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# Geochemical characteristic of Goliam Bukovets mine tailings impoundment, Chiprovtsi mining area, NW Bulgaria

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Â. Ìëàäåíîâà, Ç. Çëàòåâ. 2004. *Ãåîõèìè÷íà õàðàêòåðèñòèêà íà óòàéêîõðàíèëèùå Ãîëÿì Áóêîâåö, ×èïðîâñêè ìèíåí ðàéîí, ÑÇ Áúëãàðèÿ. – Ñïèñ. Áúëã. Ãåîë. ä-âî, 65*, 1-3, 141-150.

**Ðåçþìå.** Óòàéêîõðàíèëèùå Ãîëÿì Áóêîâåö å îñíîâíîòî äåïî çà ñúõðàíåíèå íà òâúðäèÿ îòïàäúê îò ïðåðàáîòêàòà íà ðóäèòå îò òðè òèïà íàõîäèùà â ×èïðîâñêèÿ ðóäåí ðàéîí. Ïî ðàçëè÷íî âðåìå è â ðàçëè÷åí îáåì òóê ñà íàòðóïâàíè îòïàäú÷íèòå ïðîäóêòè îò ïðåðàáîòêàòà íà Pb-Zn-Ag-Fe ðóäè îò íàõîäèùå ×èïðîâöè, Au-ïîëèìåòàëíèòå ðóäè îò íàõîäèùå Ãîâåæäà è Fe ðóäè îò íàõîäèùå Ìàðòèíîâî.

Îêèñëåíèåòî íà ñóëôèäèòå â ìèííèòå ðàéîíè å âàæåí ïðîáëåì ïîðàäè êèñåëèííîòî äðåíèðàíå, êîåòî òå ïðåäèçâèêâàò è îñâîáîæäàâàíåòî íà ïîòåíöèàëíî òîêñè÷íè åëåìåíòè. Çàòîâà äàííèòå çà ìèíåðàëíèÿ è õèìè÷íèÿ ñúñòàâ íà óòàéêîõðàíèëèùå Ãîëÿì Áóêîâåö ïîçâîëÿâàò äà ñå íàïðàâè ðåàëíà îöåíêà íà ðèñêà, êîéòî ïðåäèçâèêâàò åëåìåíòèòå, òúé êàòî òîêñè÷íîñòòà è ïîäâèæíîñòòà èì ñå ïðîìåíÿ â çàâèñèìîñò îò îêñèäíîòî ñúñòîÿíèå è åêîëîãè÷íàòà îáñòàíîâêà.

Ïîâúðõíîñòíîòî îïðîáâàíå íà òâúðäèÿ îòïàäúê å èçâúðøåíî ðú÷íî ïî äâàíàäåñåò ïðîôèëà ïðåç 20 m, ïðåñè÷àùè ãî ïî äúëãàòà îñ. Âåðòèêàëíîòî îïðîáâàíå å ïðîâåäåíî ðú÷íî ïðåç 0,25 cm íà äúëáî÷èíà äî 1,5 m â òðè ðàçëè÷íè òî÷êè â ãðàíóëîìåòðè÷íî ðàçëè÷íèòå ÷àñòè íà óòàéíèêà.

Ìèíåðàëíèÿò ñúñòàâ íà óòàéêàòà ñå îïðåäåëÿ ãëàâíî îò ñúñòàâà íà âìåñòâàùèòå ñêàëè è íà èçïóñíàòèòå îò ôëîòàöèÿòà ðóäíè ìèíåðàëè. Òå ñà îñíîâíè ôàêòîðè çà ïðîöåñèòå, êîèòî ñå èçâúðøâàò â óòàéêàòà. Ñ ðåíòãåíîôàçîâ àíàëèç âúâ âñè÷êè ïðîáè ñà óñòàíîâåíè êàëöèò, ñèäåðèò, êâàðö, õëîðèò, àìôèáîë è ðÿäêî ìàãíåòèò, à îïòè÷íî è ðåäêè çúðíà îò ïèðèò. ×ðåç ICP (AES, AAS) ñà èçñëåäâàíè K, Mg, Ca, Ag, Pb, Zn, Cu, Ni, Fe, Mn, As, Cd, Sb è Au. Çëàòîòî è ñðåáðîòî ñà â íèñêè êîíöåíòðàöèè. ßñíà êîðåëàöèîííà çàâèñèìîñò ñå óñòàíîâÿâà ñàìî çà Ca, Fe, Mg è Mn. Çà îñòàíàëèòå åëåìåíòè âðúçêèòå ñà íåçíà÷èòåëíè. Íå ñå íàáëþäàâà çîíàëíîñò íà óòàéêàòà.

Óòàéêàòà â óòàéêîõðàíèëèùåòî å â íà÷àëåí ñòàäèé íà èçâåòðÿíå ïîðàäè íåîòäàâíàøíîòî ïðåêðàòÿâàíå íà ìèííàòà è îáîãàòèòåëíàòà äåéíîñò â ðàéîíà.

*Êëþ÷îâè äóìè*: ×èïðîâñêè ìèíåí ðàéîí, óòàéêîõðàíèëèùå Ãîëÿì Áóêîâåö, ìèííè îòïàäúöè, ãåîõèìèÿ, ìèíåðàëè.

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**Abstract.** The Goliam Bukovets mine tailings impoundment is the main place for the solid waste storage from the processing of the ore from 3 types of deposits in Chiprovtsi mining area. The waste products from the Pb-Zn-Ag-Fe ore of Chiprovtsi deposit, the Au-base metal ore of Govezhda deposit and the Fe-ore of Martinovo deposit are stored here at different time and in different volume.

Oxidation of sulfides in mining environments is an important problem regarding the acid drainage it induces and the release of potentially toxic elements. Therefore mineralogical and geochemical data concerning Goliam Bukovets mine tailings impoundment enable a realistic evaluation of the risk posed by the elements because its toxicity and mobility varies with oxidation state and chemical environment

Surface sampling of solid tailings was performed manually from twelve profiles along the long axis at each 20 m. Vertical sampling was performed by hand from three pits at each 0.25 m to the depth of 1.50 m in the three granulometrically different parts of the tailings.

The ore composition floated in the factory and the host rocks types determine the mineral composition of the tailings. They are the main agents responsible for the processes in the tailings. Ñalcite, siderite, quartz, chlorite, amphibole and rarely magnetite are established by means of X-ray analysis in all samples. Optically pyrite grains were observed.

The chemical composition was analyzed using ICP (AES, AAS) for K, Mg, Ca, Ag, Pb, Zn, Cu, Ni, Fe, Mn, As, Cd, Sb and Au. The Ag and Au have low concentrations. Only Ca, Fe, Mg and Mn show relatively good correlation. The rest of elements do not show any correlation. Several factors contribute to the lack of tailing zonality.

The hypergene alteration of Goliam Bukovets mine tailings is in its early stage because of the recently finish of mining and processing activity in the region.

*Key words*: Chiprovtsi mining area, Goliam Bukovets impoundment, mine tailings, geochemistry, minerals.

## Introduction

In NW Bulgaria the mining activity is known from the Roman times. The modern mining has been active for about 50 years in the second half of the last century. The ecological problems, however, increase in the last 20 years after the closing of the part of the mines and accumulation of tones of waste in tailings impoundments and piles. Many of these wastes are now a source of low-quality drainage waters. The regions with former mining activity are now polluted with toxic metals, as As, Pb, Zn, Cd, and Sb and the transport of the products of sulfide oxidation will continue through the tailings or underlying materials for several decades. Therefore the interest in research related to mine waste remediation increases. The knowledge of tailings mineralogical and geochemical composition is the main clue to the tailings management.

Mining activity in Chiprovtsi region left waste rock dumps and 3.5 millions tones waste stored in two tailings impoundments. The older one is Mechi Dol impoundment with 500 thousands tones of tailings.

The Goliam Bukovets mine tailings impoundment is the bigger one and was selected for a detailed study because it is the main place for the waste storage from metal production at the former Ch. Mihaylov washery in Chiprovtsi mining area. At the time of sampling the tailings were dry, without any cover and thus facilitating the oxidation and weathering because of the exposure to the atmosphere and moisture and dispersing of waste through the wind.

In this paper we present the results of the investigation of Goliam Bukovets tailings, focusing on the geochemical and mineralogical characteristics of the waste products at the surface and near the surface.

The preliminary results of this study have been reported at the Annual scientific conference of Bulgarian Geological Association in 2002 (Zlatev, Mladenova, 2002).

## Description of the tailings and the studied area

Goliam Bukovets tailings impoundment is situated in Chiprovtsi mining area in Western Balkan Mountain, NW Bulgaria (Fig. 1).

The mining area is situated at an altitude of 500 m. The mean annual precipitation in the region is 756 mm/m$^2$ per year with maximum in the spring and minimum in the autumn (Koleva, Peneva, 1990). The mean temperature in the area is 10.4$^o$C (Climatic reference book…, 1983). The spring is wet and the winter is mild. The vegetation consists mostly of deciduous forest. The major soil type in the area is strongly eroded gray forest soil (Koinov et al., 1998).

The tailings impoundment occupies a natural negative relief. Its surface is approximately 0.6 km$^2$ and its volume is around à 30 million tones. The maximal depth is around 100 m. The bedrock in the area consists mostly of the rocks of the metamorphic diabase-phillitic complex (DPC) (Nikolaev, Tonev, 1961). It comprises an alternation of diabase, diabase tuffs, phillites, marbles, chlorite-sericite- and quartz-chlorite schist and diorite porphyrite. Diabase tuffs and phillites are the most widespread rocks of this complex. The bedrocks are eroded and fractured on the surface. The wall of the tailings impoundment is built up from the massive waste produced by the dry magnetic separation of the iron ore in Martinovo factory (Vesselinov et al., 1996). The tailings were uncovered until 2001.

The Goliam Bukovets impoundment stores the waste products from 3 different types of deposits in the region:

• Tailings from Govezhda gold deposit are stored in Goliam Bukovets impoundment in the period of its operation between 1950-1992.

• Martinovo magnetite mine was operated from 1962 to the beginning of 1999. The material from this mine is stored in Goliam Bukovets mine tailings after 1980.

• The Chiprovtsi deposit was operated between 1951-1996. All tailings are deposited in Goliam Bukovets.

So the Goliam Bukovets mine tailings stores mainly the waste from Chiprovtsi deposit. The upper layer is composed only from Chiprovtsi deposit waste because it was the last closed mine in the region. The waste material is entered from 12 pipes situated on the eastern wall of the tailings impoundment and from one pipe in the northern part (Fig. 1). Tailings are transported and deposited in water suspension so a natural granulometric separation in the impoundment is established. Some sedimentary structures as stratification and graded bedding are observed. In the eastern part where the pipes are situated the material has particle size of sand (20-200 μm) and in the western the material fall within particle size for silt (5-20 μm). The tailings in the central part have intermediate size. In the western part of the tailings the surface waters have produced a pond with seasonally varying volume. The streams and brooks support its existence.

## Sampling and analytical methods

Sampling of solid tailings was performed mainly in the summer of 2000 manually from surface profiles and from pits dug. Surface sampling was performed at each 20 m from twelve profiles with around 1 kg weight of each sample. The profiles were outlined from the tubes conducting the waste materials (Fig. 1). A total of 190 solid samples were collected. All of 24 samples from the surface profile No 9 were analyzed because this profile crosscuts the central part of the impoundment and is representative for the tailings.

Vertical sampling was performed by hand from three pits at each 0.25 m to the depth of 1.50 m. The manual sampling was located at 3 points of profile No 9 in the three granulometrically-different parts of the tailings.

The samples were dried, homogenized and separated for different analyzes.

The mineral composition of the samples was studied by X-ray diffraction of 30 bulk samples at the labo-

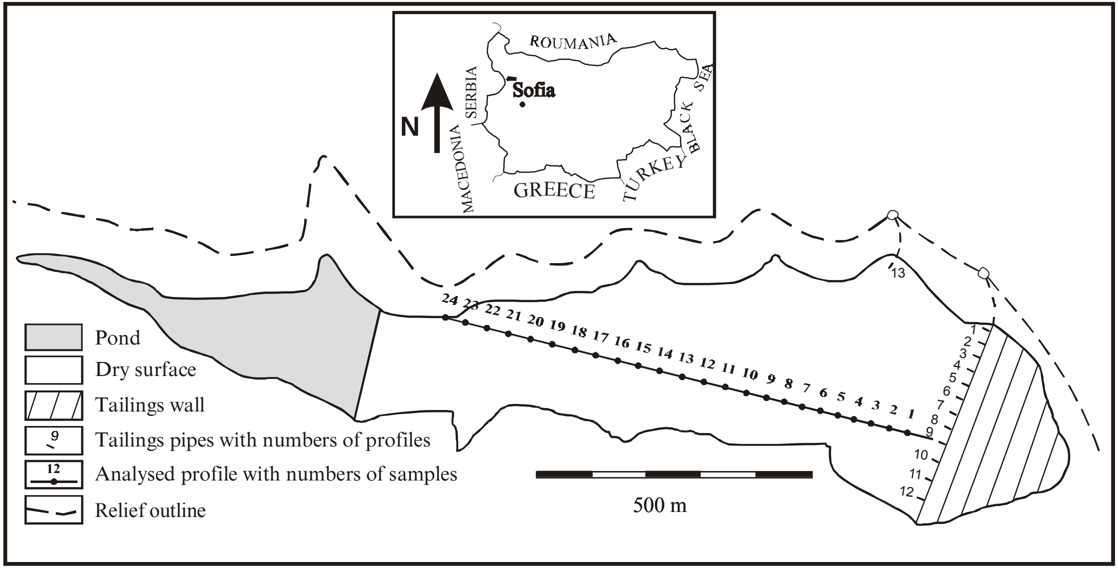


**Fig. 1. Sketch map of Goliam Bukovets tailings impoundment**

**Ôèã 1. Ñõåìàòè÷íà êàðòà íà îòïàäúêîõðàíèëèùå Ãîëÿì Áóêîâåö**

ratory of the Department of Mineralogy, Petrology and Economic Geology at Sofia University with TUR M 62 diffractometer (step width 0.05°, accumulation time 1.5s/step) using $CoK_{\alpha}$ radiation over a 2θ range from 4 to 80°.

All chemical analyzes of solid materials have been made using ICP- AES, AAS. A total of 42 samples were analyzed for K, Mg, Ca, Ag, Pb, Zn, Cu, Ni, Fe, Mn, As, Cd and Sb. All depth samples and six samples from the surface profile were analyzed for Au.

## Mineral composition of the ores

The ore composition floated in the factory is the main agent responsible for the processes in the tailings.

In Chiprovtsi deposit the ore from the main silver-base metal stage was operated. The main minerals are galena, pyrite, tetrahedrite, chalcopyrite and silver sulfosalts. Main gangue minerals are siderite, calcite and chlorite. Marble layer from the diabase – phyllitoide complex (DFK), hosts the ore. At the eastern edge of the ore field fluorite-cinnabar mineralization occurs, but this part was never operated (Dragov, Obretenov, 1974; Atanassov, Pavlov, 1982; Obretenov, 1988).

The ore from the gold deposits of Govezhda ore field consist mainly of arsenopyrite, pyrite and gold as economically important mineral with minor amounts of galena, sphalerite and antimony sulfosalts. The major gangue minerals are quartz and calcite. The ore is hosted by the rocks of the DFK composed mainly of chlorite, amphibole, micas and calcite (Nikolaev, Tonev, 1961; Mladenova et al., 2003b).

In Martinovo deposit the main mineral is magnetite with high Mn content. Pyrrhotite, arsenopyrite, pyrite, hematite, chalcopyrite and löllingite are deposited too. The ore mineralization has typical skarn paragenesis with pyroxenes, garnet, and chlorite. In Martinovo deposit siderite is widely distributed too (Velchev, 1974; Tarasova, 1987; Kanourkov, 1988).

## Mineral composition of the tailings

The tailings minerals can be classified in 4 groups: primary, secondary, tertiary and quaternary minerals (Jambor, Owens, 1993 after Jambor, 1994).

The primary minerals in the tailings are those that constitute the ore and gangue assemblages. They were deposited in the impoundment without any changes other than comminution. The primary minerals derived from the 3 types of deposit in the Chiprovtsi region are calcite, siderite, quartz, chlorite, amphiboles and magnetite. These minerals are established in all samples by X-ray analysis. Fig. 2 represents typical X-ray diffractograms illustrating the mineral assemblages of the three-granulometrically different parts of the impoundment. Sulfide minerals are not detectable in X-ray diffractograms because of their relatively low abundance. Under binocular microscope scarce grains, mainly of pyrite and rare arsenopyrite are observed.

Calcite is the most abundant mineral in the tailings because it is presented as gangue mineral in the three deposits as well as in the host rocks. Siderite occurring as main mineral in Chiprovtsi and Martinovo deposits is the second abundant mineral in the tailings. Quartz is a main gangue mineral in the deposits too and is detected in all samples. Chlorite and amphiboles from the host rocks get into the tailings through the floatation. Magnetite is the main ore mineral in Martinovo deposit. Its presence in the tailings can be explained by its omission by the flotation.

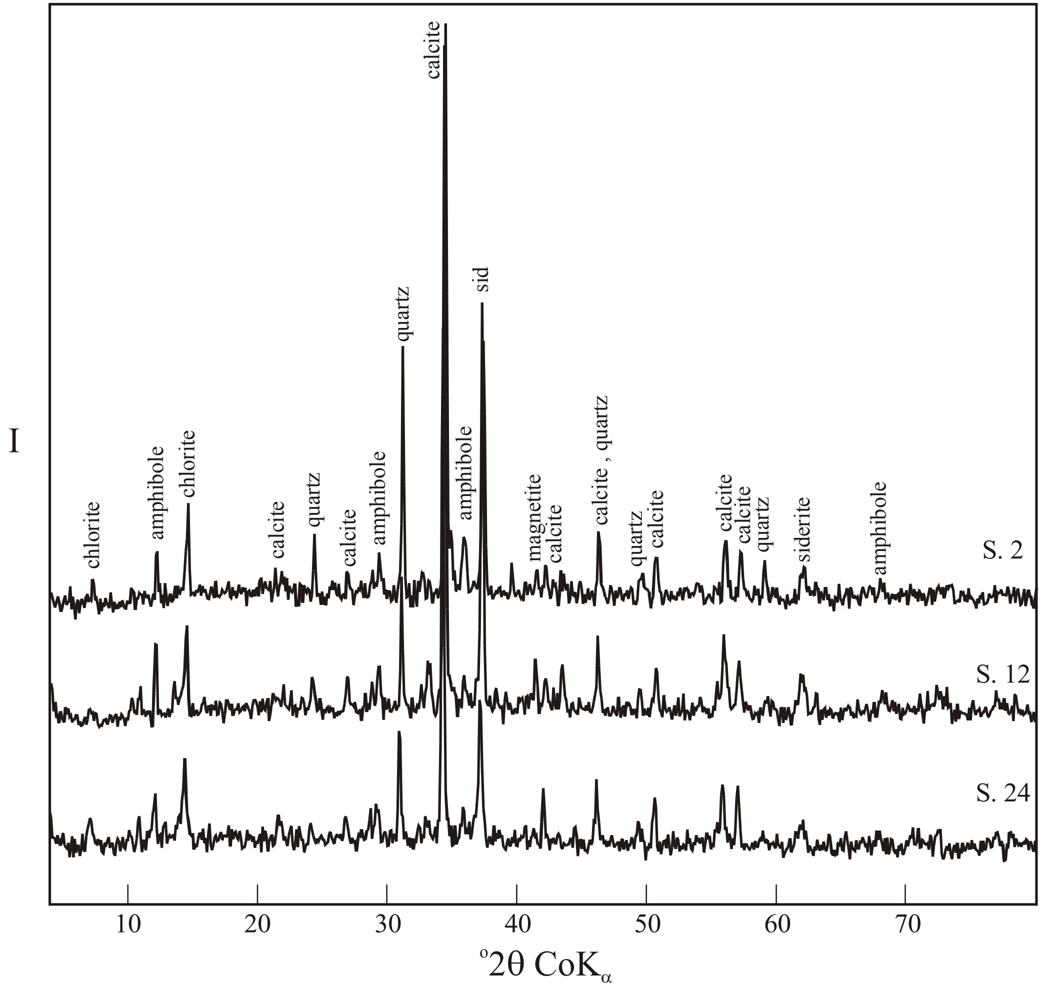


**Fig. 2. X-ray diffractograms of bulk solid tailings samples showing the assemblages in sample 2 (sand size), sample 12 (intermediate part) and sample 24 (silt size) of Goliam Bukovets impoundment**

**Ôèã. 2. Ðåíòãåíîâè äèôðàêòîãðàìè íà âàëîâè ïðîáè îò òâúðäèÿ îòïàäúê, ïîêàçâàùè àñîöèàöèè-òå â îáðàçåö ¹ 2 (ïÿñú÷íà ÷àñò), îáðàçåö ¹ 12 (ìåæäèííà ÷àñò) è îáðàçåö ¹ 24 (ãëèíåñòà ÷àñò) íà îòïàäúêîõðàíèëèùå Ãîëÿì Áóêîâåö**

From the secondary minerals that form within the Goliam Bukovets impoundment at and near the tailings-impoundment surface only gypsum is detected.

Tertiary minerals that crystallize after the tailings samples have been removed from the environment of the impoundment and quaternary minerals that form by surface oxidation during storage of the dried sample are not observed.

## Geochemical characteristic

The chemical composition of the solid tailings is summarized in Tables 1 and 2 and illustrated in Fig. 3 and 4.

Ca, Fe, Mg and Mn have high concentrations and show relatively good correlation along the whole surface profile (Fig. 3a, 3b). This correlation is not well expressed in the depth (Fig. 4a, 4b). The presence of Ca and Fe is due to the abundance of calcite, siderite and magnetite in the tailings. Chlorite and amphibole from the host rocks contain both the elements too. The significant content of Mg is due to its presence in calcite and chlorite from the host rock and gangue assemblages. The high Mn concentration in the tailings is due to the rhodochrosite component in siderite and its presence as trace element in magnetite (Velchev, 1974). In some ore bodies from Chiprovtsi deposit the Mn content reaches 8-9% (Obretenov, 1988).

The K content is due to the minerals of the host rocks and its concentrations don't vary significantly in the samples.

Pb, Zn, Cu and Cd have relatively invariable concentrations and extremely high contents are established only in single samples (Fig. 3d, 4d). Although Cd is concentrated in sphalerite, no correlation between Zn and Cd is observed (Fig. 3e, 4e).

Ag shows strong fluctuation in the investigated surface profile. In general it has low concentrations, in most samples under the detection limit of 2 ppm, but in some samples the contents are several times higher. In some cases a correlation between Ag and Pb and be-

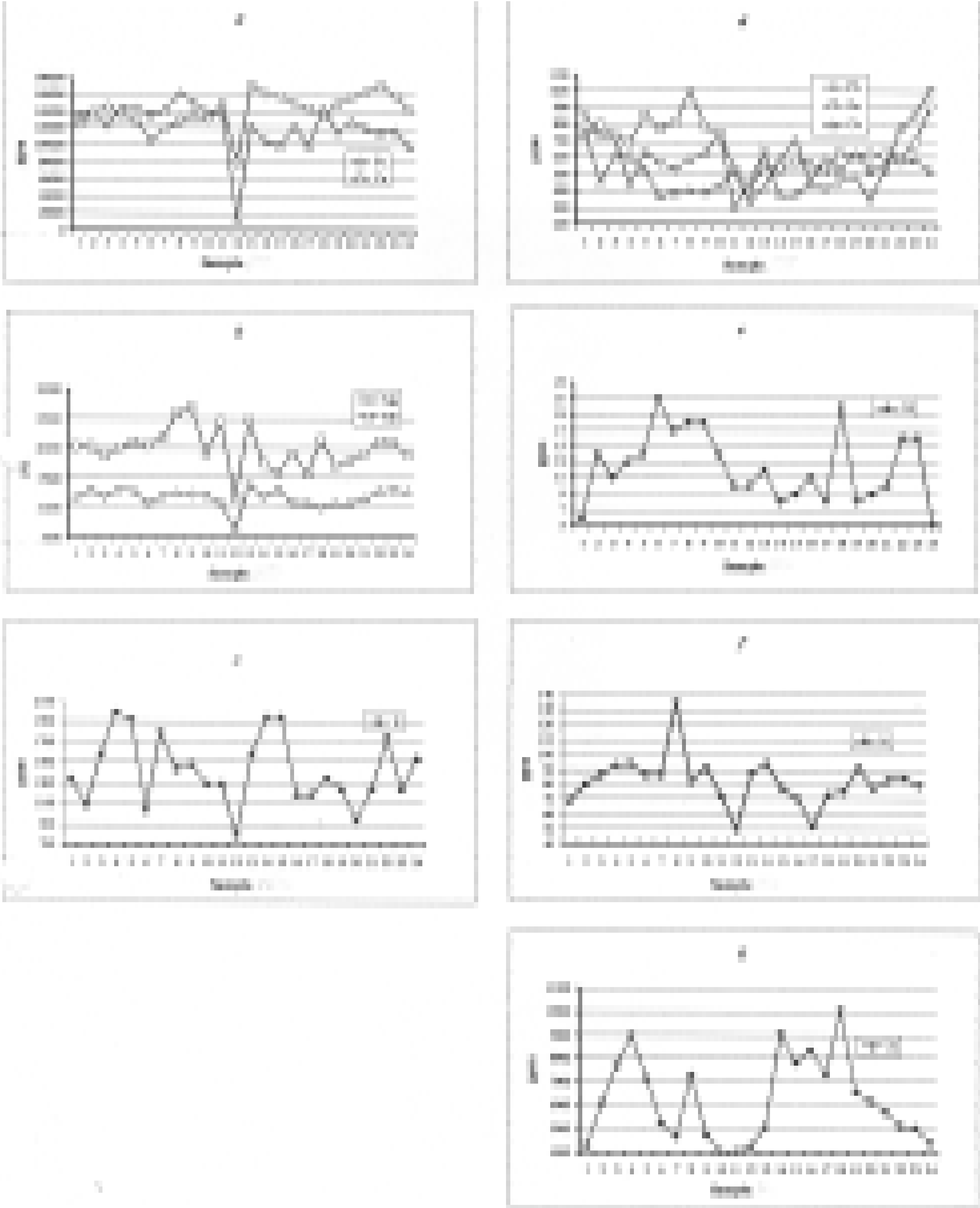

**Fig. 3 (a-g). Concentrations of analyzed elements in surface samples along the profile 9**

**Ôèã. 3 (a-g). Êîíöåíòðàöèÿ íà àíàëèçèðàíèòå åëåìåíòè â ïîâúðõíîñòíèòå îáðàçöè ïî ïðîôèë ¹ 9**

Table 1
*Concentrations of elements in samples from surface profile 9*

Таблица 1
*Концентрация на елементите в пробите от повърхностния профил № 9*

| Sample | Elements, ppm | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pb | Zn | Cu | Ni | Fe% | Mn% | As% | Cd | Sb | K% | Mg% | Ca% | Ag | Au |
| 1 | 849 | 731 | 748 | 69 | 13.60 | 2.04 | 0.43 | 6 | <10 | 0.13 | 1.18 | 12.40 | <2 | n.a. |
| 2 | 732 | 792 | 457 | 80 | 13.60 | 2.04 | 0.61 | 14 | <10 | 0.11 | 1.31 | 13.90 | <2 | 0.35 |
| 3 | 721 | 731 | 614 | 86 | 12.40 | 1.86 | 0.77 | 11 | <10 | 0.16 | 1.21 | 14.50 | 16 | n.a. |
| 4 | 433 | 685 | 606 | 93 | 14.40 | 2.01 | 0.90 | 13 | <10 | 0.20 | 1.31 | 13.70 | <2 | n.a. |
| 5 | 630 | 859 | 526 | 94 | 14.50 | 2.11 | 0.72 | 14 | <10 | 0.19 | 1.29 | 12.80 | <2 | n.a. |
| 6 | 572 | 772 | 367 | 86 | 13.60 | 2.05 | 0.52 | 21 | 76 | 0.10 | 1.08 | 10.70 | 12 | 2.03 |
| 7 | 540 | 815 | 385 | 86 | 14.10 | 2.17 | 0.47 | 17 | <10 | 0.18 | 1.20 | 11.80 | <2 | n.a. |
| 8 | 582 | 1001 | 402 | 135 | 16.10 | 2.59 | 0.73 | 18 | <10 | 0.14 | 1.25 | 13.00 | 21 | n.a. |
| 9 | 625 | 787 | 396 | 82 | 15.20 | 2.69 | 0.48 | 18 | <10 | 0.15 | 1.23 | 13.40 | 18 | n.a. |
| 10 | 753 | 744 | 428 | 91 | 13.90 | 1.92 | 0.40 | 14 | <10 | 0.13 | 1.23 | 13.20 | <2 | 0.44 |
| 11 | 295 | 533 | 518 | 72 | 13.80 | 2.45 | 0.40 | 10 | <10 | 0.13 | 1.09 | 14.90 | <2 | n.a. |
| 12 | 444 | 404 | 334 | 50 | 12.37 | 1.17 | 0.43 | 10 | <10 | 0.08 | 0.63 | 7.95 | <2 | n.a. |
| 13 | 636 | 556 | 427 | 87 | 12.20 | 2.47 | 0.51 | 12 | <10 | 0.16 | 1.38 | 17.10 | <2 | n.a. |
| 14 | 369 | 543 | 589 | 94 | 10.40 | 1.74 | 0.91 | 8 | 26 | 0.19 | 1.20 | 16.10 | 44 | 0.34 |
| 15 | 369 | 576 | 712 | 77 | 10.00 | 1.60 | 0.78 | 9 | 46 | 0.19 | 1.31 | 15.90 | <2 | n.a. |
| 16 | 444 | 570 | 458 | 70 | 12.20 | 1.92 | 0.84 | 11 | <10 | 0.12 | 1.09 | 15.00 | <2 | n.a. |
| 17 | 412 | 526 | 601 | 52 | 9.90 | 1.56 | 0.73 | 8 | <10 | 0.12 | 1.07 | 14.50 | <2 | n.a. |
| 18 | 465 | 624 | 525 | 73 | 14.40 | 2.15 | 1.01 | 20 | 81 | 0.13 | 1.01 | 13.50 | <2 | 0.43 |
| 19 | 487 | 611 | 625 | 75 | 11.70 | 1.72 | 0.66 | 8 | <10 | 0.12 | 1.07 | 14.90 | <2 | n.a. |
| 20 | 348 | 617 | 529 | 91 | 12.80 | 1.79 | 0.62 | 9 | <10 | 0.09 | 1.06 | 15.60 | 8 | n.a. |
| 21 | 534 | 619 | 560 | 77 | 12.00 | 1.92 | 0.57 | 10 | <10 | 0.12 | 1.14 | 16.30 | <2 | n.a. |
| 22 | 774 | 600 | 585 | 83 | 11.60 | 2.12 | 0.51 | 16 | <10 | 0.17 | 1.27 | 17.10 | <2 | 0.29 |
| 23 | 859 | 689 | 590 | 84 | 11.80 | 2.09 | 0.51 | 16 | <10 | 0.12 | 1.31 | 16.00 | <2 | n.a. |
| 24 | 1019 | 912 | 522 | 79 | 9.87 | 1.89 | 0.44 | 5 | <10 | 0.15 | 1.25 | 14.20 | 10 | n.a. |

Abbreviation: n.a. - not analysed
Съкращение: n.a. - не е анализирано

tween Ag and Sb is established. Probably it is due to sulfosalts in the samples. Various silver and lead-silver sulfoantimonides are established in the deposits of Govezhda ore field (pyrargyrite, proustite, owyheeite $Ag_{3+x}Pb_{10-2x}Sb_{11+x}S_{28}$) (Mladenova et al., 2003b) and in Chiprovtsi deposit (tetrahedrite with Ag) (Atanassov, Pavlov, 1982). The single correlation of Ag and Zn in sample No 8 is insufficient for making conclusions (Table 1). The Ag content is higher in depth and varies from 4 to 23.3 ppm (Table 2).

Sb shows enrichment in some surface samples but as a rule its concentration is under the detection limit of 10 ppm (Table 1). It is impossible to find strong correlations. In the samples with high Sb content parallel enrichment of Cu content is observed (sample No 15) probably due to the presence of sulphosalt minerals (bournonite, boulangerite tetrahedrite) deposited in these deposits (Mladenova, 2003b), or is due to the presence of stibnite. In other samples no correlation could be found (Table 1, sample No 18). The Sb concentration in depth is more constant (Table 2).

As has high concentration in all samples from the surface as well as in depth to 1.5 m. Its concentration is in the range 0.40-1% at the surface (Table 1, Fig. 3g). Its content is remarkably higher in the depth profile in the sand part (Table 2, Fig. 4f). The main As-bearing mineral is arsenopyrite. It is deposited in the three deposits but as main mineral only in the deposits of Govezhda ore field. Fahl ore (tennantite) and löllingite from Chiprovtsi deposit and some sulfides with As as trace element from Chiprovtsi and Martinovo deposits contribute to the high As concentrations too (Atanassov, Pavlov, 1982; Obretenov, 1988; Kerestedjian et al., 1999).

Ni is found in all samples (Tables 1 and 2; Fig. 3f and 4e). The main Ni-bearing mineral is the fine-grained and colloform pyrite from the Chiprovtsi deposit and pyrrhotite from the Martinovo deposit (Atanassov, Pavlov, 1982; Kanourkov, 1988).

Au is analyzed only in 6 samples from the surface and in all depth samples. Its concentrations are lower than 1 ppm and only in one sample it has content of

Table 2
*Concentrations of elements in depth at point 2, 12 and 24 of the surface profile 9*

Таблица 2
*Концентрация на елементите в дълбочина в точки 2, 12 и 24 на повърхностния профил № 9*

| Sample | Elements, ppm | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Au | Ag | Pb | Zn | Cu | Ni | Fe % | Mn % | As % | Cd | Sb | K % | Mg % | Ca % |
| 2-surface | 0.36 | <2 | 188 | 626 | 596 | 73.00 | 8.10 | 0.81 | 0.84 | 14.00 | <10 | 0.15 | 1.08 | 13.20 |
| 2-0.25m | 0.39 | 14 | 779 | 990 | 482 | 16.70 | 15.7 | 2.46 | 1.40 | 15.50 | 29 | 0.20 | 1.53 | 17.32 |
| 2-0.50m | 0.21 | 11.60 | 665 | 353 | 522 | 22.80 | 12.81 | 2.08 | 1.08 | 8.80 | 39 | 0.20 | 1.97 | 19.49 |
| 2-0.75m | 0.20 | 16.60 | 781 | 348 | 377 | 19.70 | 16.00 | 2.50 | 1.60 | 11.30 | 32 | 0.23 | 1.67 | 15.51 |
| 2-1.00m | 0.04 | 23.30 | 1089 | 288 | 354 | 18.80 | 18.10 | 3.63 | 0.77 | 10.20 | 19 | 0.19 | 1.93 | 16.13 |
| 2-1.25m | 0.04 | 15.60 | 495 | 193 | 578 | 19.90 | 14.10 | 2.14 | 1.34 | 9.30 | 17 | 0.26 | 1.62 | 18.90 |
| 2-1.50m | 0.31 | 18.20 | 1066 | 384 | 555 | 25.40 | 19.10 | 3.16 | 2.18 | 12.50 | 27 | 0.25 | 1.98 | 12.42 |
| 12-surface | n.a. | 21.00 | 167 | 628 | 919 | 86.00 | 8.94 | 0.95 | 0.84 | 10.00 | <10 | 0.22 | 1.57 | 16.70 |
| 12-0.25m | n.d. | 13.00 | 930 | 350 | 331 | 16.90 | 14.00 | 2.02 | 0.83 | 9.70 | 18 | 0.18 | 1.66 | 20.58 |
| 12-0.50m | n.d. | 11.40 | 644 | 662 | 391 | 15.90 | 14.40 | 2.14 | 0.83 | 13.50 | 17 | 0.17 | 1.78 | 17.78 |
| 12-0.75m | 0.07 | 14.50 | 1541 | 790 | 296 | 19.50 | 14.20 | 2.77 | 0.86 | 14.00 | 17 | 0.17 | 1.62 | 19.31 |
| 12-1.00m | 0.05 | 7.50 | 646 | 399 | 609 | 17.40 | 12.70 | 1.89 | 1.04 | 9.80 | 8 | 0.25 | 3.97 | 28.40 |
| 12-1.25m | 0.15 | 4.50 | 343 | 182 | 779 | 18.80 | 11.10 | 1.67 | 0.89 | 7.40 | 12 | 0.31 | 1.71 | 20.27 |
| 12-1.50m | n.d. | 15.70 | 786 | 453 | 382 | 19.50 | 15.50 | 2.93 | 1.07 | 10.20 | 11 | 0.23 | 1.87 | 17.63 |
| 24-surface | n.a. | 10.00 | 1019 | 912 | 522 | 79.00 | 9.87 | 1.89 | 0.44 | 5.00 | <10 | 0.15 | 1.25 | 14.20 |
| 24-0.25m | 0.08 | 11.20 | 862 | 404 | 485 | 15.00 | 11.90 | 1.78 | 0.75 | 8.90 | 25 | 0.23 | 1.73 | 18.89 |
| 24-0.50m | n.d. | 9.30 | 610 | 478 | 374 | 14.10 | 13.60 | 2.00 | 0.65 | 11.20 | 10 | 0.19 | 1.51 | 18.70 |
| 24-0.75m | 0.10 | 8.90 | 711 | 423 | 497 | 21.10 | 12.80 | 2.04 | 0.76 | 10.10 | 15 | 0.25 | 1.84 | 20.74 |
| 24-1.00m | 0.12 | 11.60 | 811 | 390 | 463 | 15.00 | 12.30 | 2.24 | 0.51 | 9.30 | 13 | 0.23 | 2.94 | 21.35 |
| 24-1.25m | 0.13 | 6.00 | 514 | 495 | 540 | 13.60 | 12.00 | 1.72 | 0.76 | 11.20 | 13 | 0.22 | 1.58 | 20.95 |
| 24-1.50m | 0.11 | 12.00 | 722 | 475 | 622 | 19.00 | 11.50 | 1.93 | 0.74 | 7.90 | 16 | 0.25 | 1.84 | 21.03 |

Abbreviations: n.a. - not analysed; n.d. - not detected
Съкращения: n.a. - не е анализирано; n.d. - не е установено

2.03 ppm (Tables 1 and 2). Probably a grain of native gold is fallen in that sample. Native gold with silver content and electrum are abundantly presented in Govezhda deposit (Velchev, Vassilev, 1966; Mladenova et al., 2003a). The insufficient data for gold concentrations in the tailings don't permit to find correlation between Au and Ag at the surface (Table 2). The depth samples don't show any correlation with Ag (Fig. 4d). Probably the reason is that Ag content is mainly due to Ag-bearing sulfides.

## Geochemical zonality

When making conclusions concerning some spatial correlations and regularities of the tailings mineral and chemical compositions several factors and processes have the responsibility.

During the live of the Goliam Bukovets impoundment the wastes of three different types of deposits were stored here. Hence the mine proceedings and flotation schedule determine some differences in the chemical and mineralogical compositions. The type of floated ore influences the differences mainly in depth. Besides, additional factors contribute to the lack of zonality too:

• First, the sampling has been performed only few years after the deposition of material.

• Second, the way of entering of material from two directions as pulp contributes the mixing and homogenizing of tailings during its deposition in the impoundment. (Vesselinov et al., 1996).

• Third, the streams in the region contribute mixing and homogenization of the material at the surface of the tailings.

Some zones, however, could be drawn. Besides the ore composition, probably graded bedding due to particle size and weight differences of the existing minerals occurs. Pb, Zn and Cu show some enrichment in depth of 0.75-1.25 m, and Ca, Mg, Fe and Mn have the same concentrations in all samples. The elements show different concentrations in the granulometrically different parts of the deposited materials. Pb, Zn and Cu show maximal concentrations in the sand and silt part and some decrease in the intermediate part of the impoundment. The rest of elements show strong fluctuations.

Hence the mineralogical and geochemical data for Goliam Bukovets mine tailings reflect the type of floated ores, probably affected in some extent by sedimentary processes and climate factors as rainfalls and streams.

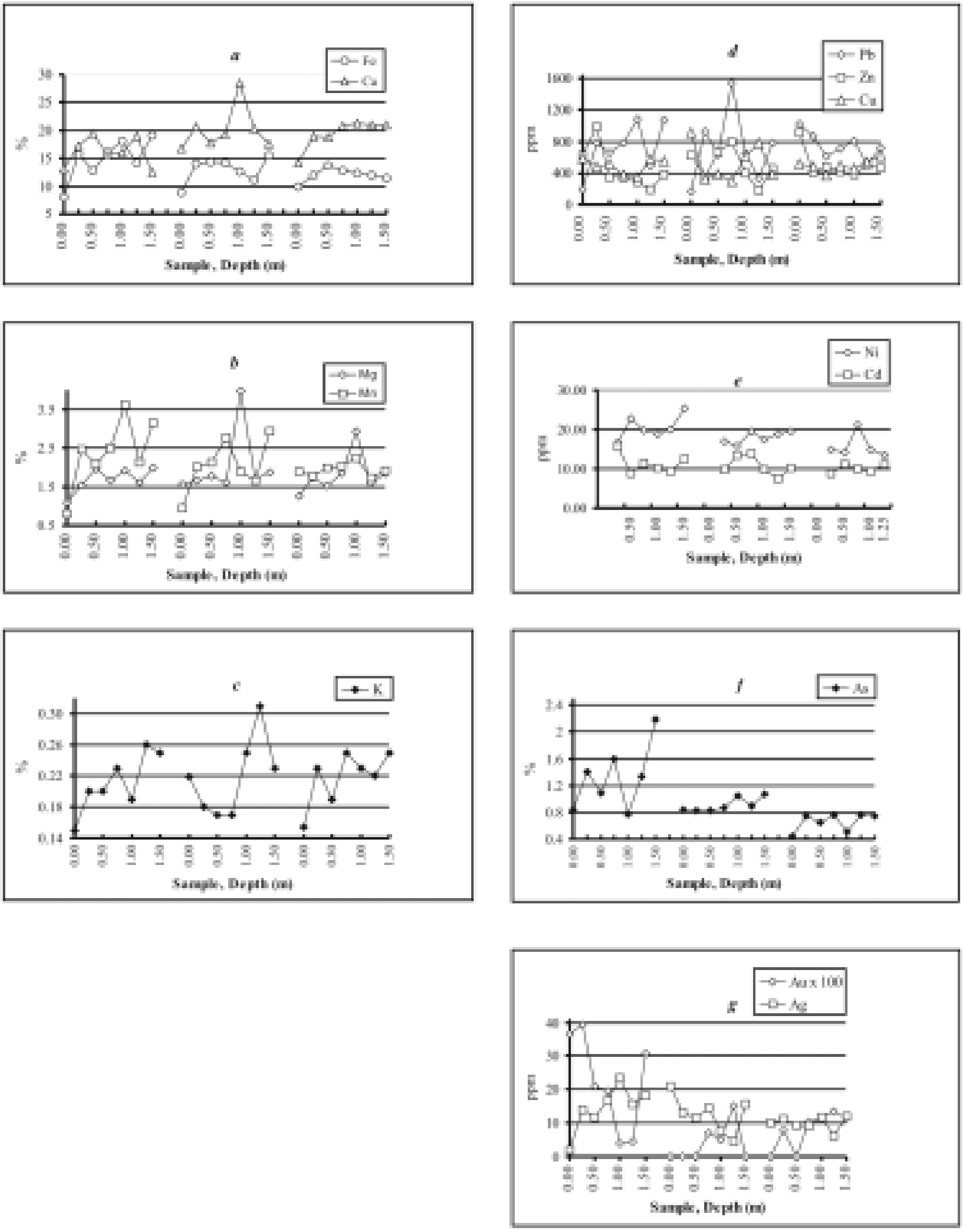


**Fig. 4 (a-g). Concentration of analyzed elements in depth to 1.5 m. Each chart is separated in three parts, which represent (from left to right) the analyzed samples at points 2, 12 and 24 on the profile 9**

**Фиг. 4 (a-g). Концентрация на анализираните елементи на дълбочина до 1,5 m. Всяка диаграма е разделена на три части, които представят (отляво надясно) анализираните проби в точки 2, 12 и 24 върху профил № 9**

## Hypergene weathering

Despite the small particle size of the material and the climate peculiarities of the region, the hypergene alteration of Goliam Bukovets mine tailings is in its early stage. By means of X-ray some secondary minerals have been detected. With naked eye it is seen that fractured surfaces exposed to water and air are covered with thin film of alteration products and only at some surfaces coating from secondary minerals are observed. Pyrite commonly develops alteration rim consisting of limonite.

Experimental investigations on minerals that constitute the ore and gangue assemblages show that Goliam Bukovets impoundment stores very susceptible to air- and water-weathering minerals. Although the development of predictive models to describe the oxidation process is specific for each tailings impoundment, some environmental factors and laboratory results can help to the modelling of this complex process.

Muir et al. (1993) determined by XPS (X-ray photoelectron spectroscopy) è AES (Auger electron spectroscopy) that one-day exposure of fresh arsenopyrite in air increased the concentration of arsenic and oxygen at the surface. At the upper 20-30Å about 35% of arsenic appeared as $As^{3+}$ and $As^{5+}$ oxides, and only a minor amount $Fe^{2+}$ was oxidized to $Fe^{3+}$. In water, however, the mineral underwent oxidation dissolution.

The alteration of pyrite surface is more rapid. Within minutes of exposure, iron sulfate formed on fresh fractured surfaces, whereas iron oxide formed on abraded surfaces. Fractured surfaces exposed to water led to the formation of iron oxide, but no sulfate (Buckley, Woods, 1987). Two oxidants are important by the alteration of pyrite: oxygen and ferric iron ($Fe^{3+}$) (Nicholson, 1994).

Upon exposure to air the initial products of oxidation of galena are lead hydroxide, oxide, and carbonate, and extended exposure to air results in the formation of sulfate (Buckley, Woods, 1984).

The weathering and dissolution of these minerals presented in dumps as well in the tailings is the reason of the pollution of waters and soils in the region.

## Discussion

Oxidation of sulfides in mining environments is an important problem regarding the acid drainage it induces and the release of potentially toxic elements (Alpers et al., 1994). A realistic evaluation of the risk posed by the elements in the tailings depends on accurate determination of different element speciation, because its toxicity and mobility varies with oxidation state and chemical environment.

The presence of carbonate minerals in the tailings is very important. When carbonate minerals as calcite, siderite, dolomite and ankerite are present in the waste, their dissolution helps to prevent the formation of low-pH drainage from the waste containment areas (Blowes, Ptacek, 1994). Solubility differences between calcite and siderite lead to calcite dissolution and siderite precipitation during acid neutralization (Al et al., 2000). On the other hand, the surfaces of carbonate minerals are highly, reactive (Stipp, Hochella, 1991) and co-precipitation and adsorption reactions at carbonate-mineral surfaces are likely to influence the concentrations of dissolved metals in these systems (Morin, Cherry, 1986; Bruno et al., 1998).

The remedial programs focus of sulfide-oxidation control by creating of oxygen-diffusion barriers. Although the early stage of weathering of tailings in Goliam Bukovets impoundment the soils and water in the region are polluted mainly with As and Pb. From the beginning of 2000 the Chiprovtsi mining area is an object of different programs in order to resolve the ecological problems. In 2001 Goliam Bukovets tailings impoundment was covered with coating of an insoluble, non-reactive synthetic precipitate that inhibits oxygen ingress. The ability of these barriers to prevent sulfide oxidation over short time periods is proved but over the longer term (decade to centuries) remains unknown (Jambor et al., 2000).

At the moment the Mechi Dol impoundment in the same area is in process of covering with soil layers and stabilizing of its dams.

Besides the resolve of ecological problems the impoundments conservation in the region will help to preserve the tailings as low-grade raw material for the future.

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