|---|
| Mean grain size [μm] | 13.12 | 12.09 |
| Median diameter [μm] | 11.66 | 9.51 |
| RSD [μm] | 10.01 | 9.72 |
| Nominal surface [$cm^2.g^{-1}$] | 3030 | 3114 |

Under the nominal surface parameter should be understood the calculated nominal surface of the ball with the equivalent diameter not taking into the account the shape coefficient.

From the above stated results, that this material consists of very fine grains therefore the name "slurry" corresponds to this state.

From the other factors of importance, influencing the leaching process, are those which are in a certain manner

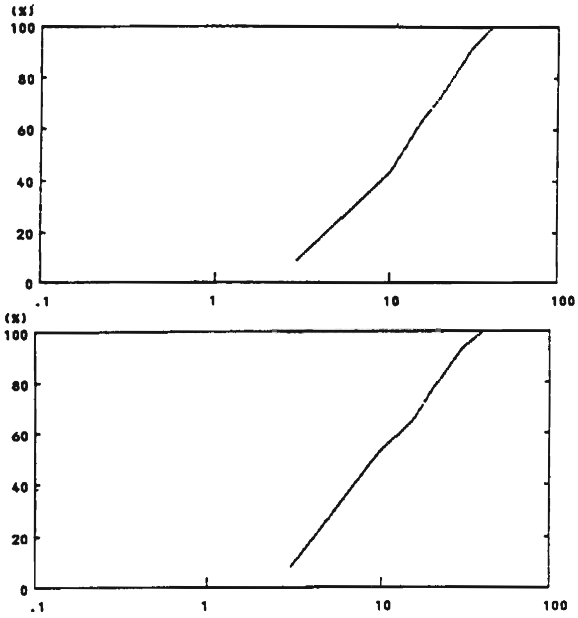

Fig. 1. The grain size distribution of the slurry samples, (the grain size is expressed in μm).

related to the energy state of the phase interface. Therefore the selected electrochemical phenomena should be taken into the consideration when executing the experimental estimation of the process conditions.

### Electrochemical specification of the slurries

The energy state of the particles influences up to the essential degree their behavior in technological processes. The slurries mineralogical composition was not estimated. It is assumed, that the slurry is composed of the compounds of which it was produced. Variety of wastes was used for the production of the zinc salts, as the zinc residue, waste dust, channel paint (slag from paint production factory Košeca) and so on.

The alternations in the slurries composition confirm the results of the Zeta potential measurements. Zeta potential shows the particle surface charge size and its character, with the regard to the surrounding environment. The results of Zeta potential measurements, shown in Figs. 2 and 3, were estimated with the instrument of fy Brockhaven Instruments Corporation (USA).

Zeta potential is shown in the individual figures for the following conditions.

pH = 6 represents the natural environment, which originated the slurry mixing in the distilled water. Zeta potential reaches the value -1,70 mV for majority of the grains.

In Fig. 3 is shown the course of Zeta potential for pH = 4 after sulphuric acid addition ($H_2SO_4$).

The interpretation of the demonstrated results leads to the following statement:

- The value of Zeta potential is very low, it oscillates around 0 and it points on the isoelectric point.
- The value of Zeta potential indicates that the particles surface is passivated and therefore it is necessary to apply the mechanical or chemical surface activation.

### Sample chemical composition

The sample of the slurry in dry state, we had at our disposal, was of the following composition: 21 Zn %, 9,5 Fe %, 4,8 - 5,2 Pb %, 0,95- 1,0 Cu %.

Remaining elements and compounds like Co, Ni, Sb, Cl, $SiO_3^{-2}$, $SO_4^{-2}$, $SO_4^{-2}$, and so on, were not taken into the consideration.

The slurry composition subject to the producer evidence is highly alternative and varies in the wide diapason: 12,1 - 37,0 Zn %, 0,18 - 12,0 Fe %, 0,5 - 6,5 Pb %, 0,01 - 1,35 Cu %, 18,0 - 51,0 $H_2O$ %.

### Acidic and base leaching of the slurries

The hydrometallurgical procedure was selected for the slurries processing among the other possible pyro- and hydrometallurgical processes. The pyrometallurgical met-

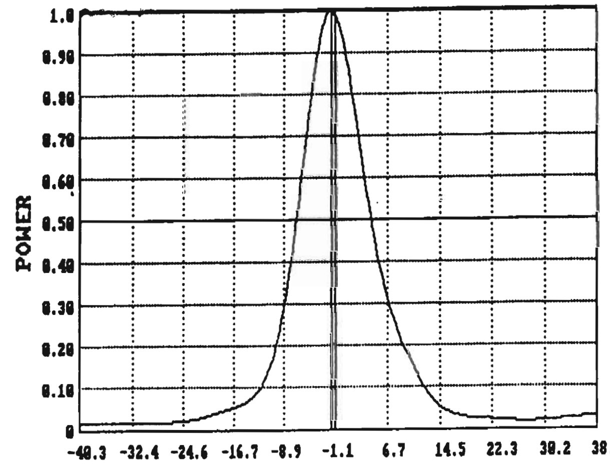

Fig. 2. Zeta potential of the slurry for natural pH = 6.

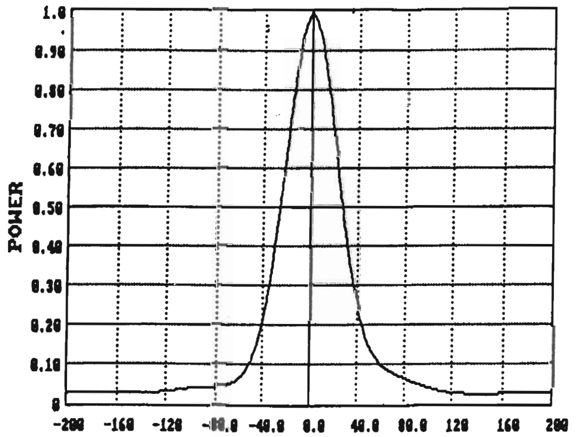

Fig.3. Zeta potential of the slurry for pH = 4, sulphuric acid addition.

hods were omitted while the pure pyrometallurgical process does not represent the suitable solution and the hydrometallurgical process seems to be more convenient. With the regard to the preceding technology, which resulted in the slurry as the by-product, the leaching in the acidic environment is the most suitable procedure. This selection enables to avoid the complications in the operation connected with the circulation of two or more kinds of solutions. The ammonium mode of leaching was verified with the aim of the approach complexity.

For the hydrometallurgical processing of Zn wastes, there was selected the leaching under normal pressure and under the temperature up to 50 °C (Výskumné správy). As the constant parameters for leaching, selected were the following ones: amount of dry substance (25, 50, 100 g - subject to the vessel size), rotations of the mixer and the slurry grain size distribution.

Variable parameters were as follows:

- temperature 25, 50 °C, slow heating
- the leaching agent concentration 50, 40, 30, 20, 10, 5 %
- the leaching time.

The results of the verifying series of the leaching agent are given in the Tab. 1.

The leaching was realized under the conditions which are given in the table. When the needed amount of the leaching agent was stated, principal was the complete (100 %) - stoichiometric addition of the leaching agent, calculated on the basis of the metal content in the residual slurry.

. It is obvious from the table that the leaching temperature does not influence essentially the metal content in the leach. It is in spite of the fact that the sulphuric acid concentration influences up to the essential degree the content of Pb and partially even that of Zn in solid residue.

Tab. 1
The results of the slurry leaching by the sulphuric acid and by the ammonium hydroxide

| No. | Leaching agent concentration (in %) | Metal concentration | | Solid residue (in %)<br>Extract ($g.dm^{-3}$) | | Leaching temperature (in °C) |
|---|---|---|---|---|---|---|
| | | Zn | Cu | Fe | Pb | |
| | | Leaching in sulphuric acid | | | | |
| 1 | 20 | 4.20<br>7.65 | 0.30<br>0.40 | 3.16<br>3.25 | 13.92<br>0.002 | 25 |
| 2 | 40 | 3.50<br>8.80 | 0.20<br>0.40 | 2.60<br>4.50 | 7.78<br>0.002 | 25 |
| 3 | 20 | 4.00<br>7.85 | 0.20<br>0.40 | 2.80<br>4.00 | 12.56<br>0.0025 | 50 |
| 4 | 40 | 3.00<br>8.15 | 0.28<br>0.44 | 2.82<br>4.10 | 7.68<br>0.003 | 50 |
| | | Leaching in ammonium hydroxide | | | | |
| 5 | 12 | 10.40<br>6.40 | 1.04<br>0.30 | 17.26<br>- | 8.26<br>0.005 | 25 |
| 6 | 11 | 5.80<br>6.85 | 0.58<br>0.30 | 18.88<br>- | 8.76<br>0.005 | 25 |
| | Sample | 21.00 | 1.00 | 10.00 | 5.20 | |

The amount of the slurry: 25 g of the dry substance, the leaching time: 30 min.

Tab. 2
The leaching results as related to the leaching time and to the sulphuric acid concentration

| No. | Leaching agent concentration (in %) | Metal concentration | | Solid residue (in %)<br>Extract ($g.dm^{-3}$) | | Weight of the residue (g) |
|---|---|---|---|---|---|---|
| | | Zn | Cu | Fe | Pb | |
| | | t = 30 min. | | | | |
| 1 | 10 | 4.8<br>8.9 | 0.70<br>0.373 | 7.34<br>3.727 | 15.48<br>0.009 | 16.40 |
| | * | 9.781 | 0.481 | 4.857 | 2.392 | |
| | | t = 45 min. | | | | |
| 2 | 10 | 4.40<br>8.9 | 0.74<br>0.379 | 6.36<br>3.854 | 15.28<br>0.01 | 15.68 |
| | * | 9.59 | 0.487 | 4.788 | 2.253 | |
| | | t = 60 min. | | | | |
| 3 | 10 | 4.4<br>20.5 | 0.60<br>0.844 | 3.66<br>8.6 | 16.78<br>$7.31.10^{-3}$ | 14.10 |
| | * | 10.87 | 0.507 | 4.82 | 2.373 | |
| 4 | 20 | 3.5<br>19.4 | 0.46<br>0.896 | 3.32<br>8.3 | 16.84<br>$5.08.10^{-3}$ | 14.12 |
| | * | 10.19 | 0.513 | 4.62 | 2.385 | |
| | | t = 120 min. | | | | |
| 5 | 10 | 3.4<br>18.5 | 0.50<br>0.853 | 3.46<br>8.4 | 15.06<br>$6.79.10^{-3}$ | 14.14 |
| | * | 9.731 | 0.497 | 4.689 | 2.136 | |
| 6 | 20 | 3.6<br>19.1 | 0.34<br>0.91 | 3.28<br>8.3 | 16.56<br>$5.34.10^{-3}$ | 14.11 |
| | * | 10.06 | 0.503 | 4.613 | 2.342 | |
| | | t = 180 min. | | | | |
| 7 | 10 | 3.7<br>18.5 | 0.54<br>0.833 | 3.64<br>8.0 | 16.56<br>$7,16.10^{-3}$ | 14.24 |
| | * | 9.78 | 0.493 | 4.518 | 2.365 | |
| 8 | 20 | 3.4<br>19.5 | 0.62<br>0.916 | 3.08<br>8.6 | 15.94<br>$5.08.10^{-3}$ | 14.38 |
| Balance of the realized experiments: | | | | | | |
| | *<br>** | 10.24<br>10.5 | 0.547<br>0.475 | 4.743<br>4.750 | 2.297<br>2.40 | |

* calculated weight of the metal subject to the balance of the insoluble residue and solution
** amount of the metal in the sample calculated from the analysis results

The leaching with the ammonium hydroxide was carried out and in the test No. 6 there was used the mixture of the ammonium hydroxide and ammonium sulphate. The results given in the Tab. 1 confirm that from the point of Pb the leaching by ammonium hydroxide does not represent any progress in comparison with the sulphuric acid. When stating this, other possible advantages of the ammonium leaching are not taken into the consideration. The most significant is the fact that it is not necessary to explore two leaching agents in one technological unit.

It is obvious from the provided verifying measurments that the leaching with the sulphuric acid is more convenient. For these reasons it is necessary to examine the kinetics of the leaching.

## Leaching kinetics

The leaching in the acidic environment provides the certain possibility to gain the success. Therefore it was necessary to estimate the leaching rate. The experiments were carried out in the laboratory with the dry substance from 50 g sample weight. The sulphuric acid concentration was 5, 10 and 20 % with the leaching time of 30, 45, 60, 120, 180 min. The leaching results are presented in Tab. 2.

The relative deviation of the measurement ranges in the interval 2.5 - 7.3 % and this value complies with the given type of the experiments. The leaching temperature was alternating and no thermostat was used. The temperature ranged from 40 °C at the start after the suspension mixing - which is the result of the exothermic process, up to 25 - 27 °C at the end of the experiment.

When filtering the suspension, for the certain ratios s:l when leaching with 5 and 10 % sulphuric acid, the problems arised from rather large amount of the precipitate of the iron hydroxide. It was necessary to transfer to the leaching with the sulphuric acid of the higher concentration, i. e. to reduce the solution pH, or to increase the ratio s:l in favor of the liquid phase.

## Conclusion

It is possible to conclude from the results of the realized experiments that the acidic leaching leads partially to the goal, i. e. it leads to the metals content reduction in the residual slurry. However the problem is not solved completely while the leaching does not solve the problem of Pb content in slurry. Iron behaves in the similar manner. To reduce to Pb and Fe content the multistage leaching would be required, or explored should be for the leaching of the sulphuric acid of the higher concentration.

As the convenient leaching seems to be introducing the further stage of the leaching only, which complicates the entire technological system. Under the conditions of the normal operation, the activity of the solution diminishes as the result of the permanent circulation and the amount of the accompanying elements is increasing. This fact is highly demanding in pure products production. It is one of the problems of the multistage leaching. Another problem results from the substance of the technological processes. This problem can be formulated in such a manner, that in the given stage of the technological system, the final waste is not processable by the given method, in our case the residual slurry. As the physical methods showed to be ineffective, its further exploitation is possible when applying other, more suitable technologies, as the pyrometallurgical, hydrometallurgical or their combination. In any case such a solution leads to the complex technology and to the costs increase and the efficiency (with the given amount of the slurry) obviously reduces. Therefore it is problematic to recommend above solution of this problem.

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# Oxidation of solutions with content of Sb, Hg and As

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## Abstract

Knowledge about the pressure oxidation experimental study of the components present in the solution, resulting from the tetrahedrite concentrate basic leaching, are presented in this paper. Antimony, mercury and arsenic were selectively separated in the form of thio-compounds by leaching of the concentrate in natrium sulphide solution. This solution was oxidized during 150 minutes at 154 °C and the initial pressure of oxygen 1.6 MPa, which resulted in the forming of the crystalline sodium hexahydroxoantimonate (V) $Na[Sb(OH)_6]$. It has been proved that due to the increased partial pressure of oxygen, the sulphur changes its valency up to (VI) and $Na_2S_6O_{19}$ crystallizes. Owing to the excessive concentration through evaporation (over 20 % of water), $Sb_2O_5$ forms at the end of the pressure oxidation. Figs. 1-4 show the changes in the quality of the crystalline product obtained at individual experimental conditions.

**Key words:** leaching, oxidation, pressure oxidation, solution, solution of antimony

### Oxidácia roztokov s obsahom Sb, Hg a As

V práci sú uvedené získané poznatky z experimentálneho štúdia tlakovej oxidácie zložiek roztoku pochádzajúceho zo zásaditého lúhovania tetraedritového koncentrátu. Lúhovanie koncentrátu prebiehalo v roztoku sulfidu sodného, čím sa selektívne oddelil antimón, ortuť a arzén do roztoku vo forme tiozlúčenín. Tento roztok sa počas 2,5 hodín oxidoval pri teplote 154 °C a počiatočnom tlaku kyslíka 1,6 MPa za účelom získania kryštalického hexahydroxoantimoničnanu sodného $Na[Sb(OH)_6]$. Výsledky oxidácie dokazujú, že pri zvýšených parciálnych tlakoch kyslíka dochádza k preoxidovaniu síry až do šesťmocnej formy, pričom sa z roztoku vylučujú kryštály $Na_2S_6O_{19}$. Pri nadmernom odparení vody z roztoku (nad 20 %) dochádza na konci tlakovej oxidácie k tvorbe oxidu $Sb_2O_5$. Zmeny v kvalite získaného kryštalického produktu sú pre jednotlivé experimentálne podmienky znázornené na obr. 1 až 4.

A mutual separation of antimony from copper is a serious problem of a complex processing of tetrahedrite raw materials. By many years of research in the area of pyrometallurgical selection of the stated elements, a conclusion that separation is not possible by a simple metallurgical process, was drawn. Due to a composition attractiveness of tetrahedrite concentrates, which sometimes contain up to 5500 g/t Ag, 10 g/t Au and 22 to 28 weight % Cu, hydrometallurgical processes of their complex processing are being developed. Using alkaline respectively chemical leaching in the sodium sulphide ($Na_2S$) solution in the first step seems to be a real possibility. Results of the works (Baláž et al., 1995; Javorka and Fröhlich, 1996; Baláž et al., 1994) prove it.

By leaching of tetrahedrite concentrate in $Na_2S$, the selective separation of antimony, mercury and arsenic from other parts of the concentrate is completed. An ability of some sulphides to dissolve themself in the solutions of alkaline sulphides and to create thiosalts is taking advantage in the process. Due to antimony content in the original raw material, 5 to 18 weight %, the creating solutions contain mostly antimony. Their composition is on the basis of sodium thioantimonate (V) ($Na_3SbS_4$) and residual sodium sulphate ($Na_2S$) and sodium hydroxide (NaOH).

It is possible to process these solutions by different ways. By an electrolytic way gaining metallic antimony or by oxidation processes gaining crystalline sodium hexahydroxoantimonate ($Na[Sb(OH)_6]$). Both processes require previous rafination of the solution from mercury. The rafination is usually carried out by cementation by the means of metallic iron or antimony what lowers mercury content in the solution to cca 0.1 g/t. Arsenic remains in the solution together with sodium thioantimonate as thioarsenite or thioarsenate. Arsenic is excluded from the process in dumping from in the final phase of processing.

By oxidation of the stated solution, the oxidation of sulphur from $S^{2-}$ to $S^{2+}$ and $As^{3+}$ to $As^{5+}$ will be reached. Sulphur present in the solution in the form of dissoluble sulphides and polysulphides will change by oxidation to thiosulphate according to the reactions 1 to 6:

$$Na_3SbS_4 + 2NaOH + 4O_2 + 2H_2O = Na[Sb(OH)_6] + 2\,Na_2S_2O_3 \quad (1)$$

$$2\,Na_2S + 2\,O_2 + H_2O = Na_2S_2O_3 + 2\,NaOH \quad (2)$$

$$Na_2S_2 + 1{,}5\,O_2 = Na_2S_2O_3 \quad (3)$$

$$2\,Na_2S_3 + 4\,O_2 + 2\,NaOH = 3\,Na_2S_2O_3 + H_2O \quad (4)$$

$$Na_2S_4 + 2{,}5\,O_2 + 2\,NaOH = 2\,Na_2S_2O_3 + H_2O \quad (5)$$

$$2\,Na_2S_5 + 6\,O_2 + 6\,NaOH = 5\,Na_2S_2O_3 + 3\,H_2O \quad (6)$$

Antimony begins to precipitate from the solution in the form of crystalline sodium hexahydroxoantimonate already in the course of oxidation. The precipitation takes place due to a low solubility of antimony in the solution. The value of solubility product is $4.10^{-8}$. After finishing the oxidation it is possible to achieve its final crystallization by a partial thickening of the solution. By using this method it is possible to lower content of antimony in the oxidized solution from the values of tens g/l to the values of $10^{-3}$ g/l and gain saleable antimony product.

Aging of water solution $Na_2S$ leads to polysulphide formation by oxidation of hydrolytically formed ions $HS^-$. Sodium sulphide hydrolytically splits in water, in 1N solution up to 90 %, what considerably increases a possibility of polysulphide formation. The splitting takes place according to the reaction (7):

$$Na_2S + HOH = NaOH + NaHS \qquad (7)$$

Leaving the solution in the air with high concentration of $HS^-$ ions causes gradual polysulphide formation, for example:

$$2\ NaHS + 0{,}5\ O_2 = H_2O + Na_2S_2 \qquad (8)$$

The more concentrated $Na_2S$ solutions are, the more they incline to gradual oxidation and formation of polysulphides.

Oxidation of polysulphides and sodium sulphide takes place according to the reaction schemes (2) and (6) with high negative value of Gibbson energy (Tab. 1), therefore their complete oxidation can be expected.

Tab. 1
ΔG reactions (2) to (6) at the temperature of 20 and 140 °C

| Reaction | $\Delta G^{20}$ | $\Delta G^{140}$ |
|---|---|---|
| | kJ | kJ |
| (2) | -773.14 | -772.34 |
| (3) | -603.14 | -569.86 |
| (4) | -1639.88 | -1558.85 |
| (5) | -1038.24 | -990.55 |
| (6) | -2515.37 | -2405.64 |

In this work there are stated the notions from experimental study of oxidation of real solution coming from leaching of tetrahedrite concentrate. The oxidation was done in the rotatory autoclave.

Tab. 2
Oxidation condition

| Conditions of experiment | Experiment number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Amount of solution (ml) | 500 | 1000 | 500 | 500 |
| Initial pressure of oxygen (MPa) | 1,6 | 1,6 | 1,6 | 1,6 |
| Temperature of oxidation °C | 154 | 154 | 154 | 154 |
| Period of oxidation (hour) | 2,5 | 2,5 | 2,5 | 2,5 |

## Experimental study

A solution with antimony content of 7.8 g/l, 179 g/l $Na_2S$, 20.4 g/l $Na_2S_2O_3$, under 0.02 g/l As and 0.024 g/l Hg was used for the oxidation. The solution underwent cementation of mercury by iron powder.

Oxidation conditions in each experiment are shown in Tab. 2.

### *Process of the experiments*

### Experiment No. 1

After filling the autoclave with the solution and its space rinsing with pure oxygen and subsequent pressurizing of oxygen to a pressure of 1.6 MPa, heating was turned on. A decrease of total pressure was observed in the autoclave already during heating as a result of oxygen consumption for oxide reactions. After remaining at the temperature for 2.5 hours, the total pressure became stable at the value of 1.3 MPa. The autoclave was then cooled down by gradual cooling. The cooling took place under pressure of non-consumed oxygen whose value at the temperature of 20 °C was 0.78 MPa. Condensated water gathered between the wall of autoclave and liner in which oxidation of the solution took place. The condensate corresponded with the evaporation and thus with the concentration of the liquor solution. Products of the reaction were separated and after drying of precipitated crystal were subsequently quantificated.

### Experiment No. 2

The process of the experiment was the same as in the former experiment. Only amount of the initial solution was doubled and the system of cooling, respectively turning the autoclave off was changed. Due to the used amount of the solution it was necessary to refill consumed amount of oxygen after 30 minutes of oxidation process. The total pressure decreased to the value of 0.8 MPa and was supplemented to the total pressure in the autoclave of 1.7 MPa. It was necessary to repeat this process after 70 minutes. The total pressure decreased to the value of 1.0 MPa and was supplemented to the value of 1.8 MPa. In the course of the further oxidation it was settled at the value of 1.2 MPa. The pressure later remained unchanged. Cooling of the autoclave was carried out by loosening the pressure valve after expiration of the determined period of solution oxidation. Accumulated, respectively remnant gases were led to the atmosphere through a condensation system. The seized condensates from the interspace of the liner and the autoclave and from the condenser of condensation system equaled to the vapored water from the solution.

### Experiment No. 3

The stated experiment was similar to the experiment No. 1. The only difference was that after reaching 95 °C accumulated gaseous products, created during the healing, were led out to the atmosphere. Already after then the autoclave was pressured to the initial pressure of 1.6 MPa. The total pressure was stabilized at the value of 1.2 MPa in the course of the oxidation. Cooling of the autoclave was the same as in the former experiment.

### Experiment No. 4

Oxidation conditions were completely the same as in the former experiment. The only change was in the speed of cooling what caused a different degree of water evaporing from liquor at the end of the process.

### *Discussion of obtained results*

Needed amounts of oxygen for carrying out the main oxidation process (the reaction (1)) were calculated from each experiment. The difference between the real oxygen consumption and the calculated one showed oxygen consumption for the process of the additional oxidation reactions of the excess sodium sulphide and the present polysulphide. The values are shown in Tab. 3.

Tab. 3
Oxygen consumption

| Exper. No. | for the oxidation of $Na_3SbS_4$ | real consumption | for the oxidation of $Na_2S$ and $Na_2S_x$ | |
|---|---|---|---|---|
| | g | g | g | % |
| 1 | 4.095 | 107.8 | 103.705 | 96.2 |
| 2 | 8.19 | 101 01 | 92.82 | 91.9 |
| 3 | 4.095 | 112.76 | 108.67 | 94.6 |
| 4 | 4.095 | 112.76 | 108.67 | 94.6 |

As it follows from the Tab. 3, 91 up to 96 % of the oxygen is consumed in the process of the additional reactions. If the whole oxygen needed for the additional oxidation reactions was allowed to oxide only $Na_2S$, there had to be about 255 g/l of it in the initial solution. This situation did not reflect the reality. Therefore a reason for the increased oxygen consumption was searched for. A composition of the crystalline phase was studied in detail. The study showed that created crystalline phase in all experiments contained another component belonging to the $Na_2S_6O_{19}$ phase. Fig. 1 up to Fig. 4 depict the situation.

Non-requested phase is most likely formed by $Na_2S$ oxidation according to the reaction:

$$6\,Na_2S + 12\,O_2 + 5\,H_2O = Na_2S_6O_{19} + 10\,NaOH \qquad (9)$$

According to the reached oxygen consumption and to the chemical analysis of the initial solution up to 40 % of oxygen is used for the reaction process (9). The stated amount equals to 14 % of $Na_2S$ oxidation to $Na_2S_6O_{19}$ which is partially secreted from the solution to the crystalline phase. The oxidation was most likely caused by the high partial pressure of oxygen in the autoclave as well as by the temperature of oxidation process. From the

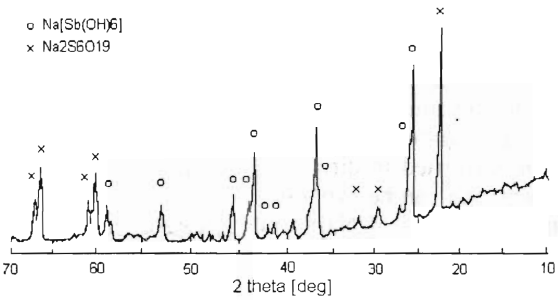

Fig. 1. X-ray diffractogram of experiment No. 1.

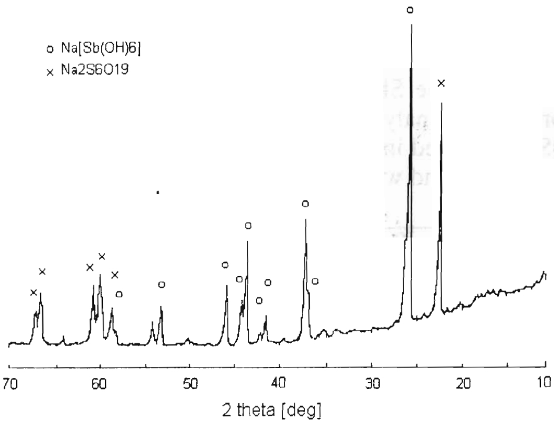

Fig. 2. X-ray diffractogram of experiment No. 2.

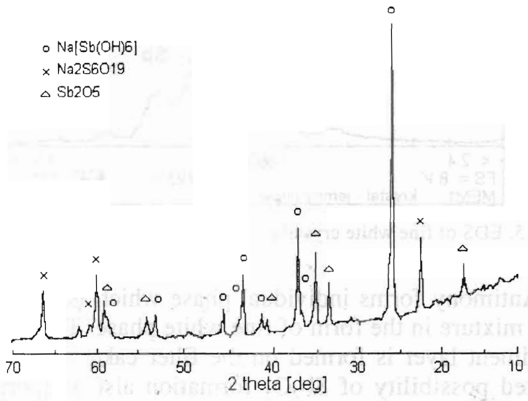

Fig. 3. X-ray diffractogram of experiment No. 3.

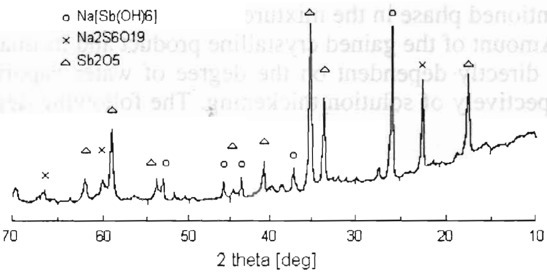

Fig. 4. X-ray diffractogram of experiment No. 4.

quality view of the forming crystals these are important parameters of the process. At the present time oxidation experiments at lower partial pressures of oxygen and at lower temperatures are carried out.

Another phase that is free antimony pentoxide ($Sb_2O_5$) can be identified in diffractograms in Fig. 3 and Fig. 4. Its formation can be explained by the following deliberation. A molecule of $Na[Sb(OH)_6]$ crystal can be written in the form:

$$2\,Na[Sb(OH)_6] = Na_2O.Sb_2O_5.6H_2O$$

Formation of a bound among $Na_2O$, $Sb_2O_5$ a $H_2O$ and creation of the recquired crystal occur at a sufficient amount of water. Lack of water causes weakness of the bound and free $Sb_2O_5$ precipitates from the solution. From a microanalysis of the crystalline phase part, whose EDS is depicted in Fig. 5, there follows that antimony is not in the bound with sodium.

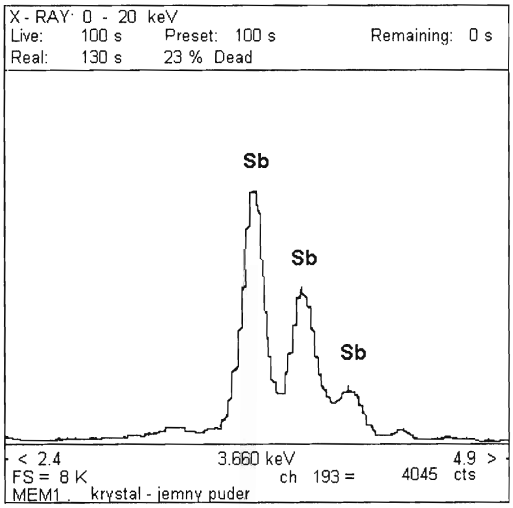

Fig. 5. EDS of fine white crystals.

Antimony forms individual phase which is situated in the mixture in the form of fine white phase. The filtering sediment layer is formed on the filter cake surface. The stated possibility of $Sb_2O_5$ formation also supports the fact that with an increasing degree of water vaporing, the amount of the secreted phase is increasing. This situation is shown in Fig. 3 and Fig. 4. Intensity of diffraction lines increases what reflects concentration relations of the mentioned phase in the mixture.

Amount of the gained crystalline product and its quality are directly dependent on the degree of water vaporing, respectively of solution thickening. The following degrees of vaporing were reached under conditions of the experiments No. 1 up to No. 4 what is shown in Tab. 4.

Tab. 4
Degree of water vaporing (in %)

| Exper. No. | vapored water | amout of crystal |
|---|---|---|
| 1 | 54 | 87.5 |
| 2 | 16 | 94.4 |
| 3 | 35 | 124.2 |
| 4 | 66 | 200.3 |

Note: amount of crystal is compared to a theoretical amount of sodium hexahydroxoantimonate

Despite a considerable solution thickening (54 %) there was not a phase of antimony pentoxide formed in the experiment No. 1. This can be connected with conditions of the autoclave cooling. Influence of pressure of gasseous atmosphere has most likely major effect on this process. If the autoclave cools down at atmospheric pressure, formation of oxide phase occurs after vaporing of 20 % of water from the processed solution.

Necessary selectivity of arsenic and mercury separation between liquor and gained crystal was ensured by the oxidation conditions of the processed solution in all experiments. A chemical analysis showed that the crystal was practically pure. Arsenic and mercury concentration were under the detection limit, that is under 0.002 weight %. Arsenic, in the liquor, concentrated to the values of 1 g/l up to 2 g/l and mercury to 0.1 g/l up to 0.2 g/l. Besides, liquour contained only 0.002 g/l up to 0.09 g/l of antimony.

## Conclusion

Notions from the pressure oxidation of the solution originated in alkaline leaching of tetrahedrite concentrate are published in the paper. Oxidation of the stated solution is carried out to obtain saleable antimony product - crystalline sodium hexahydroxoantimonate.

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# Pressure leaching of tetrahedrite raw materials

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### Abstract

The paper deals with the treatment of tetrahedrite concentrate by pressure leaching i. e., by leaching at higher temperatures. The objective of this work was to achieve the selective solubility of antimony into the solution at the given leaching conditions and to achieve that copper together with silver and gold remained in the solid residue. Selective leaching of antimony from the tetrahedrite concentrate can be achieved by the pressure leaching in autoclave, which has been proved by the results of our work. Comparatively high leaching efficiencies of antimony into the solution have been achieved (up to 90 %). The process can be optimized further, so that the efficiency of Sb leaching would be over 95 % and the process economic at the same time.

**Key words:** leaching, pressure leaching, tetrahedrite, leaching of sodium sulphide, antimony

### Tlakové lúhovanie tetraedritových surovín

Príspevok sa zaoberá spracovaním tetraedritového koncentrátu tlakovým lúhovaním, t. j. lúhovaním pri zvýšených teplotách. Cieľom práce bolo, aby sa antimon pri daných podmienkach lúhovania selektívne rozpúšťal do roztoku a meď zostala v podobe využiteľného koncentrátu spolu so striebrom a zlatom v pevnom zvyšku. Z výsledkov možno konštatovať, že vhodnou metódou pre selektívne lúhovanie antimonu z tetraedritového koncentrátu sa javí tlakové lúhovanie v autokláve. Dosiahla sa relatívne vysoká účinnosť lúhovania antimónu do roztoku, blízka hodnote 90 %. Uvedený proces je možné ďalej optimalizovať a tak dosiahnuť pri ekonomickej únosnosti procesu účinnosť lúhovania antimonu nad 95 %.

Tetrahedrite concentrates are formed in the process of siderite or barite raw materials flotating regulation. They are sulphidic polycomponent concentrates on the basis of Cu-Sb-Fe-sulphide with a share of polluting elements such as As, Hg, Bi and Zn. Valuable parts of tetrahedrites are Ag and Au.

Processing of tetrahedrite raw materials has its importance in Slovakia due to a considerable content of individual utility metals, mainly Sb, Cu, Ag and Au.

One of the ways of tetrahedrite concentrate processing is hydrometallurgical one. A perspective way seems to be pressure leaching that is leaching at increased temperatures. The aim of the mentioned leaching of flotating tetrahedrite concentrate is to achieve selective dissolution of antimony and remaining of copper together with silver and gold in the solid residue in the shape of a useful concentrate.

There are two ways of tetrahedrite concentrate processing by alkaline hydro-way, respectively by pressure leaching:

a) by using sodium sulphide,
b) by using sodium sulphide prepared by reaction between NaOH and S in the liquid solution.

With regard to price relations and amounts of chemicals needed for the process of the stated alternative ways of leaching, the most convenient way seems to be (b). In this process the following reactions between elementary sulphur and sodium suphide in the liquid solution take place:

$$4\ S^{\circ}_{(s)} + 6\ NaOH(1) = 2\ Na_2S_{(1)} + Na_2S_2O_{3(1)} + 3\ H_2O \quad (1)$$

As it follows from the reaction, natrium sulphide and sodium thiosulphide are created. Leaching-wise sodium thiosulphide is ineffective. During the reaction process (Okáč, 1961), when creation of $Na_2S$ occurs, free sulphur reacts with sodium sulphide and according to the reaction scheme (Brown, 1982) polysulphides $Na_2Sx$ are formed:

$$(x-1)\ S^{\circ}_{(s)} + Na_2S_{(1)} = Na_2Sx_{(1)} \quad (2)$$

where x = 2 to 5

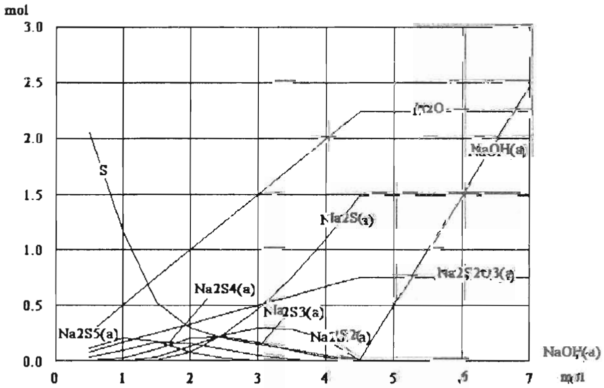

Fig. 1. Material bilance of the reactions (1) and (2).

A diagram which is presented in Fig. 1 shows the process of reactions between sulphide and sodium hydroxide.

There is material bilance of the reactions (Okáč, 1961) and (Brown, 1982) depicted in the diagram and it is possible to observe reaction of sulphur depending on concentration of sodium hydroxide in the liquid solution.

Sodium sulphide, which was created as the result of reaction between sulphur and sodium hydroxide, reacts with tetrahedrite, that is with sulphide whose simplified formula can be written in the $Cu_2S.Sb_2S_3$ form. The reaction takes place according to the schemes:

$$Cu_2S.Sb_2S_{3(s)} + Na_2S_{(l)} = Cu_2S_{(s)} + 2\ NaSbS_2 \qquad (3)$$

$$NaSbS_{2(l)} + Na_2S_{(l)} = Na_3SbS_{3(l)} \qquad (4)$$

Due to the oxidation ability of the present polysulphides in the solution, major amount of antimony (+V) is situated in the soluble form:

$$Na_2Sx_{(l)} + (x-1)\ Na_3SbS_{3(l)} = (x-1)\ Na_3SbS_{4(l)} + Na_2S_{(l)} \quad (5)$$

Antimony selectively dissolves and copper remains in the solid residue as it follows from the reaction scheme (3).

There was influence of change in concentration of parts of leaching solution and in leaching period on the total effectiveness of antimony dissolving at the temperature of 150 °C observed in the paper by experimental tests.

## Experimental study

### *Equipment and methodics of experiments*

Rotatory autoclave from a company Lampart was used for the leaching tests of tetrahedrite flotating concentrate. The process of leaching was following: weighed amount of concentrate was poured into the autoclave, solution which contained reagents of sodium hydroxide and sulphur was added, the autoclave was closed, heating and stirring in the autoclave was turned on. After reaching a desired pressure and temperature the period of leaching process was measured. The autoclave was cooled down by water after leaching. The content of autoclave was poured into beaker after being opened. The solution was separated from the solid part by filtering. The solid part was washed by water. Concentrated solution, washing solution and solid part were formed after the process of leaching was over. Each solution was measured, the solid part was dried and weighed. After all, the three products underwent chemical analysis.

### *Characteristics of the raw material*

Flotating tetrahedrite concentrate from an area of Rožňava was used for the experimental tests. Chemical composition of the concentrate was following (weight %): Cu 27.36; Sb 15.93; S 27.67; Fe 14.58; Na 0.43; Bi 0.33; As 1.02; Hg 0.74; Ag 3900 g.t$^{-1}$; Au 5.7 g.t$^{-1}$.

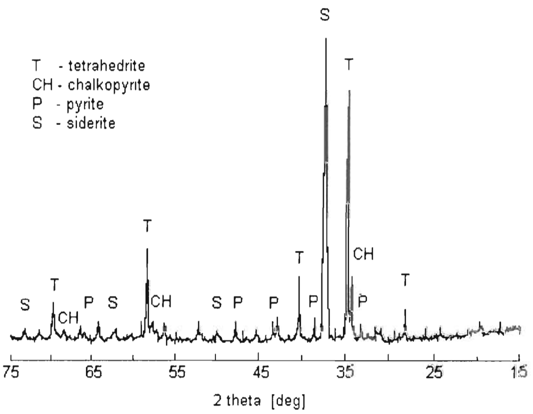

Fig. 2. X-ray diffractogram of Rožňava's tetrahedrite concentrate.

A presence of tetrahedrite, chalcopyrite, pyrite, siderite and quartz was proved by X-ray qualitative phase analysis. Belonging X-ray photograph of the presented concentrate is shown in Fig. 2.

### *Experimental tests and conditions of experiments*

The experimental tests of pressure leaching of flotating tetrahedrite concentrate in the solution which contained reagents of sodium hydroxide and sulphur were realized under these conditions. Two periods of leaching were chosen for the experiments. It was 1 hour for the first serie of experiments and three hours for the second one. A temperature was 150 °C and total vapor pressure was 0.6 MPa. Liquid/solid ratio was 10:1 in all experiments. The amount of concentrate in each experiment was 50 g. Ratio between amount of sodium hydroxide and sulphur was changing what can be observed in Tab. 1 and Tab. 2. There is also effectivity of antimony dissolving shown in the tables.

Tab. 1
Period of pressure leaching = 1 hour

| Sample | NaOH | S | NaOH/S | Sb |
|---|---|---|---|---|
| | mol/l | mol/l | - | % |
| L - 3 | 0.750 | 0.470 | 1.595 | 4.33 |
| L - 6 | 2.400 | 1.875 | 1.280 | 20.59 |
| L - 9 | 3.300 | 2.563 | 1.288 | 71.45 |
| L - 12 | 3.750 | 3.000 | 1.250 | 53.17 |
| L - 15 | 5.475 | 3.000 | 1.833 | 71.71 |

Tab. 2
Period of pressure leaching = 3 hour

| Sample | NaOH | S | NaOH/S | Sb |
|---|---|---|---|---|
| | mol/l | mol/l | - | % |
| L - 18 | 3.300 | 2.563 | 1.288 | 71.46 |
| L - 22 | 5.475 | 3.000 | 1.833 | 74.73 |
| L - 28 | 3.300 | 2.563 | 1.288 | 89.21 |

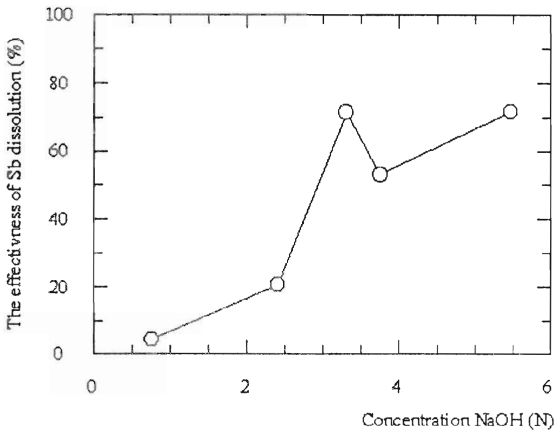

Fig. 3. Efficiency dependence of Sb dissolving on NaOH concentration in the leaching solution, time of leaching = 1 hour.

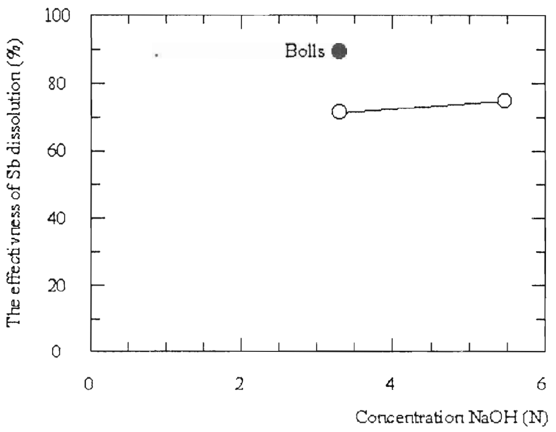

Fig. 4. Dependence of efficiency of Sb dissolution on NaOH concentration in the leaching solution, time of leaching = 3 hours.

## *Analysis of obtained results*

The following facts can be derived from the results of pressure leaching of tetrahedrite concentrate:

Efficiencies of antimony dissolving were in a wide range of values in the first part of the work when the period of pressure leaching was 1 hour. The values were from 4.33 % to 71.71 %, as it shows Tab. 1. The values are drawn in the graph in Fig. 3 and depict dependence of efficiency of antimony dissolving to the solution on NaOH concentration in the solution. On the basis of a graphic dependence it can be said that by increasing NaOH concentration in the solution the efficiency is increasing up to a certain value whereby further increasing of concentration has no effect on efficiency of antimony dissolving. It was proved that increasing NaOH concentration over the value of 3.3 N had not brought satisfactory results.

Notion of influence of increasing leaching time of two different NaOH concentrations on Sb dissolving was gained in the second part of the work. On the basis on the results of the preceding experiments NaOH concentrations of 3.3 and 5.475 N were chosen. The best efficiency of Sb dissolving during one hour of leaching was reached with these concentrations.

The results are shown in Tab. 2. As it can be seen, increasing leaching time does not have an essential effect on Sb dissolving. Due to the fact that experiments of leaching were realized in the rotatory autoclave, where only generating process of the material took place, to make the leaching of the sample L 28 more intense, steel balls were used. Two effects were achieved by doing so. The material was stirred more intense and at the same time surface activation of tetrahedrite particles occurred by removing reactant products. The effect of mechano-chemical pressure leaching was expressed quite distinctively and efficiency of antimony dissolving reached a level of 90 %. The efficiencies of antimony dissolution achieved in dependence on NaOH concentration are shown in Fig. 4.

## Conclusion

From the results achieved in this work it can be stated that a convenient way of selective antimony leaching from the tetrahedrite concentrate seems to be the pressure leaching in the autoclave. Relatively high efficiencies of antimony dissolution were reached, close to the value of 90 %. The results of the tests can be taken as the first approximation to real values and a question of increasing efficiency of antimony dissolving over 90 % needs to be dealt with in more detailed way in further works concerning pressure leaching, respectively mechano-chemical leaching in the autoclave.

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# Influence of microwave radiation on the leaching of tetrahedrite

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## Abstract

The microwave radiation has a positive influence on the course of many technologic processes. On account of this reason it was examined also for improvement of the efficiency of tetrahedrite concentrates leaching, which are not utilized up to the present time in our country. The leaching experiments with these materials were carried out in the basic medium of sodium sulphide both before and after microwave irradiation of samples. The recoveries of searched metals in the leachate have attested the positive effect of microwave radiation on the following leaching process of Sb and As from tetrahedrite, which has been expressed by the higher recovery of Sb about 6 % and As about 15 %. There were gained little expressive results in the case of tetrahedrite concentrate leaching and of Hg recovery in the leachate. For tetrahedrite concentrate it would be explained with the presence of gangue constituents and by absorption of the great part of microwave radiation and its heating effect in them. The positive effect of microwave radiation on the results of tetrahedrite leaching cannot be connected with phase changes in the samples. Its explanation demands further detailed research.

**Key words:** microwave radiation, leaching, tetrahedrite, complex electric permittivity

### Vplyv mikrovlnného žiarenia na lúženie tetraedritu

Mikrovlnné žiarenie pozitívne ovplyvňuje priebeh početných technologických procesov. Z tohto dôvodu bolo odskúšané aj pre zvýšenie účinnosti lúhovania tetraedritu a tetraedritových koncentrátov, ktoré nie sú u nás doteraz využívané. Pokusy lúhovania týchto materiálov boli urobené v zásaditom prostredí sírnika sodného bez a po predchádzajúcom ožiarení vzoriek mikrovlnami. Výťažnosť sledovaných kovov do výluhu potvrdila pozitívny účinok mikrovlnného ožiarenia na následný proces lúhovania Sb a As z tetraedritu, ktorý sa prejavil zvýšením výťažnosti u Sb až o 6 % a pri As až o 15 %. V prípade lúhovania tetraedritového koncentrátu a výťažnosti Hg do výluhu boli získané výsledky málo výrazné. Pri tetraedritovom koncentráte sa to dá vysvetliť prítomnosťou jalových zložiek a absorpciou veľkej časti mikrovlnného žiarenia a jeho tepelného efektu. Pozitívny účinok mikrovlnného ožarovania na výsledky lúhovania tetraedritu nesúvisí s fázovými zmenami vzoriek. Jeho vysvetlenie vyžaduje ďalší podrobnejší výskum.

## Introduction

Deposits of tetrahedrite, situated in the Spiš-Gemer ore mountains, form an important part of the reserves of Slovak copper ore. Mining of this ore was concentrated in localities Rudňany and Rožňava. Tetrahedrites are sulphides characterized by fluctuating content of main metallic components (Cu, Sb and As) and they frequently contain also other additives (Hg, Ag, Zn, Fe). Tetrahedrite from Rudňany shows especially high content of Hg for which specific name schwazite is used. Extracted tetrahedrite ore is thus a polymetallic raw material, which was treated by flotation in the mining plant of Iron Ores Mines Rudňany. By chloridizing roasting of the flotation concentrate mercury was obtained, but no feasible technology was available for further processing of the roasted tetrahedrite ore. Leaching of Sb, As and Hg from the tetrahedrite concentrate and subsequent hydrometallurgical processing of the obtained leachate seems to be an acceptable solution from the technological point of view. However, this process becomes effective only when it includes also mechanochemical activation which substantially increases efficiency of leaching (Baláž et al., 1995).

The problem of increasing the efficiency of technological processes is significant especially in the branch of mining industry in which part of useful component is irrecoverably lost in the waste. In order to decrease these losses various technical inovations are applied, among which the use of electromagnetic radiation, especially that in the microwave range, becomes more and more attractive. This type of radiation is already used for a number of industrial applications, above all for drying and heating of various materials. Application of microwaves for treatment and processing of minerals was tested by a number of authors. These applications include microwave drying of brown coal (Standish et al., 1988), continuous measurement of coal moisture content (Cutmore et al., 1989) and coal desulphurization (Jacobs et al., 1982). It was established that microwave radiation has positive influence on the flotation of fluorite (Roussy et al., 1986), on the grindability of iron ore (Walkiewicz et al., 1988), on the magnetic properties of iron ore (Florek et al., 1996) as well as on the leaching of gold-arsenopyrit concentrates which are difficult to dress (Hague, 1987). Catalytic influence of microwaves in the course of chemical reactions has been described already in many papers (Toma, 1993) even when its theoretical basis is still unclear. In this paper we summarize the results of experiments whose aim was to influence the process of leaching the tetrahedrite and its concentrate in an alkaline medium by the microwave irradiation. These experiments were evaluated on the basis of the recovery of metals in the leachate and by studying the phase changes in tetrahedrite irradiated with microwaves.

## Theoretical part

Microwaves are in fact high-frequency electromagnetic radiation in the millimetre and centimetre wavelength which is used mainly due to its heating effect. Advantage of microwaves is, when compared with traditional sources of heat, their rapid and volume effect on the irradiated material. Heat is generated within the whole volume of material, what is of great importance from the technological point of view.

Microwave irradiation may initiate three types of interactions, depending on the electric properties of given material. In materials with high electric conductivity the reflection of microwaves takes place, while in dielectrics the microwave radiation is absorbed. In other materials effects connected with the transmission of radiation through the material may be observed. From the practical point of view, including ore dressing, above all the interactions are of interest which result in the absorption of the microwave radiation and its conversion into heat.

Absorption of microwaves in dielectrics with subsequent increase of their temperature may be observed on microstructural level as an influence of the high-frequency electric field. Due to the influence of this field electrically charged particles of material tend to align with the direction of the field. After the field has decayed, they return back into neutral positions, the corresponding part of their potential energy being transformed into the thermal energy. In the time-dependent electric field the polarization of particles is proportional to the field intensity. At low frequencies polarization changes synchronously with the changes of electric field, while at high frequencies the inertia of molecules causes delay and phase shift leading to the absorption of energy and its transformation into heat. These phenomena are closely connected with the type of dielectric polarization relevant for particular case. Main types of dielectric polarization are:

- electron polarization caused by the change of positions of electrons around the nucleus;
- atomic polarization caused by positional shifts of the nucleus due to the non-uniform distribution of the charge within the molecule;
- orientation polarization caused by the reorientation of permanent dipoles due to the influence of electric field;
- spatial charge polarization observed when material contains free electrons whose distribution is limited by the grain surface (Maxwell-Wagner mechanism).

In the range of microwave frequencies the electron and atomic types of polarization basically do not contribute to dielectric heating. Such a heating is produced by two other types of polarization, i. e. orientation and spatial, which cause both the phase shift and the heat effect mentioned above. Thermal effect of the microwave radiation can be determined from the absorbed power which is given by the formula

$$P = 2\pi \varepsilon_0 f \varepsilon'' E^2 \tag{1}$$

where

$\varepsilon_0$ - permittivity of vacuum

$f$ - frequency of microwave radiation

$\varepsilon''$ - imaginary part of complex electric permittivity

$E$ - intensity of local electric field.

Considering practical use of microwaves it is important to characterize the properties of materials, mainly those of dielectrics, in the time-dependent electric field. In alternating electric field the value of complex electric permittivity ($\varepsilon^*$) is given by the relation:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' - j\sigma/\omega \tag{2}$$

where

$\varepsilon$ - relative permittivity of material

$\sigma$ - conductivity of dielectric

$\omega$ - angular frequency

$j = \sqrt{-1}$

Value of dielectric losses may be expressed also in terms of a loss angle using equation (3).

$$\tan \theta = \varepsilon'' / \varepsilon' \tag{3}$$

On the basis of (1) and (3) it is possible to assess the effect of microwave radiation on materials. Higher value of these quantities means higher efficiency of microwave irradiation of a certain material.

This theoretical basis may be used to assess the feasibility of the microwave irradiation of tetrahedrite or its concentrate. This materials is, like other sulphides, electrically conductive ($10^{-3}$ - $10^4$ $\Omega$ m). This is confirmed also by the imaginary part of complex permittivity which was determined by the reflection method (Florek et al., 1996). At a frequency of 2,45 GHz, which is reserved for microwave appliances, and at an electric field mean intensity of 1400 $\mathrm{Vm^{-1}}$ the absorbed power of microwave radiation in tetrahedrites is, according to equation (1), 253 800 $\mathrm{Wm^{-3}}$. Such a power may be obtained in normal microwave oven used in kitchen. Depth of penetration of electromagnetic radiation into material may be determined from the equation (Florek and Lovás, 1995).

$$d = \frac{c}{2\pi f} \sqrt{\frac{2}{(\varepsilon'^2 + \varepsilon''^2)^{1/2} - \varepsilon'}} \tag{4}$$

where c - velocity of light, $\varepsilon'$ - real part of complex electric permittivity.

For the values 2,19 and 0,95 of the real and imaginary parts, respectively, of the permittivity of tetrahedrite the penetration depth of microwave radiation is 0,06 m. This means that when the tetrahedrite with flotation granularity is irradiated, the microwave radiation will sufficiently penetrate through the grains. These parameters thus confirm that tetrahedrite may be efficiently irradiated with microwaves.

## Experimental procedures

In leaching experiments samples of tetrahedrite and its concentrate with granularity class below 0.2 mm were used. Table 1 gives chemical composition of samples.

Tab. 1
Chemical composition of tetrahedrite samples

| Sample | Metal content [%] | | | | |
|---|---|---|---|---|---|
| | Cu | Sb | As | Hg | Fe |
| Tetrahedrite | 28,50 | 7,69 | 2,17 | 0,73 | 6,42 |
| Tetrahedrite concentrate | 27,36 | 15,93 | 1,02 | 0,71 | 14,58 |

Samples were irradiated with microwaves before leaching in a Panasonic microwave oven with a frequency of 2.45 GHz and a power output of 900 W. Samples were placed in evacuated glass tubes. Pure tetrahedrite was irradiated for 30 seconds while samples of tetrahedrite concentrate were irradiated for 30 and 80 seconds.

The influence of microwave irradiation on the samples of tetrahedrite and tetrahedrite concentrate was investigated by the method of X-ray diffraction analysis using a DRON 2,0 apparatus. Phase changes in irradiated samples were evaluated on the basis of obtained diffractograms.

Leaching of tetrahedrite with the aim to leach Sb together with As and Hg into the leachate, with Cu concentrate in the form of solid phase being separated by filtration, may be performed either in acid or in basic medium. We have used the method of leaching in the basic solution of sodium sulphide, which is widely used also in industry. In this process the leaching of Sb from tetrahedrite by sodium sulphide takes place according to the equation

$$Cu_2S.Sb_2S_3 + 3Na_2S \rightarrow Cu_2S + 2Na_3SbS_3 \qquad (5)$$

The obtained copper sulphide ($Cu_2S$) represents solid phase and Sb is leached into the solution in trivalent form ($Na_3SbS_3$), from which it oxidizes in the presence of polysulphides into a pentivalent form ($Na_3SbS_4$) (Baláž et al., 1995). Simultaneously with Sb also As and Hg are released into the solution. Disadvantage of this procedure is relatively low recovery of Sb, As and Hg in leachate even when leaching is prolonged over long time. Irradiation with microwaves could have a positive influence on the process of leaching, similarly as in the case of gold-arsenopyrite concentrates (Haque, 1987). To verify this assumption we have made experiments consisting of leaching tetrahedrite and tetrahedrite concentrate samples in the basic medium of sodium sulphide both before and after they were irradiated with microwaves. Samples with a mass of 10 g were leached in 200 ml of an $Na_2S$ solution at a temperature of 90 °C under permanent agitation. Concentration of the $Na_2S$ solution used for leaching was 300 $gl^{-1}$. The kinetics of leaching was observed only during 15 minutes since for longer time intervals the observed differences between the irradiated and non-irradiated sample remained almost the same. Results of these experiments were evaluated on the basis of the obtained recovery of selected metals (Sb, As, Hg) in dependence on the time of leaching.

## Discussion of results

The influence of microwave radiation on the leaching of tetrahedrite and its concentrate was evaluated by studying the phase changes in the irradiated matter and also on the basis of the obtained recovery of Sb, As and Hg in the leachate.

Thermal effect caused by microwave irradiation of tetrahedrite samples, which represents the main effect of the irradiation, indicates that we should concentrate on the possibility that phase changes occur due to irradiation. By the formation of new phases we can easily explain also the changes in the efficiency of leaching. Diffractograms of original and irradiated tetrahedrite do not show significant differences (see Fig. 1).

On the basis of these diffractograms we can state that:

- in the irradiated sample no such new phases were formed whose fraction would exceed 5 %;
- a decrease in the intensity of the diffraction radiation of individual components of the irradiated sample was observed, particularly that of the line corresponding to tetrahedrite;
- a shift of peaks of diffraction radiation lines amounting to about 3° was observed in irradiated samples.

The absence of phase changes in irradiated samples may be explained by their lower warming-up due to short time of irradiation. Selection of such a time was motivated by the need to suppress the phase changes in order to observe the leaching of tetrahedrite and not that of newly created Cu oxides. Decrease of the intensity of diffraction radiation may be probably connected with the formation of hot centers due to volume heating from tetrahedrite and the resulting partial decomposition of the tetrahedrite component. In the irradiated sample a shift of diffraction peaks was observed, a phenomenon which might be connected with irreversible changes of the parameters of elementary cell and which we will investigate in detail.

Diffractograms of the tetrahedrite concentrate before and after irradiation with microwaves show still smaller differences than those of tetrahedrite itself and so we are neither showing nor commenting them. Results of leaching the tetrahedrite and its concentrate are presented as the dependence of the recovery of Sb, As and Hg in the leachate

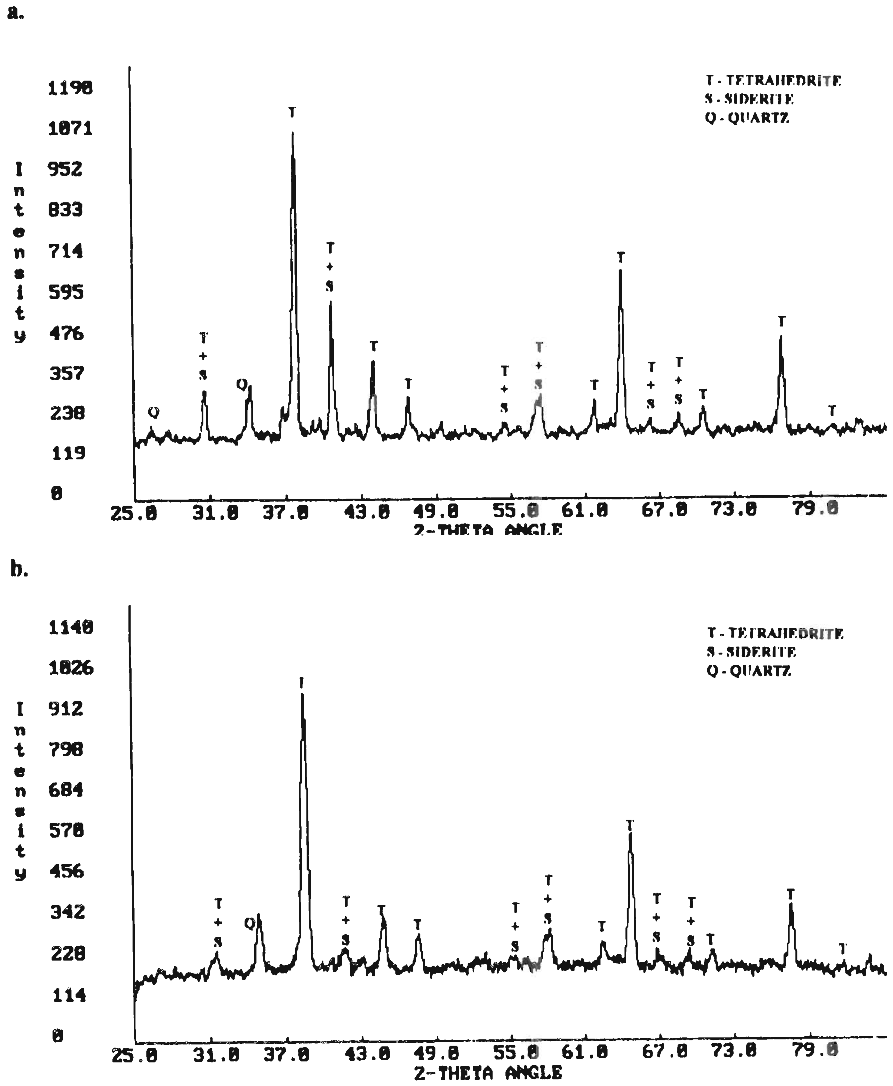

Fig. 1. Diffractograms of the tetrahedrite before (a) and after (b) the irradiation by microwaves.

on the time of leaching. These dependences thus represent also the kinetics of leaching of in a given time interval. It may be concluded from these dependences that microwave irradiation of samples has different influence on both the process of leaching and the obtained recovery of selected metals. The most apparent differences obtained in leaching of the irradiated and non-irradiated samples of tetrahedrite are seen in the recovery of As and Sb (Figs. 2 and 3). The recovery of As from the irradiated sample is higher by about 15 % when compared with the non-irradiated sample, from which the recovery stabilizes already after 5 minutes (Fig. 2). The difference of recovery for Sb is somewhat lower - about 6 % in favour of the irradiated sample - and the course of leaching indicates that the selected time is not long enough to leach the high fraction of Sb in tetrahedrite (Fig. 3). Contrary to the results mentioned above, leaching of Hg from irradiated and non-irradiated sample does not show any significant difference (Fig. 4).

Experiments with leaching the tetrahedrite concentrate did not lead, however, to results similar to those obtained for pure tetrahedrite, even when two different times of irradiation were used. There are only small differences, in favour of the irradiated samples, in the recovery of metals As and Hg. Apparent differences were observed only for Sb, indicating that prolonged irradiation is not effective (Fig. 5).

## Conclusion

Positive influence of the microwave radiation with a frequency of 2.45 GHz and power of 900 W, lasting for 30 s, on the leaching of tetrahedrite in a basic medium of sodium sulphide was experimentally proved in terms of higher recovery of As and Sb. In irradiated samples of tetrahedrite the observed increase of the As recovery in the leachate was about 15 % while for Sb

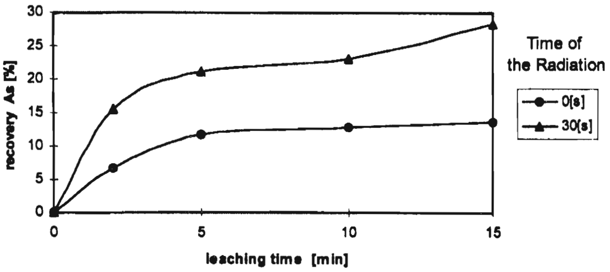

Fig. 2. Recovery of As in leaching of tetrahedrite.

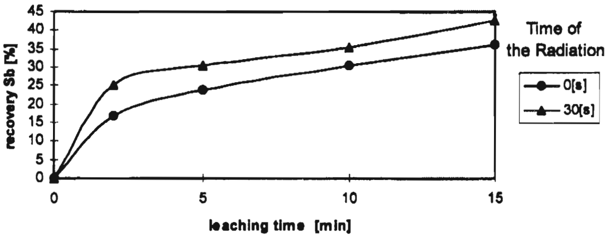

Fig. 3. Recovery of Sb in leaching of tetrahedrite.

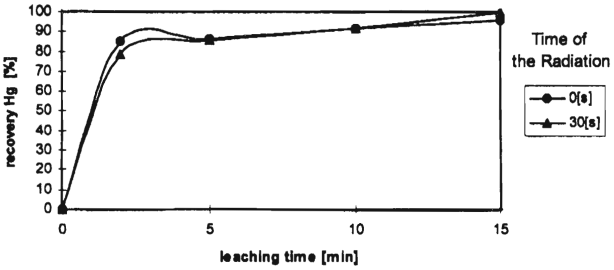

Fig. 4. Recovery of Hg in leaching of tetrahedrite.

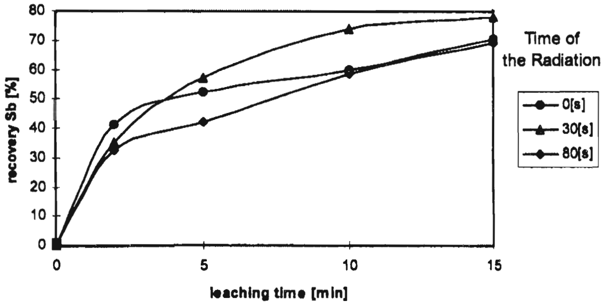

Fig. 5. Recovery of Sb in leaching of tetrahedrite concentrate.

it was about 6 %. There was a small apparent positive influence of the microwave radiation on the recovery of Hg, nor on the leaching of As and Hg from tetrahedrite concentrates.

This result may be caused by great part of the other minerals in the concentrate, which absorb the microwave radiation and its heating effect. Different influence of irradiation on the recovery of selected metals cannot be connected with phase changes in the sample, since these were not observed. A more detailed research is needed to explain this influence using either the concept of breaking the compactness of leached grains by the formation of microcracks after irradiation or the concept of weakening coupling forces in individual components of the leached material.

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GeOvestník

Informačný spravodajca pre geológiu, baníctvo, úpravníctvo a životné prostredie

Príloha časopisu Mineralia Slovaca, roč. 28, č. 5

## Obsah

# Geologicko-ekonomické problémy magnezitových ložísk Slovenska

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Roku 1995 sa v súlade s vyhláškou SGÚ č. 6/1992 Zb. prehodnotili zásoby magnezitu tých ložísk, ktoré boli v evidencii a ochrane bývalej Slovenskej geológie, š. p., Spišská Nová Ves a bývalého Geofondu Bratislava. Ide o známe ložiská v ochtinskom súvrství (vrchný karbón, namúr?) dobšinskej skupiny gemerika - Dúbravský masív-hĺbka, Dúbravský masív-Jedľovec, Ochtiná, Lubeník, Poproč - Rovné a Košice-hĺbka. Z niektorých z nich sa paralelne s výpočtom podľa klasických podmienok využiteľnosti zásob (kondícií) urobil aj variantný výpočet, ktorý ponúka optimistickejší pohľad na ekonomický význam overených zásob magnezitu. Tak napríklad v hĺbkovom a východnom pokračovaní významného ložiska Jelšava - Dúbravský masív-hĺbka a Jedľovec sa variantným výpočtom zistilo 225,5 mil. t magnezitu, z toho sa 162,3 mil. t kvalifikovalo ako bilančná a 63,2 mil. t ako nebilančná zásoba. Podľa pôvodných podmienok využiteľnosti (kondícií) by bolo možno ako bilančnú zásobu hodnotiť len 21 mil. t z celkového množstva overených geologických zásob.

Z analýzy pôvodného a nového výpočtu zásob vyplýva, že hlavným dôvodom neopodstatneného vykazovania značného množstva nebilančnej zásoby ložiska Dúbravský masív bola metodika určovania kondícií v minulosti. Doterajšie chápanie podmienok využiteľnosti zásob (ďalej PVZ) ako podkladu na hodnotenie a výpočet zásob výhradného ložiska podľa vopred určených podmienok využiteľnosti očakávaných zásob vedie k metodickým postupom, ktoré sa v istých prípadoch pri ekonomickom oceňovaní ložiska prejavujú nepriaznivo. Každé ložisko nerastnej suroviny je neopakovateľným prírodným objektom s akumuláciou hospodársky využiteľných nerastov, a preto nie je účelné ani možné vopred definovať jeho PVZ slúžiace na rozdelenie na bilančnú a nebilančnú zásobu. Ložisko overené po skončení vyhľadávacieho prieskumu je svojimi parametrami (zásoba, kvalita) vopred neznáme, preto sa dá ekonomicky zhodnotiť až potom, keď sa na základe variantného výpočtu zásob definujú jeho „statické" geologickoložiskové parametre, (Z - zásoba, $x_o$ - medzná kvalita, x - priemerná kvalita) a zmeny Z a x v závislosti od zmeny $x_o$.

Doterajšia filozofia vopred určených PVZ nebrala do ohľadu funkčnú závislosť medzi geologickoložiskovými, technicko-technologickými a ekonomickými parametrami, a preto neumožňovala určiť optimálnu kontúru bilančnej zásoby ložiska a jeho maximálnu cenu, často ani racionálne stanoviť množstvo a kvalitu nebilančnej zásoby.

Predpokladáme, že cena ložiska (C) ako ekonomická hodnota jeho overenej zásoby závisí nielen od ceny suroviny (c), výrobných nákladov (n), technicko-technologických parametrov (tp), ale aj od geologickoložiskových pomerov (Z, $x_o$, x), ktoré zásadne ovplyvňujú dynamické, technicko-technologické a ekonomické vlastnosti ložiska C f (Z, $x_O$, x, n, c, tp). Z uvedeného vychodí, že maximálnej cene ložiska pri konštantnej cene suroviny, konštantných výrobných nákladoch a technicko-technologických parametroch zodpovedajú len presne určené zásoby, definované hodnotou medznej kvality ($x_O$), priemernej kvality (x) a geologickými zásobami (Z).

Druhým závažným nedostatkom v doterajšej metodike určovania PVZ ložísk magnezitu (ale aj mastenca a rudných surovín) je spoločné určovanie „okrajovej vzorky" (medznej kvality $x_O$) bilančnej aj nebilančnej zásoby ložiska. Takýto prístup má za následok, že sa pri nevhodnej, nízkej hodnote okrajovej vzorky zásoby zvyšujú, ale znižuje sa ich priemerná kvalita s pochopiteľným negatívnym vplyvom na bilančnosť overených zásob. V prípade ložiska Dúbravský masív (časť Jedľovec a hĺbka) sa nevhodná (nízka) hodnota okrajovej vzorky ($x_O$) prijatá v kondíciách z roku 1979 spoločne pre bilančné aj nebilančné zásoby (35 % MgO) stala hlavným dôvodom nebilančnosti viac ako 100 mil. t magnezitu v tejto časti ložiska. Nový, variantný výpočet zásob realizovaný pri troch rôznych hodnotách medznej kvality $x_o$ (35 % MgO, 41 % MgO, 43 % MgO) umožnil vyčleniť v magnezitových polohách úseky s vyššou kvalitou (> 41 % MgO), ktoré majú zároveň nižší obsah škodlivín (CaO, $SiO_2$, $Fe_2O_3$) a ktoré možno právom kvalifikovať ako bilančné zásoby. Týmto novým metodickým postupom bolo možno v časti ložiska Dúbravský masív-Jedľovec a hĺbka vyčleniť 162,3 mil. t bilančnej zásoby (kategórie Z-3) s priemernou kvalitou 42,51 % MgO, 2,35 % CaO, 0,70 % $SiO_2$ a 3,71 % $Fe_2O_3$.

Je veľmi pravdepodobne, že kontúry zásob magnezitu, kde sa v minulosti aplikovala okrajová vzorka 35 % MgO, sú kontúrami, v ktorých sú a vykazujú sa nebilančné zásoby spolu s bilančnými. Za magnezit sa spravidla označuje surovina s obsahom nad 40 % MgO a pod 4 % CaO. Z tohto hľadiska bolo zaraďovanie chudobnej zásoby s kvalitou 35 - 40 % (zmes magnezitu a dolomitu) jednoznačne do zásob magnezitu (> 40 % MgO) z technologického aj ekonomického hľadiska neadekvátne.

Skúsenosti z prehodnocovania zásob magnezitu, ale aj ďalších nerastných surovín (mastenca, rúd Cu, Sb, Mo, Sn, Au, Ag, Hg, Pb, Zn, ako aj keramických surovín, zeolitu, bentonitu ai.) potvrdzujú veľký význam určenia optimálnych kontúr (medznej kvality) osobitne bilančných ($x_{OB}$) a osobitne nebilančných zásob ($x_{ON}$).

Ekonomický význam prehodnotenej zásoby magnezitu ložiska Dúbravský masív sa orientačne zhodnotil prostredníctvom súčasných svetových cien magnezitu, slinku a bázických stavív (55 - 280 USD/t), ako aj priemerných výrobných nákladov. Ak sa cena 1 t bilančnej zásoby magnezitu odhadne prostredníctvom diferenciálnej banskej renty len na 100 Sk, potom hodnota novo vypočítanej a preklasifikovanej zásoby ložiska Dúbravský masív-Jedľovec a hĺbka je okolo 16 mld. Sk.

Celkové geologické zásoby ložiska Dúbravský masív odhadujeme na 538 mil. t, čím sa - spolu s ložiskom magnezitu Košice - 516 mil. t - zaraďuje medzi veľké a významné svetové ložiská s možnosťou dlhodobej rentabilnej ťažby.

Okrem týchto dvoch veľkých magnezitových ložísk a ťaženého magnezitového ložiska Lubeník (s malou perspektívou overiť novú zásobu v hĺbkovom pokračovaní) možno medzi stredne veľké ložiská zaradiť aj ložisko Burda - Rovné, kde sa overená a prognózna zásoba odhaduje na 60 mil. t. Ostatné magnezitové ložiská (Podrečany, Sirk, Ochtiná) patria medzi malé ložiská so zásobou 1 - 10 mil. t, resp. medzi ložiskové výskyty (Ružiná, Cinobaňa, Ploské, Hlinka, Amág, Veľká Šteť, Hrádok - Hŕbky, Biela skala, Kavečany) so zásobou pod 1 mil. t a nepredpokladáme ich väčší priemyselný význam.

Veľké zásoby magnezitu (93 mil. t) v staršom paleozoiku gemerika, ktorý je sprievodnou surovinou ekonomicky významného mastencového zrudnenia (Gemerská Poloma - Henclová), sa v súčasnosti pre vysoký obsah $Fe_2O_3$ a $SiO_2$ prakticky nevyužívajú, ale ich priemyselnú exploatáciu ako významnej ekologickej suroviny zo zmesi magnezitu a mastenca v budúcnosti nemožno vylúčiť.

## Záver

Magnezitové a magnezitovo-mastencové ložiská Slovenska sú jedným z ekonomicky najvýznamnejších zdrojov nerastného bohatstva Slovenskej republiky. Magnezit má pre ekonomiku Slovenska veľký strategický význam okrem iného aj preto, že Slovensko patrí medzi popredných svetových producentov (2 - 3 mld. Sk/rok) a jeho overené geologické zásoby (> 1 mld. t) predstavujú domácu surovinovú základňu pre ďalší intenzívny rozvoj magnezitového priemyslu. Z uvedených hľadísk možno magnezit pokladať za jednu z našich najvýznamnejších nerastných surovín a ďalší rozvoj výroby (vrátane MgO, kovového Mg ai.) pre nízke až stredné produkčné, dopravné a obchodné riziko považovať za mimoriadne efektívny. V súčasnosti je malé aj riziko zmien a použitia, pretože magnezitu ako žiaruvzdornému materiálu zatiaľ vážne nič nekonkuruje. Možná konkurencia zo strany morskej vody ako zdroja Mg bude závisieť od ceny energie. V súčasnosti je hlavným konkurentom nášho magnezitového priemyslu lacný čínsky export.

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# Geografický informačný systém pri riešení environmentálnych problémov

Software Geografického informačného systému (GIS), ktorý umožňuje spracovanie a analýzu priestorových dát, je dnes vo svete počítačov jednou z najdynamickejšie sa rozvíjajúcich oblastí. Podľa toho, čo kategória GIS zahŕňa, možno ročný obrat v obchode s jeho aplikáciami odhadnúť na 550 miliónov až jednu miliardu USD ročne a rast v rovnakom období 15 - 24 %.

Veľký podiel na komerčnom úspechu majú programy využívajúce sa v marketingu, ktoré umožňujú efektívne lokalizovať a triediť potenciálnych zákazníkov. Ale významnou na trhu GIS je aj environmentálna oblasť s aplikáciami, medzi ktoré patrí monitoring znečisťovania, analýza geologicky ohrozených území, mapovanie vegetácie, správa a sledovanie prírodných rezervácií, oceňovanie územia z hľadiska možnej výstavby a rozličné verejné informácie. GIS dnes využíva mnoho riadiacich pracovníkov spoločností zaoberajúcich sa využívaním prírodných zdrojov a už v rámci univerzitného štúdia sa s nimi zoznamuje množstvo vysokoškolákov.

„Sila GIS spočíva v tom, že dodáva informácii priestorovú zložku," hovorí Mark Lehnertz, spoluzakladateľ americkej spoločnosti Environmental Database, Inc. „Väčšina ľudí nemôže nosiť v hlave celú mapu a práve GIS dáva možnosť triediť informácie do systému veľmi blízkemu skutočnosti."

Lehnertzova firma pracuje priamo podľa želaní zákazníkov: vytvára primárne mapy pre environmentálnych inžinierov a konzultantov, právnické firmy, chemické spoločnosti a i. Väčšina dát, ktoré na takúto analýzu používa, sú v USA verejne prístupné. Napríklad informácie o úniku látok z podzemných uskladňovacích nádrží možno získať zo štátnej agentúry pre životné prostredie, hydrologické údaje z Geologickej služby Spojených štátov (U. S. Geological Survey, ďalej USGS) a pôdne mapy z miestnych alebo federálnych poľnohospodárskych úradov. Bez veľkej námahy môže GIS všetky dáta kombinovať a vytvárať mapy najpravdepodobnejších miest znečistenia podzemnej vody.

Takéto mapy boli, samozrejme, prístupné už pred nástupom počítačov, ale technológia GIS ich tvorbu zjednodušuje a urýchľuje a umožňuje kombinovať najrozmanitejšie druhy informácií a poľahky sledovať ich vzájomnú súvislosť.

Geografické informačné systémy integrujú priestorové údaje a manipulujú s tými, ktoré boli „geokódované", čiže fixované na reálny geografický priestor. Môže to zahŕňať napr. dáta zo sčítania ľudu, poštové smerové čísla alebo digitálne fotografie. Výskumníci v oblasti životného prostredia môžu využiť údaje o hranici povodí, miestnom zaťažení krajiny pesticídmi, správy o kvalite ovzdušia alebo o rozmiestnení chemických tovární. Pre program GIS je typické umiestňovanie takýchto pestrých atribútov do „vrstiev", tie potom navzájom porovnáva a kombinuje s cieľom odhaliť vzájomné väzby, ako je hoci aj vzťah medzi výškou príjmu domácností a vzdialenosťou od miesta úniku toxických látok.

Jedným z dôvodov rastúcej popularity GIS je aj zvýšenie dostupnosti rozličných geografických podkladov v elektronickej forme. Ešte donedávna bolo nevyhnutné vytvárať vlastné priestorové databázy, a to či už digatalizáciou máp, alebo skanovaním leteckých záberov, ale v súčasnosti už americké štátne inštitúcie digitalizujú svoje údaje o prírodných zdrojoch v masovom meradle, a tak sa informácie stávajú prístupnejšími, a preto aj lacnejšími. Množstvo agentúr, univerzít, ale aj súkromných spoločností dnes ponúka geopriestorové údaje zadarmo alebo za relatívne nízku cenu.

USGS napríklad poskytuje rozličné druhy kartografických údajov, ako sú topografické a hydrografické informácie, využívanie pôdy, vegetačný pokryv a multispektrálne fotografie z družice Landsat alebo iných satelitov. Medzi projektmi, ktoré teraz USGS realizuje, je aj tvorba ortofotografických štvorcových digitálnych obrazov založených na leteckých snímkach, ktoré odstraňujú skreslenie spôsobené fotografickým zariadením a terénom. Takéto snímky bude možno použiť ako podkladové mapy pre GIS namiesto doterajších ilustrovaných máp.

Vládne agentúry si často vymieňajú údaje, prispôsobujú ich, príp. kombinujú so svojimi. Hydrologické dáta USGS sú napríklad podkladom na vytvorenie tzv. „reach" súborov agentúry EPA. Ide o digitálnu databázu povrchových vodných tokov v mierke 1:100 000 so všetkými ich vzťahmi k celkovej odvodňovacej sieti. Už niekoľko výskumov využilo túto databázu na sledovanie migrácie znečisťujúcich a výživných látok vo vodných tokoch.

GIS nielenže ovplyvňuje spôsob, akým sa geopriestorové údaje analyzujú, ale mení aj metódy ich zhromažďovania. Dnes sa už často využívajú prenosné prijímače globálneho systému lokalizácie (GPS), ktoré vďaka satelitnej navigácii dokážu veľmi presne určovať polohu pri operáciách v teréne, a tak spresňovať vytváranie modelu pomocou GIS. V teréne sa začínajú používať aj ľahké prenosné počítače a často aj software na rozoznávanie reči, ktorý umožňuje vytvárať digitálne terénne poznámky a priamo ich zabudúvať do databázy GIS, a tak sa už aj sama databáza postupne stáva nielen vstupom, ale aj produktom GIS.

Tak ako sa GIS stáva bežným v environmentálnych a iných aplikáciách, začína sa inkorporovať do viacerých hlavných typov softwaru. Nové verzie CAD a databázové programy, ako je AutoCAD či Oracle, majú možnosť analyzovať dáta GIS, či manipulovať s nimi. Niektoré spoločnosti použili GIS ako základ na vytváranie modernejších programových balíkov špeciálne určených na ochranu životného prostredia. Napríklad systém GIS/Key spája GIS, databázu a CAD a je schopný ukladať a integrovať hydrologické, chemické, geologické a iné údaje s cieľom monitorovať úložiská nebezpečného odpadu. Medzi používateľov GIS/Key patrí aj NASA alebo DuPont Chemical, podľa ktorých sa pri použití tohto systému cena prieskumu a hodnotenia úložiska redukuje o 30 - 60 %.

Ako každá technológia, aj GIS má isté obmedzenia. Doteraz to bola najmä konverzia máp a iných údajov na formát využiteľný GIS. Tak sa často stávalo, že sa projekty využívajúce GIS realizovali pomalšie ako projekty založené na tradičnejších metódach, a vznikali aj konceptuálne rozdiely medzi modelmi založenými na analógových dátach získaných priamo v teréne a modelmi GIS vychádzajúcimi z digitálnych údajov.

Pri využívaní produktov GIS hrozí aj nebezpečenstvo prílišnej interpretácie. Ako príklad možno uviesť mapy radónového rizika väčších území, ktoré napr. hovoria veľmi málo o situácii v jednotlivých budovách. Každý používateľ GIS by si mal uvedomovať všetky predpoklady a zjednodušenia, ktoré sprevádzali tvorbu mapy, medzi ktoré patrí najmä mierka a kvalita vstupných údajov.

Napriek spomenutým obmedzeniam expanzia GIS pokračuje a v súčasnosti má vďaka Internetu a WWW možnosť preniknúť aj k oveľa širšiemu publiku, ako je environmentálna komunita. Vznikajú uzly, z ktorých bude možno získať mapy, obrazy, historické letecké zábery a iné kompatibilné údaje GIS. Vďaka prepojeniu pracovísk a úradov bude sa pravdepodobne dať získavať a využívať lokálne informácie a vytvárať stále podrobnejšie súbory.

Ďalším krokom vo vývoji GIS by mohlo byť spojenie trojrozmerných aplikácií GIS s počítačovými technikami vedeckej vizualizácie, ktoré poskytujú štvrtý rozmer - čas. Toto spojenie by časom mohlo produkovať štvorrozmerné animácie zobrazujúce komplexné environmentálne procesy, akým je napríklad pohyb látok vo vodnom ekosystéme meniaci sa v priestore aj čase.

Mnohým sa to zdá ako prirodzený vývoj GIS, najmä ak sa splní predpoklad, že sa s ním bude zoznamovať postupne čoraz viac používateľov. Podľa vývoja v posledných dvoch rokoch, keď bol rast záujmu oň priam revolučný, sa to zdá dosť pravdepodobné.

*Zdroje:*
(1) List of GIS software packages: http://triton.cms.udel.edu/~oliver/gis_gip/gis_gip_list.html
(2) Federal Geographic Data Committee Internet Site: http: //fgdc.er.usgs.gov
(3) EPA Internet data sites: http://nsdi.epa.gov/nsdi and http: //www.epa.gov/ docs/grd.
(4) GIS data publishers: http: //www.esri.com/products/arcdata/publishers/html

*Podľa ES&T, August 1996 spracoval M. G.*

R. SCHMIDT: **Aplikácia graficky orientovaného software v geológii. MicroStation** (Košice 23. 1. 1996)

V geologickej praxi sa dokumentujú a analyzujú originálne objekty (vzorky, geologické štruktúry atď.) vyznačujúce sa konkrétnou priestorovou pozíciou. Pritom vzniká potreba zostavovať grafickú dokumentáciu, mapy, priestorové modely, textové opisy a výsledky analýz, ako sú grafy, tabuľky ap. Zefektívniť takúto činnosť umožňujú programy typu CAD, medzi ktoré patrí aj produkt firmy Bentley Systems Inc. MicroStation.

MicroStation umožňuje vytvárať grafický výkres v priestore 2D alebo 3D, vektorizovať rastrové podklady a spájať prvky vo výkrese s negrafickými textovými informáciami z databáz (napr. DBASE). Výkres sa začína zostavovať vstupom podkladov, ktorými môžu byť už hotové mapy, napríklad topografická alebo banská mapa pri tvorbe geologickej mapy, mapy odberu vzoriek a pod. Takéto podklady možno spracovať pomocou digitalizačného tabletu alebo zvektorizovať po zoskanovaní do podoby rastrovej snímky. Na prácu s rastrovými súbormi sú k dispozícii nadstavbové aplikácie IRAS a BRAS. Vstupný podklad možno zadať aj v podobe súboru súradníc, napríklad výsledkov geodetických meraní. Po spracovaní podkladu nasleduje vlastné kreslenie a kompletizácia výkresu v pracovnom okne programu pomocou širokej ponuky grafických prvkov a funkcií. Medzi najbežnejšie patria rozličné typy čiar, kriviek, kružníc, uzatvorených objektov, škála farieb a funkcie na manipuláciu s prvkami výkresu. Uzatvorené plochy sa dajú vypĺňať šrafami podľa potreby. Trojrozmerný model možno prostredníctvom vizualizácie opláštiť ľubovoľným rastrovým povrchom, a tak vytvoriť fotorealistickú snímku. Veľmi praktické je vkladanie textov. Výkres môže obsahovať 63 vrstiev, čo je vlastne 63 na seba položených výkresov, ktoré sa dajú spracúvať a plotrovať samostatne alebo v ľubovoľnej kombinácii. Spracúvanie prebieha v reálnej mierke, takže do výkresu možno presne vkladať detaily akejkoľvek veľkosti, odčítavať z mapy súradnice alebo merať presné vzdialenosti. Negrafické textové informácie sú pripojiteľné k vybratým prvkom v podobe štítkov (akejsi visačky) alebo databázovej tabuľky. Ako príklad uvádzame pripojenie číselných výsledkov chemických analýz k miestam odberu vzoriek. Dostupná je široká škála špecializovaných nadstavbových aplikácií. Dajú sa programovať aj vlastné aplikácie v programovacom prostredí. Základná filozofia využívania programu MicroStation vo výskume spočíva v postupnom zostavovaní komplexného systému grafických a negrafických informácií a vo využívaní nadstavbových aplikácií, a to až po vytvorenie geoinformačného systému, z ktorého možno produkovať rozličné výstupy podľa zamerania výskumného projektu alebo ho používať na podporu kombinačných schopností.

LADISLAV TOMETZ: **Jur nad Hronom - ropná havária. Prieskum geologických činiteľov životného prostredia** (Košice 27. 2. 1996)

Podľa základnej charakteristiky geologických činiteľov životného prostredia, ktorá hovorí o faktoroch priaznivo a nepriaznivo ovplyvňujúcich život a dialo človeka, sa rozlišujú geopotenciály a geobariéry. Z geopotenciálov sú pre život človeka potrebné zdroje nerastných surovín, energetické zdroje, podzemná voda, úrodná pôda a dobrá základová pôda. Geobariéry sa v podstate dajú rozdeliť do troch základných skupín. V 1. skupine ide o činitele ohrozujúce život človeka (sopečná a seizmická činnosť, zosuny veľkého rozsahu, rozsiahle záplavy a pod.), v 2. sú to činitele hodnotiace interakcie medzi technickými zariadeniami a geologickým prostredím a 3. skupinu charakterizuje nepriaznivý vplyv činnosti človeka na geologické prostredie (nadmerná ťažba nerastných surovín, ukladanie rozličného odpadu a pod.).

Prednáška sa zaoberala poslednou z uvedených skupín a poukázala na vplyv takého technického zariadenia na geologické prostredie, akým je ropovod Družba. Táto líniová stavba prechádza celou SR od Čiernej nad Tisou až po Bratislavu. Prevádzka ropovodu v minulosti viac ráz negatívne ovplyvnila životné prostredie, niekedy so značným negatívnym vplyvom hlavne na kvalitu pôdy a podzemnú vodu. Častým zdrojom znečisťovania sú prečerpávacie stanice, kde sa v minulosti riešili, ale aj v súčasnosti riešia úlohy súvisiace so znečistením pôdy a vody spôsobeným ich prevádzkou (Budkovce, Moldava nad Bodvou).

Nemalým problémom je aj sám ropovod, ktorého potrubie je vystavené korozívnemu vplyvu prostredia, v ktorom je uložené, ale aj nepriaznivému vplyvu prepravovaného média. Zrejme nie je ďaleko čas, keď sa celá trasa ropovodu podrobí rozsiahlej rekonštrukcii.

Jednou z najväčších ropných havárií, na ktorej riešení sa zúčastnil aj prednášateľ, bol výron ropy z porušeného potrubia pri Jure nad Hronom v okrese Levice. Znečistenie spôsobil dlhodobejší výtok ropy cez otvor na skorodovanom zvare potrubia, ktorého priemer nepresahoval 5 cm, cez ktorý sa rozliala ropa na poľnohospodársku pôdu (s ozimnou pšenicou) a vytvorila škvrnu v dĺžke viac ako 800 m a v priemernej šírke okolo 30 m. Únik ropy z potrubia sa zistil 25. októbra 1993, zrejme po dlhšom čase. Prevádzkovateľ (Transpetrol - Ropovod Šahy) potom začal asanačné práce, ktoré sa skladali (okrem odstránenia poruchy na potrubí) z odčerpávania ropy z povrchu terénu, kde sa vo väčších depresiách začali vytvárať kaluže miestami v hĺbke aj 20 až 30 cm. Potom bola ropná škvrna zapálená, aby sa zabránilo jej postupu do pôdy. Po predbežnej sanácii najvrchnejšej časti terénu sa v zmysle legislatívnych opatrení mal vykonať prieskum na zistenie rozsahu znečistenia. V tejto fáze prieskumu, ktorý predchádzal projektovej dokumentácii (v havarijných prípadoch sa môže prieskum začať bez projektu), sa vykonali plytké sondážne (vrtné) práce. Celkove sa takto odvŕtalo 95 sond a odobralo 125 vzoriek zeminy. Na základe uvedených prác a laboratórneho rozboru vzoriek zeminy sa určila miera znečistenia. Miestami bola pôda kontaminovaná až do hĺbky 2,0 m pod terénom a obsah NEL sa v nej pohyboval od 30 000 do 150 000 mg.kg$^{-1}$ sušiny.

Po určení plošného a hĺbkového rozsahu znečistenia zeminy sa vykonali asanačné práce. Tvorilo ich odťaženie zeminy do hĺbky 0,5 až 1,0 m a jej odvezenie na dekontamináciu do rašelinových závodov. Po vyťažení zeminy bolo dno vzniknutej jamy rozorané hlbokou orbou a do takto rozrušenej pôdy sa aplikoval biopreparát na degradáciu ropných látok v pôde. Neskôr sa celá jama zaviezla čistou zeminou.

Po nevyhnutných geologickoprieskumných prácach na zistenie rozsahu znečistenia na povrchu terénu a plytko pod jeho povrchom sme s fázovým posunom navrhli ďalšiu etapu prieskumných prác, ktorá sa mala zamerať na prípadné znečistenie podzemnej vody. Bezprostredný prieskum na tento cieľ po havárii nebolo vhodné vykonať, aby sa v dôsledku vrtných prác nevytvorili preferované cesty na postup kontaminantu.

Prieskumné práce sa vykonali v údolnej nive Hrona pri obci Jur nad Hronom. Reliéf má charakter nivy so zmiešaným tvarom vysokej riečnej terasy a sprašovej tabule. Z pôdnych typov sa tu vyskytuje černozem degradovaná na spraši (priestor kontaminácie) a poriečnu nivu sčasti pokrýva nivná glejová pôda na nekarbonátových sedimentoch. V poriečnej nive prevláda silne skeletnatá a v miestach kontaminácie ílovito-hlinitá pôda.

Z geologického hľadiska sa z predkvartérnych útvarov na stavbe záujmového územia zúčastňujú sedimenty neogénu. Najrozšírenejší je vápnitý íl panónu, v menšej miere piesčitý íl s polohami piesku, ojedinele aj štrku. Naše vrtné práce v hĺbke viac ako 10 m pod terénom zachytili polohy zelenomodrého piesčitého a žltohnedého ílu. Celková hrúbka tohto súvrstvia tu presahuje niekoľko 100 m.

Kvartérne sedimenty, na ktoré sa náš prieskum zameral, v prvom rade predstavujú v prirečnej časti najvrchnejšie holocénne fluviálne sedimenty vo forme málo vyvinutej povodňovej hliny, pod ktorou je pleistocénny piesčitý štrk. Vo väčšej vzdialenosti od Hrona (postihnuté územie) tvorí najvrchnejšiu vrstvu spraš, pod ktorou je piesčitý štrk.

Podzemná voda sa viaže na fluviálne štrkovo-piesčité sedimenty, ktorých priepustnosť zodpovedá III. triede priepustnosti s koeficientom filtrácie okolo $1,10^{-4}$ m.s$^{-1}$. Hladina podzemnej vody je v hydraulickej spojitosti s hladinou vody v povrchovom toku a má charakter voľnej hladiny. Podľa zisteného hydraulického gradientu je smer prúdenia podzemnej vody SSZ - JJV. Hladina podzemnej vody kolíše v rozmedzí 8 - 9 m pod terénom. Z hydraulického hľadiska má podzemná voda zvýšenú mineralizáciu (1020 mg.l$^{-1}$). Prevládajú v nej katióny Na, Ca, z aniónov $HCO_3$, $SO_4$, Cl a podľa Palmerovej - Gazdovej klasifikácie ju hodnotíme ako nevýrazný kalciovo-bikarbonátový základný typ.

Ďalšia etapa prieskumu sa zamerala na overenie šírenia sa znečistenia vo vertikálnom, ale aj horizontálnom smere, najmä vo vzťahu k hladine podzemnej vody. Na to sa vyhĺbilo päť hydrogeologických vrtov s označením MP-1 až MP-5, každý s hĺbkou 12 m, vystrojených rúrou PVC s priemerom 110 mm a s perforovanou časťou v úrovni prítoku podzemnej vody. Vrty sa realizovali ako hydraulicky dokonalé, čiže prešli celou dĺžkou zvodneného prostredia až do nepriepustného podložia. Počas vŕtania sa z každého metra odobrali vzorky zeminy a z hladiny podzemnej vody aj jej vzorky na zhodnotenie miery znečistenia. Vo vrtoch ju najlepšie charakterizujú predmetné grafy, z ktorých je zrejmý obsah NEL v zemine a podzemnej vode. Po zhodnotení laboratórnych rozborov sme stanovili mieru a rozsah kontaminácie a podľa odporúčania komisie pre životné prostredie SR, ktorá hovorí, pri akom znečistení geologického prostredia sa má začať s prieskumnými a asanačnými prácami, sme navrhli ďalší postup prác. Výsledky analýz poukázali na zvýšené znečistenie zeminy najmä vo vrtoch situovaných v miestach intenzívneho sústredenia sa ropy bezprostredne po havárii, keď obsah ropných látok v zemine aj napriek predchádzajúcej asanácii dosahovali v hĺbke m pod terénom hodnotu okolo 1000 mg.kg-1 sušiny. Smerom do hĺbky miera znečistenia zeminy klesá a jej rast je badateľný až v úrovni hladiny podzemnej vody, čo súvisí so šírením sa znečistenia po hladine podzemnej vody.

Obsah ropných látok v podzemnej vode v tomto štádiu prieskumu mal hodnotu od 1,2 do 10,5 mg.l$^{-1}$.

Z prieskumných prác jednoznačne vyplynula potreba vykonať sanačné práce aj v zvodnenom prostredí. Na to sa v záujmovom území vybudoval hydraulický sanačný systém z troch nalievacích a troch odberových vrtov. Odčerpávaná voda sa dopravovala cez filter, v ktorom sa okysličila rozstrekovaním a prešla aktívnym filtrom, ktorým bola zeolitová drvina vo frakcii 6 - 8 mm. Z filtra sa voda vypúšťala do nádrže a odtiaľ sa prečerpávala vsakovacím systémom späť do horninového prostredia. Účinnosť degradácie ropných látok v podzemnej vode sa prejavila ihneď po začatí čerpania, keď analýzy odobraných vzoriek pred filtrom vykazovali obsah NEL okolo 1 mg.l$^{-1}$ a za filtrom menej ako 0,1 mg.l$^{-1}$. V monitorovacom systéme, ktorý sa skladal z vrtov prvej etapy prieskumu (MP-1 až 5), sa obsah ropných látok v podzemnej vode pohyboval v rozmedzí 0,1 (MP-5) až 18,25 mg.l$^{-1}$ (MP-1) na začiatku sanačných prác a na ich konci po roku nepretržitého čerpania hodnota NEL vo vode vstupujúcej do filtra klesla na úroveň 0,07 mg.l$^{-1}$, na výstupe z filtra 0,03 mg.l$^{-1}$.

Na základe dosiahnutých výsledkov sa sanačné čerpanie skončilo v marci 1996.

### M. KOŠUTH: **Poznatky o superhlbokom vrte KTB** (Košice 27. 3. 1996)

Prednáška bola súhrnom poznatkov autora z osobnej návštevy a z periodík o unikátnom geologickom projekte, ktorý sa v minulom roku úspešne skončil.

Keď bol roku 1980 v Nemeckej spolkovej republike schválený program Kontinental tiefbohrung, sledovali sa najviac tieto tri ciele:

1. vedecký výskum záujmovej časti zemskej kôry,
2. prezentácia technických schopností Nemeckej spolkovej republiky,
3. technické odskúšanie možností vŕtať pri 300 °C a tlaku zodpovedajúcom 10 km.

Roku 1985 vybralo federálne ministerstvo pre výskum a technológie spomedzi štyroch miest Windischeschenbach v hornom Falcku. Skúmaná oblasť s anomálnou elektrickou vodivosťou, geofyzikálnymi, gravimetrickými a magnetickými anomáliami leží na predpokladanom križovaní franckej línie a litoměřického zlomu. Vrt bol založený v hraničnej zóne dvoch hercýnskych tektostratigrafických jednotiek - silne metamorfovaného moldanubika a slabo premeneného saxotüringika s ich predpokladanými násunmi.

Pozícia vrtu KTB geologicky spadá do devónskej (moldanubikum) tektonickej jednotky Erbendorf - Vohenstrauss (ZEV), budovanej striedavo pararulami a metabazitmi (metagabrá a dvojaké amfibolity). V podloží pravdepodobne alochtónnej jednotky ZEV je tzv. erbendorfská zóna zelených bridlíc. Obidve jednotky sú penetrované malými telesami ultramafických hosbachitov a menšinovými vsuvkami grafitických bridlíc a kvarcitov, ortorúl so šošovkami eklogitov. V tesnej blízkosti na V a S vystupujú na povrchu telesá variského, prevažne posttektonického granitu. Na Z za franckou líniou prilieha k paleozoickým jednotkám mezozoikum.

Dovtedy známe a predpokladané poznatky mal potvrdiť alebo vyvrátiť vrt, ktorý bol výnimočný predovšetkým technickým zabezpečením. Vŕtaniu predchádzal vývoj samonosného kábla dĺžky 15 km a radu prístrojov kalibrovaných na pracovnú teplotu do 300 °C. S trojročným predstihom sa odvŕtal pilotný vrt hlboký 4000 m. Parametre 83 m vysokej vrtnej veže KTB dovoľovali označiť ju za najdokonalejšiu na svete. Jej zdvižná sila 800 t dvojnásobne prekročila hmotnosť vrtnej kolóny dlhej 10 000 m. Motor s výkonom 9500 kW a ostatné elektrické zariadenia sa napájali vlastným vedením vysokého napätia s príkonom 4 MW. Bezodpadový výplachový systém s celkovým objemom 450 000 l poháňali pumpy s výkonom 1000 až 4000 l/min. Jeho integrovanou súčasťou bol aj vyvinutý tzv. downhole motor, automaticky registrujúci a korigujúci deklinácie smeru vŕtania. Okrem valivých dlát s jadrovacou medzerou uprostred a diamantových koruniek sa špeciálnym zariadením vzorkovali na jadro aj aktuálne steny vrtu. Doň sa v pravidelných intervaloch spúšťali prístroje na meranie teploty, elektrickej vodivosti, rádioaktivity a na vzorkovanie fluid, ako aj kamery na snímanie stien vrtu.

Na vzorky a merané údaje netrpezlivo čakalo 40 vedeckých pracovníkov v dokonale vybavenom poľnom laboratóriu na ploche vrtu, najmä z Geologického prieskumu v Hannoveri. Do interpretácie poznatkov sa zapojilo ďalších 350 osôb z dvanástich krajín. Úzka spolupráca geológov, petrografov, geochemikov a geofyzikov poľného laboratória umožnila rýchlo porovnávať rozbory jadier, drviny a výplachového kalu. Vrtné jadrá sa po odfotografovaní a výbere fragmentov na zhotovenie mikroskopických preparátov postúpili na podrobný štruktúrny výskum. Petrofyzikálne parametre sa získavali najmä z úlomkov hornín, zisťovala sa hustota, tepelná vodivosť, magnetická susceptibilita, prirodzená rádioaktivita a študovali sa i napäťové polia. Rtg. fluorescenčným spektrometrom a kvantitatívnymi rtg. difrakčnými rozbormi úlomkov sa do 60 minút zistilo chemické a minerálne zloženie. Všetky uvedené údaje sa kontinuálne vynášali v sérii grafov v závislosti od aktuálnej hĺbky. Takto sa zaznamenávali aj výsledky analýzy plynov rozpustených vo výplachu, automaticky stanovované hmotovým spektrometrom každé tri minúty. Výsledky rozborov a zistenia autorov 140 napojených výskumných projektov sa zaznamenávali do databázy a pravidelne publikovali v bulletine KTB-Report.

Vŕtanie v rámci projektu KTB sa skončilo podľa plánu začiatkom prvého štvrťroku 1995. Vrt splnil všetky technické predpoklady, čo nemožno povedať ohľadne potvrdenia očakávaných geologických teórií. Počas celej dĺžky nenarazil na nijaké výrazné geologické rozhrania a nezaznamenávali sa ani násunové štruktúry moldanubika na saxotüringikum, príp. na slabometamorfované rhenohercynikum (vyše 200 km na SZ). Profil vrtu prechádzal cez pripovrchové biotitické pararuly, a najmä monotónne partie bázických hornín postihnuté metamorfnými vplyvmi zodpovedajúcimi strednotlakovej amfibolitovej fácii pri teplote maximálne do 650 - 720 °C. Hrubozrnné až masívne metagabrá (alterovaný plagioklas, amfibol, +biotit) sa striedali s dvoma druhmi amfibolitov: prúžkované bez granátu s „flaseramfitmi" (plagioklas ol./and; amfibol, granát). Aj preto sa napriek technickým možnostiam prekročiť 12 000 m vŕtanie skončilo v plánovaných 10 000 m.

### J. KONDELA: **Geochemické anomálie Ag a Te na lokalite Remata** (Košice 28. 5. 1996)

V súčasnosti sa na svetových ložiskách veľmi pozorne sledujú aj stopové prvky. Ide najmä o ich ekonomické zhodnotenie, ale často bývajú aj indikátormi niektorých typov zrudnenia. Na lokalite Remata boli práve anomálne hodnoty Ag a Tl dôvodom na podrobnejšie štúdium.

Lokalita Remata leží asi 2 km na SV od Handlovej, v prevažnej miere ju tvoria karbonáty chočského príkrovu a v menšej miere paleogén. Študované územie sa tektonicky stýka s andezitmi rematskej formácie a je aj tektonicky značne prepracované. Karbonátové horniny sú často rozpukané a pukliny potom vyhojené kalcitom. Samým stredom územia prebieha hlbšie založená tektonická línia smeru V-Z. Z geochemického hľadiska je významný prienik telesa dioritového porfyritu cez karbonátové súvrstvie chočských dolomitov, ktorý spôsobil silnú areálovú premenu karbonátov - silicifikáciu. Premena prebehla do takého štádia, že kremeň tvorí až 99 % horniny. Ale najzaujímavejšie na lokalite je, že premenou nepostihnuté, prípadne iba slabo silicifikované karbonátové horniny (kremeň tvorí menej ako 25 % horniny) majú zvýšený obsah Ag a Tl. Priemerný obsah Ag v nealterovaných alebo slabo silicifikovaných karbonátoch je 3,5 ppm, maximálny 53 ppm, priemerný obsah Tl je 41 ppm a maximálny 53 ppm. Analyzovalo sa 42 vzoriek odobratých z povrchu. Tvar geochemických anomálií výrazne kopíruje už spomenutú tektonickú líniu smeru V - Z, ktorá bola pravdepodobne prívodným kanálom týchto elementov, ale ich zdroj je diskutabilný. Ag možno vysvetliť migráciou z blízkeho kremnického rudného poľa, ktoré je od študovaného územia vzdialené asi 6 km na V. Pôvod Tl sa nateraz nedá uspokojivo vysvetliť, veď z kremnického rudného poľa jeho výskyt nie je známy. Pozoruhodná je však jeho pozitívna korelácia s Ag.

Pre vyšší obsah Tl a ďalšie pozitívne kritériá (geologické, magmatické, petrologické) bola koncom 80. a 90. rokov práve lokalita Remata zaradená medzi oblasti s možnosťou výskytu Au impregnačnej mineralizácie (Knéslová, 1991), ale obsah Au takýto predpoklad nepotvrdil (Kondela, 1994).

S. W. FARYAD a G. HOINKES: **Korelácia vysokotlakových jednotiek východných Álp a Západných Karpát a polymetamorfóza austroalpínskych jednotiek** (Košice 29. 6. 1996)

Už druhý rok pokračuje spolupráca medzi katedrou geológie a mineralógie F BERG TU v Košiciach a mineralogicko-petrologickým a geologickými ústavmi univerzity v Štajerskom Hradci (Grazi), Innsbrucku a Salzburgu. Jej východiskom je projekt Korelácia vysokotlakových jednotiek východných Álp a Západných Karpát, ktorý financuje rakúsky Úrad pre zahraničnú výmenu vedeckých a pedagogických pracovníkov a Slovenská akademická informačná agentúra. Projekt zahŕňa terénny a laboratórny výskum, prednáškové pobyty a terénne exkurzie študentov. Pre nás sú takéto pobyty cenné aj preto, že nám hostiteľské ústavy umožňujú vykonávať merania na mikrosonde, čo je u nás veľmi ťažké a drahé.

Z rakúskej strany sme v júni v Košiciach privítali prof. G. Hoinkesa z ústavu kryštalografie, mineralógie a petrológie Univerzity v Grazi. Prednáškou Polymetamorfóza austroalpínskych jednotiek nás informoval o najnovších petrologických a geochronologických výskumoch kryštalického podkladu v oblasti Öztall (na Z od Innsbrucku), ako aj vo východnej časti Rakúska pri hranici so Slovinskom. V oblasti Öztall sa potvrdila prítomnosť variských eklogitov postihnutých alpínskou metamorfózou. Podľa vzťahov medzi minerálmi sa predpokladá ešte staršia (kaledónska ?) metamorfná etapa. K podobnému záveru dospel spoločný projekt Mineralogického ústavu v Innsbrucku a vo Viedni, ktoré na základe kombinácie Nd-Sm a Rb-Sr údajov získali 520 - 530 mil. vek intrúzie gabier a 340 - 370 mil. vek eklogitovej fácie öztallských metabazitov. Intenzita alpínskej metamorfózy zvyčajne rastie smerom na J, kde dosahuje až stupeň eklogitovej fácie, a podobná situácia je aj v južnej a jv. časti Taurského okna. Okrem akutálnosti dosiahnutých výsledkov bola prednáška pre študentov našej univerzity zaujímavá aj preto, že predchádzala ich exkurzii do východných Álp.

# Recenzia

AMOS SALVADOR (Ed.): **International Stratigraphic Guide.** 2nd ed., IUGS and Geol. Soc. of America (Boulder, Colorado), 214 p.

Známy Hedbergov kód (H. D. Hedberg bol editorom prvého vydania) vyšiel roku 1976 a ako vidno z grafu v tomto druhom vydaní, počet prác o stratigrafickej klasifikácii a terminológii po tomto roku nápadne poklesol. Je to výsledok stabilizácie koncepcií a princípov stratigrafickej klasifikácie, terminológie a postupov.

V druhom vydaní je nová kapitola o magnetostratigrafii. Na rozdiel od prvého vydania sa údajne viac pozornosti venuje vyvretým a metamorfovaným horninám, ale v skutočnosti sa na dvoch im venovaným stránkam nič nové neobjavuje. Osobitne sa uvažuje o jednotkách oddelených nesúhlasnosťami (unconformities). Postoj k sekvenčnej stratigrafii, ktorá ako hovorí J. Remane v predslove, je teraz veľkou módou v ropnom prieskume, sa nezaujíma. Zároveň si kladie otázku, ktorý z dvoch prístupov prežije a či sa v budúcnosti nevytvorí ich syntéza. A. Salvador sa v úvode vyjadruje skromne: „Kniha má byť návodom, a nie kódom; nikto nie je nútený postupovať podľa nej, kým sa sám nepresvedčí o jej logike a hodnotách."

Materiál publikácie je rozvrhnutý do desiatich kapitol: 1. Úvod; 2. Princípy stratigrafickej klasifikácie; 3. Definície a postupy; 4. Stratotypy a typové lokality; 5. Litostratigrafické jednotky; 6. Jednotky oddelené nesúhlasnosťami; 7. Biostratigrafické jednotky; 8. Magnetostratigrafické jednotky polarity; 9. Chronostratigrafické jednotky; 10. Vzťahy medzi rozličnými druhmi stratigrafických jednotiek. Na 38 stranách je užitočný slovníček stratigrafických termínov. Zoznam literatúry zaberá úctyhodných 55 strán.

Ďalej sa obmedzíme iba na poznámky, ktoré by mohli byť užitočné v našej praxi. Špeciálne požiadavky sú na stanovovanie jednotiek z vrtov, tunelových prác atď. (podpovrchové jednotky - subsurface units). Typovou lokalitou sa stáva daný vrt, hĺbkové rozmedzie, jeho geologický opis (kolónka) a karotážny záznam. Opis sa zakladá na štúdiu vzoriek jadra. Treba vyznačiť miesto ich uloženia s ľahkou dostupnosťou. Slabo odkryté povrchové typové lokality sa môžu doplniť podpovrchovými parastratotypmi a hypostratotypmi.

Na prekvapenie sa odporúča zachovať tradičné a zaužívané mená, aj keď nie sú odvodené od geografických názvov, napr. Millstone Grit, Kupferschiefer, Belemnite Marls. Pri zmene názvu charakteristickej zónovej fosílie sa odporúča neuvádzať zónu pod novým názvom, ale dať starý do úvodzoviek, napr. zóna „Rotalia" beccarii.

Stanovenie alebo revízia stratotypu má obsahovať tieto náležitosti: 1. meno a jeho odvodenie, 2. typový profil (stratotyp) s jeho vyznačením v detailnej mapke s prístupovými cestami, 3. opis jednotky v typovom profile (litológia, mocnosť, biostratigrafická charakteristika, hiáty, povaha rozhraní, charakteristické odlišovacie znaky, geomorfologická charakteristika, povaha rozhraní oproti podložnej a nadložnej jednotke), 4. geografický rozsah, regionálne variácie v mocnosti, litostratigrafii a biostratigrafii, vzťahy k susedným jednotkám, 5. relatívny geologický vek a pokiaľ možno aj vek pomocou rádiometrických a iných metód, 6. korelácia s inými jednotkami, 7. genéza, podmienky vzniku horniny vymedzenej jednotky, 8. odkazy na literatúru.

Z uvedených bodov sa u nás zvyčajne vynecháva geografické rozšírenie novovymedzenej jednotky, spravidla preto, lebo v čase jej definovania nebýva jej rozsah dostatočne preskúmaný. Vymedziť areál jednotiek ľahko možno na platformách, ale ťažšie v alpinotypných terénoch. Predpokladá sa, že areál rozšírenia je súvislý, čo niekedy ťažko preukázať. Takúto ťažkosť máme napríklad pri aplikovaní názvu czorsztynský vápenec na výskyty červeného hľuznatého vápenca dogeru - malmu krížňanskej jednotky (Borza a Michalík, 1987, Geol. zborník, 38, 3), kde pôvodnú priestorovú kontinuitu sotva možno predpokladať. Veľmi často sa stáva, že tá istá litostratigrafická jednotka sa v jednom štáte pomenúva inak ako v susednom; otázky prestíže sa tu miešajú s otázkami priority. Novšie vymedzenie jednotky v inej typovej lokalite totiž zvyčajne prevádza dôkladnejší opis podľa nových pravidiel, čo tézu o priorite oslabuje. Vždy možno nájsť nejaké odchýlky medzi dvoma porovnávanými typovými profilmi a to spolu s rozčleňovaním súvrstvia (formation) na menšie jednotky - členy (members) môže postupne viesť k syndrómu babylonskej veže. Opačná tendencia je aplikovať vymedzené jednotky na veľkú vzdialenosť, čo sa vzhľadom na prekvapujúcu zonárnosť fácií v pásmových pohoriach hojne uplatňuje napr. pri prenášaní mezozoických jednotiek z Álp do Karpát (ojedinele aj opačným smerom, napr. tisovecký vápenec). Aj to sa však niekedy preexponúva, napr. identifikácia hallstattských vápencov či zlambašských slieňov vo Východoindickom súostroví (Kristan a Tollmann et al., 1987: Pötschenschichten, Zlambachmergel (Hallstätter Obertrias) ... in Zentraltimor ..., Mitt. österr. geol. Ges., 80). Postupné laterálne prechody medzi litostratigrafickými jednotkami sú ďalším faktom, ktorý nedovoľuje vylúčiť subjektivitu v „krstení" a chápaní litostratigrafických jednotiek.

V knižke sa spresňujú niektoré pojmy: holostratotyp - originálny stratotyp vymedzený autorom; parastratotyp - doplnkový stratotyp použitý pôvodným autorom na ilustráciu rozmanitosti a takých čŕt, čo nie sú zastúpené v holostratotype; lektotyp - zvolený pre staršie používané jednotky, pre ktoré sa konkrétny a primeraný stratotyp nestanovil; neostratotyp - nový stratotyp ako náhrada za zničený stratotyp (napr. ťažbou, zaplavením priehradnou nádržou); hypostratotyp - neskôr stanovený stratotyp na rozšírenie poznatkov alebo na lepšiu definíciu hraníc pôvodného holostratotypu.

Publikácia je k dispozícii pre záujemcov na katedre geológie a paleontológie Prírodovedeckej fakulty Univerzity Komenského.

*M. Mišík*

# Eugen Jablonský

## významný geológ a botanik

*** 1892**
**† 1975**

Zdá sa, že slovenská historiografia má viac nezmapovaných oblastí, a preto sa čas od času náhodne a neočakávane vynorí zo zabudnutia osobnosť, ktorá má slovenský pôvod či vzťah k Slovensku a za svojho života patrila medzi pozoruhodné postavy európskej, ba i svetovej vedy. Medzi takéto osobnosti nesporne patrí aj dr. Eugen Jablonský (Jablonski), ktorého 105. výročie narodenia pripadá na 5. apríl 1997. Aj keď je pravda, že dr. E. Jablonský je skôr Stredoeurópan než írečitý Slovák, o tom, že jeho korene siahajú aj na Slovensko, vonkoncom nemožno pochybovať.

Jablonka na Orave, kde zapustila korene rozvetvená zemianska rodina Jablonských, je dnes na poľskom území a jej obyvatelia Gorali tvoria autonómne etnikum, ktorého časť inklinovala k Slovákom. Aj viacerí vzdelanci z rodu Jablonských sa pokladali za Slovákov. Napríklad jeden zo strýkov dr. E. Jablonského, miestny učiteľ a kantor rímskokatolíckeho farského kostola Jozef Jablonský, po rozpade Rakúsko-Uhorska a pričlenení Jablonky k Poľsku sa na protest proti zákazu spievať v kostole slovenské piesne vzdal svojho miesta v rodnej Jablonke a až do smrti pôsobil v Oravskom Veselom, teda v tej časti Oravy, ktorá patrila Československu. Na Slovensku zakotvili aj mnohí ďalší členovia tohto rozvetveného rodu.

Dr. E. Jablonský bol potomkom rodovej vetvy Jablonský - Šuvada. Jeho otec, vysokoškolsky vzdelaný intelektuál, pôsobil ako profesor reálneho gymnázia v Uhorsku a v Miškolci sa mu narodil syn Eugen. Intelektuálske rodinné prostredie modelovalo mladého Eugena a nasmerovalo jeho záujmy do prírodovednej sféry. Po skončení stredoškolských štúdií sa zapísal na budapeštiansku univerzitu (7. septembra 1909). Hlavným objektom jeho záujmu bola botanika, vedný obor, ktorý v tom čase nemal na budapeštianskej univerzite vysokú úroveň, a preto si odišiel prehĺbiť botanické vzdelanie k profesorovi Paxovi na univerzitu vo Vratislavi (Wroclawi) a k profesorovi Englerovi do Berlína. Jeho študijný pobyt v Berlíne bol mimoriadne úspešný. Tam spracoval do IV. dielu edície Das Pflanzenreich Regni vegetabilis conspectus čeľad Euphorbiaceae, Phyllanthoidaceae a Bridelieae. Po šiestich rokoch štúdia, krátko pred vypuknutím 1. svetovej vojny, obhájil na budapeštianskej univerzite dizertáciu (23. mája 1914) a získal titul doktora botaniky, kozmografie a geológie-paleontológie. Počas štúdia spracoval miocénnu flóru ryodacitových tufov z dnes svetoznámej lokality Ipolytarnócz. Na základe odtlačkov listov opísal okolo 30 rastlinných druhov, medzi nimi päť nových a stanovil spodnomiocénny vek ryodacitových tufov, čo je poznatok platný dodnes.

Po obhájení doktorskej dizertácie nastúpil do služieb Kráľovského geologického ústavu v Budapešti. Jeho práve začínajúcu vedeckú kariéru náhle prerušila 1. svetová vojna. Narukoval k pluku tirolských horských strelcov, v Karpatoch bol zranený a dostal sa do ruského zajatia. Bol internovaný v zajateckom tábore pri Caricyne, kde sa mu podarilo dostať k odbornej literatúre, takže pokračoval v štúdiu. Pred skončením vojny roku 1918 ušiel zo zajateckého tábora a vrátil sa do Budapešti a už 4. decembra toho istého roku vystúpil v Maďarskej geologickej spoločnosti s prednáškou o riasach karbónskych vápencov Bukových vrchov, Velebitu a zo Srbska. Výskumný materiál pochádzal zo zbierok E. Vadásza, F. Kocha a ml. L. Lóczyho. V deň svojich 27. narodenín (5. apríla 1919) sa oženil s priateľkou z vysokoškolských štúdií Máriou Krčméryovou z ružomberskej vetvy rodu Krčméryovcov.

Mladomanželia krátko po svadbe natrvalo opustili krvavým červeným a potom bielym terorom a biedou zmietané Maďarsko. E. Jablonský sa vrátil do rodiska svojich dedov do Jablonky a s pomocou poľských priateľov získal zamestnanie v Poľskom geologickom ústave. Neskôr prijal miesto geológa v ropnej spoločnosti Galicia Oil Co. v Czechowiciach. Spoločnosť sa čoskoro dostala do finančných ťažkostí a splynula s americkou Vacuum Oil Co. V jej službách vykonával rutinnú prácu ropného geológa a vrtného technika. V jednom liste prof. Vadászovi, s ktorým sa spriatelil počas vysokoškolských štúdií, píše: „praktická geológia dáva obživu, ale to nie je veda". Jeho záujmy v oblasti botaniky a paleontológie museli nadlho ustúpiť. Roku 1926 ho zavolali do New Yorku na ropnú konferenciu a ponúkli mu prácu v Texase. Chopil sa príležitosti pracovať vo svete, kde ropná geológia prežívala mimoriadny rozvoj. Ropnú prospekciu v zámorí začal v západnom Texase na hraniciach s Novým Mexikom v údolí Rio Grande a Pecos. Skúmal roponosnosť kolektorov algonkia, paleozoika, triasu a kriedy a ložiská ropy našiel vo vrchnopermských dolomitoch. Získal rešpekt amerických ropných spoločností a v marci roku 1930 ho mamutia spoločnosť Standard Oil vyslala ako vedúceho expedície do Austrálie a Tasmánie. Krátko pobudol na Novom Zélande. Potom opäť nasledovali terénne práce v Texase, Kalifornii, Kanade a v štáte New York. V auguste 1931 odišiel do Mexika, kde pracoval v ťažko prístupných územiach zamorených komármi. V marci 1933 sa služobne vrátil do Európy, aby študoval roponosnosť zechsteinu v Nemecku. Do tohto obdobia spadá jeho dvojtýždňová exkurzia v Karpatoch. Ešte v tomže roku viedol prospektorskú expedíciu na severný ostrov Nového Zélandu. Roku 1938 sa stal hlavným geológom transformovanej spoločnosti Socony - Vacuum v New Yorku. Viedol úspešnú prieskumnú expedíciu zavŕšenú objavením nových ropných polí na Blízkom východe (Egypt, Líbya, Libanon, Irak, Saudská Arábia), do Južnej Ameriky (Venezuela, Columbia, Ekvádor, Peru, Argentína), severnej Kanady a na Aljašku. Neskôr sa stal manažérom pre prieskum a potom koordinátorom prieskumu.

Po 2. svetovej vojne pôsobil v Európe, hlavne v Rakúsku, kde bol poradcom spoločnosti Mobil a manažérom prieskumu rakúskej odnože spoločnosti Mobil-Shell (Rohöl - Aufsuchung - Ges.m.b.H). Do ropnej prieskumnej praxe v Rakúsku zaviedol modernú metódu „tucker-seismic" a začal vyhľadávací ropný prieskum v rakúskej molase, v rámci ktorého sa vyhĺbil vrt Puchkirchen-1, prvý úspešný vrt v tejto oblasti.

Svoju brilantnú kariéru ropného geológa dr. E. Jablonský skončil roku 1957, keď ako 65-ročný odišiel do výslužby. Súkromnú bibliotéku a bohaté zbierky venoval trom nemeckým univerzitám, ktoré boli cez vojnu zničené leteckým bombardovaním.

Utajovanie poznatkov z vyhľadávania ropy bolo hlavnou príčinou, pre ktorú sa dr. E. Jablonský vo vedeckom svete po roku 1918 odmlčal. K vedeckej práci sa opäť vrátil na dôchodku. Po dvojročnom štúdiu flóry na SV Spojených štátov sa pripojil k osadenstvu herbária v newyorskej botanickej záhrade. Roku 1960 ho vymenovali za čestného kurátora tropickej botaniky. Bol v aktívnom styku s veľkými botanickými záhradami celého sveta. Vrátil sa k problematike, ktorej sa venoval počas vysokoškolských štúdií. Pokračoval v monografickom spracúvaní čeľade Euphorobiaceaea a jeho meno sa opätovne objavuje medzi autormi vedeckých publikácií. V rokoch 1963-1969 publikoval na túto tému päť prác.

Ako dôchodca sa často vracal do Európy. Zdržiaval sa vo Viedni, často u profesora Janoscheka a vo viedenskom prírodovednom múzeu mal rezervovaný pracovný stôl. Navštevoval aj dcéru Wandu, ktorá prechodne žila v Möldingu pri Viedni, ako aj svojich príbuzných zo svojej aj manželkinej strany na Slovensku a v Jablonke.

Úspešnú vedeckú i praktickú kariéru dr. E. Jablonského viac ráz ocenili. Jeho alma mater budapeštianska univerzita si ho uctila udelením zlatého diplomu, Maďarská geologická spoločnosť ho vymenovala za čestného člena (1969), od newyorskej botanickej záhrady dostal za mimoriadny vedecký prínos v oblasti lesníctva a botaniky Distinguished Service Award (1971).

Dr. E. Jablonský bol veľmi inteligentný, priateľský, jemný a veľkorysý človek, vedec a priateľ. O jeho odbornej a vedeckej erudícii svedčí nielen vedecké dielo, ktoré po sebe zanechal, množstvo úspešne realizovaných ropných projektov a objavených ropných polí, ale aj fakt, že aktívne ovládal deväť jazykov. Ľudskú dimenziu dr. E. Jablonského dokresľuje jeho vzťah k rodnému kraju predkov. Oravu miloval. Ako študent letné prázdniny pravidelne trávieval v Jablonke, v Roháčoch, na Babej hore. Osvojil si reč, piesne a tance ľudu tohto kraja. Keď bol v Európe, nezabudol navštíviť Oravu. Často prichádzal už ako dôchodca. V Amerike podporoval tanečný folklórny krúžok Goralov a bol jeho aktívnym členom.

Zomrel tri roky po smrti manželky Márie 24. apríla 1975 vo veku 83 rokov. Je pochovaný v New Yorku.

Medzičasom zomrela i jeho dcéra Wanda, ktorá nebola vydatá a pracovala v oblasti blízkej otcovej profesii. Bola redaktorkou týždenníka Petroleum Intelligence Weekly, vychádzajúceho v New Yorku. Patrila medzi iniciátorov založenia Združenia krajín vyvážajúcich ropu (OPEC). Požívala veľkú úctu a tešila sa priateľstvu významných ťažiarov ropy na Blízkom východe a v iných krajinách s bohatými ropnými náleziskami.

*D. Vass*

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# Terminologický stĺpček

## Slovo a termín troska

Hneď v úvode bude azda užitočné upozorniť na to, že v spisovnej slovenčine sú dve slová s podobou troska, dve samostatné slovníkové (lexikálne) jednotky, tzv. homonymá.

Napísať túto poznámku nás prinútil častý výskyt slova *struska* v rukopisných, ale niekedy aj v publikovaných vedecko-náučných, ako aj populárno-náučných textoch z niektorých geologických disciplín, ale najmä prekvapujúca vehemencia, s akou časť autorov toto neobhájiteľné slovo - osobitne vo funkcii termínu - bráni, kým slovo **troska** - opäť najmä ako termín - odmieta. Ešte horšia situácia je v odborných oblastiach, ktoré s tým, čo sa spomenutými dvoma slovami pomenúva, narábajú častejšie. Neprípustné nesprávnosti sa - isto nie zámerne - kde-tu dostávajú aj do jazykového povedomia širšej slovenskej verejnosti. Ostatnú konštatáciu možno ilustrovať napríklad článkom o najnovších archeologických nálezoch v Košiciach, v ktorom archeologička tvrdí: „Ryha pre (!) plyn a vodu ... prerezala ... objekt ... súvisiaci s výrobou železa - svedčila o tom hrubá vrstva s obsahom strusky."

Nedorozumenie pri slove troska a struska zrejme vychodí 1. z nepochopenia rozdielov medzi jazykmi vo významovej a formálnej rovine, v našom prípade medzi slovenčinou a češtinou ako príbuznými, ale samostatnými jazykmi, 2. z presvedčenia alebo aspoň z tušenia, že homonymá nie sú ako termíny veľmi vhodné a 3. zo stotožňovania profesionálneho slangu s vedecko-náučným štýlom spisovného jazyka.

Pri prvom bode treba mať na pamäti fakt, že proti dvom českým významom aj formou odlišným slovám, a to troska a struska, stoja dve slovenské významom sa odlišujúce a navzájom nesúvisiace slová, ktoré však majú rovnakú formu, čiže ide o tzv. lexikálne homonymá, a to v podobe troska. Lexikograficky (v slovníkoch) sa, prirodzene, spracúvajú v samostatných heslách.

Českému slovu troska (pozri napr. Slovník spisovné češtiny pro školu a veřejnost. Praha, Academia 1978, s. 571, ďalej SSČŠV), ktoré sa používa častejšie v pluráli a má význam „pozostatky zničenej stavby alebo iného diela ap.", napr. v spojení trosky hradu, trosky letadla ..., s príznakom expresívnosti aj význam „telesne alebo duševne zoslabnutý človek", zodpovedá slovenský ekvivalent troska$^1$. Toto slovenské slovo sa podobne ako české častejšie objavuje v pluráli a má aj približne rovnaké lexikálne významy. Časté je napr. spojenie trosky hradu vo význame zrúcaniny, rumy, ruiny ..., ale sú aj trosky šťastia, ľudská troska ap. (pozri Krátky slovník slovenského jazyka. Bratislava, VEDA, VSAV 1987, s. 470, ďalej KSSJ; podrobnejší, ale z obsahovej stránky totožný výklad hesla troska$^1$ má Slovník slovenského jazyka IV. Bratislava, VSAV 1964, s. 383 - 384, ďalej SSJ IV).

Proti českému slovu struska, ktoré SSČŠV (op. cit., s. 524) v samostatnom hesle vysvetľuje ako „odpadky při tavení rud; tuhé zbytky paliva po spálení; vypouštět z pece strusku; vysokopecní struska; uhelní struska ..." (podrobnejšie pozri Slovník spisovného jazyka českého V. 2. vyd. Praha, Academia 1989, s. 571 - 572), stojí slovenský ekvivalent, a to slovo, ale zároveň, ba častejšie termín, ktorý nás zaujíma, troska$^2$.

SSJ IV (op. cit., s. 594) pri tomto hesle uvádza, že jeho knižná a zastaraná podoba je truska (nie struska!), že ide o hutnícky termín s významom „odpadkový materiál z výroby železa ...", že sa používa napr. v spojení železná troska, zásaditá troska, že jestvuje troskový otvor pece atď. Ak v tomto hesle nie je práve taký terminologický význam, v akom ho niektorý z autorov v odbornom texte potrebuje použiť, nejde o chybu slovníka, lebo je jazykový, nie terminologický, ale názov troska platí. Navyše je v SSJ IV (ibid., s. 309) heslo struska, lenže vysádzané obyčajným typom písma čiže ako nesprávne a jednoznačne sa pri ňom konštatuje, že správne slovo je troska.

Hodno si povšimnúť, že takto primerane hodnotí slovo struska ako neslovenské a nepotrebné slovník, ktorému sa právom vyčítovalo politicky motivované úsilie o umelé a jazykovým zákonitostiam odporujúce zbližovanie češtiny a slovenčiny. Z toho okrem iného rezultuje, že slovo struska v slovnej zásobe spisovnej slovenčiny ani ako obyčajné, ani ako termín nikdy nebolo.

Doterajšie úvahy v plnom rozsahu potvrdzuje aj Česko-slovenský slovník (Bratislava, VEDA, VSAV 1979, s. 535 a 578), ako aj Slovensko-český slovník Ž. Gašparíkovej a A. Kamiša (Praha, SPN 1967, s. 630).

Očakávaná námietka, podľa ktorej nie sú homonymá ako termíny veľmi vhodné, je závažnejšia. To isté možno tvrdiť aj o polysémantických termínoch (porovnaj napr. morfológia - termín v botanike, geológii, lingvistike a i., asimilácia - v biológii, sociológii, lingvistike a i.), lebo pri homonymách aj pri polysémantických termínoch je jednoznačnosť a presnosť termínu naozaj oslabená. Lenže prirodzeného jazyka (slovenčina nie je výnimkou) bez homonymie a polysémie niet. Termín je vždy súčasťou istého systému termínov, a tak podľa ďalších termínov v odbornom texte je vždy jasné, z ktorej vednej, technickej či inej oblasti termín pochádza. Preto námietky takého druhu, že čitateľa môže zmiasť, či je v texte reč o troske ako o úbohom človekovi, alebo o látke, o ktorú nám ide, nemožno brať vážne. Mätúce, dvojzmyselné texty sa tvoria zámerne, ale to už je záležitosť hry s jazykom, napr. enigmatiky.

Stotožňovanie profesionálneho slangu, t. j. prostriedkov a spôsobov vyjadrovania, ktoré sú prirodzené a vhodné iba na komunikáciu v úzkom kruhu odborníkov jednej špecializácie, s vedecko-náučným štýlom je dosť všeobecný jav, ale nedotýka sa len sféry geologických vied. Časť používateľov nevhodného a neprijateľného pseudotermínu struska v slovenských textoch naozaj môže trpieť falošnou predstavou, že ten, kto hovorí, a najmä píše troska, obchádza odbornú terminológiu.

Zhŕňame. V spisovnej slovenčine sú dve slová (homonymá) v podobe troska. Slovo troska$^1$ má význam „zvyšok, zvyšky niečoho zničeného ...", troska$^2$ s významom „odpad pri tavení rúd ap." sa používa jednak bežne, jednak ako odborný názov čiže termín a v slovenských textoch ho v nijakom prípade neslobodno nahrádzať českým slovom struska.

*P. Kušnír*

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