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MINERALOGICAL ANALYSIS OF SAMPLES FROM THE OLD BOR MINE FLOTATION TAILING, REPUBLIC SERBIA

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Abstract. The mineralogical analysis of the samples from the Bor’s mine tailings, which were taken from boreholes, was realized in two stages. As a qualitative ore microscopic and quantitative X-ray structural analysis. About a dozen ore minerals, of higher intensity, were detected by ore microscopic analysis, such as chalcopyrite, magnetite, pyrite, bornite, molybdenite, native gold, etc. Quantitatively, with the help of the scanning-electron microscope, the compositions of all significant ore minerals were determined, from which it should be emphasized that in most of them there are no major deviations from the reference values. For chalcopyrite as the most intense mineral, the copper concentration ranged from 33.24 to 36.33% Cu, iron from 29.78 to 32.13% Fe and sulfur from 32.40 to 35.73% S, while in bornite those concentrations ranged from 61.99 to 64.01% Cu, from 11.40 to 13.01% Fe and from 23.69 to 25.43% S. The quantification of XRD confirmed the presence of pyrite, quartz, nacrite, alunite, anorthite, hornblende and others.

Key words: ore minerals, tailings, Bor mine, quantification and mineralogical analysis.

МИНЕРАЛОШКИ АНАЛИЗИ НА ПРИМЕРОЦИ ОД СТАРОТО ХИДРОЈАЛОВИШТЕ НА РУДНИКОТ БОР, РЕПУБЛИКА СРБИЈА

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Апстракт. Минералошката анализа на примероци од Борските хидројаловишта, кои беа земени од дупчотини, беше реализирана во две етапи. Како квалититативна рудно-микроскопска и квантитативна рендгено-структурна анализа. Околу десетина рудни минерали беа дијагностицирани со рудно-микроскопската анализа, а со понагласен интезитет се халкопирит, магнетит, пирит, борнит, молибденит, самородно злато и други. Квантитативно со помош на Скенинг-електронскиот микроскоп беа одредени составите на сите позначајни рудни минерали од кои треба да се потенцира дека во најголем дел од нив нема некои поголеми отстапувања од стандардните вредности. За халкопиритот како најинтензивен минерал концентрацијата на бакарот се движи од 33.24 до 36.33 % Cu, на железото од 29.78 до 32.13 % Fe и сулфурот од 32.40 до 35.73 % S, додека кај борнитот тие концентрации се движат во опсег од 61.99 до 64.01 % Cu, од 11.40 до 13.01 % Fe и од 23.69 до 25.43 % S. Квантификацијата на XRD го потврди присуството на пирит, кварц, накрит, алунит, анортит, хорнбленда и др.

Клучни зборови: рудни минерали, хидројаловиште, рудник Бор, квантификација и минералошка анализа.

1. Introduction

Tailing dams as storage sites for tailings from active mines, mainly of polymetallic mineral raw materials are usually located near the mines with open pit or underground exploitation and they have long been treated as potential environmental contaminants, but lately as economically potential raw materials, also. The latter is gaining importance in the last few years when the circular economy is looking for added value in many directions, but also in the mineral resources in-situ or in the immediate vicinity of the active mines or those with already completed regular exploitation. Large quantities of processed material are actually stored in those tailings and their quantities are expressed in millions of tons. The duration of the exploitation of the mines directly proportionally affects the size of the tailings or tailings material. The variable degree of utilization of the ore components from the primary ores during the processing, mostly the flotation concentration, contributed to the part of the unused quantities of polymetals and associated components to be deposited in the existing tailings. Most often in the World and in our country the tailings are continuously extended and upgraded, so in today's conditions there is usually a group of old tailings and newer tailings that have their own economic value. That the concentrations of certain metals such as copper, gold, silver, rhenium, palladium, osmium, selenium and especially the group of rare earth elements, can be interesting in the copper tailings as it was shown by the latest studies, where these types of tailings are also called technogenous deposits [1], [2]. Research and studies of the Buchim tailing dam [3] have shown a number of positive results, especially in terms of gold content distributed in 3 horizons within a tailing dam characterized with a 140 million tons of tailings material. The positive influences of the technogenous deposits are noted in the work of [2], as well as in the works of [4], [5] and others. According to the above, in this paper are presented data from the mineralogical study of samples from boreholes drilled in the old tailings of the Bor mining complex. The main motive for this is to contribute to a closer understanding of the positive impacts of the tailings, specifically the old tailings in the mining complex in Bor. The identified mineral species, their intensity and manner of occurrence and preservation open the possibility for further detailed analysis and utilization of these potential raw materials supported by European projects that are active in the last few years.

2. Materials and methods

Within the current ore minerals study of the old Bor old tailing were analyzed samples taken from cores of 6 exploration drill holes preformed at the Field 1 and Field 2. Of the total obtained and shortened specimens, a total of 12 samples from 4 drill holes were evenly selected for the needs of the mineralogical study so that different levels could be enclosed and studied within the drilled area. From those 12 samples, 12 polished sections were made and further treated under study optical microscopes and scanning electron microscope. For the purpose of more complex mineralogical study and quantification of materials from the 12 samples for mineralogical testing we have selected 6 samples for further analysis (two from B-1 and B-2 and one from B-3 and B-4 borehole), but from different levels. Those 6 samples were analyzed at the XRD laboratory of the Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia. Prepared 12 polished sections were previewed on the polarizing optical microscope Zeiss Axiolab Pol in reflected light mode. The chemical compositions of the major mineral phases were determined by scanning electron microscope (SEM). The SEM analyses were recorded on the scanning electron microscopy VEGA3 LMU and INCA Energy 250 Microanalysis System, located at the “Goce Delčev” University in Štip, for quantitative analyses of the samples. First, the samples were cleaned and then a small piece was put on the sample holder with carbon double adhesive tape on it. The sample’s surface was coated with gold on Modular Coater, Quorum Q150R ES and then analyzed in high vacuum mode with more than 0.018 Pa. For SEM, the VegaTC software was used. The energy dispersive X-ray (EDX) system for SEM is a fully quantitative SDD with excellent performance at low and high count rates, which is capable of achieving a resolution better than 125 eV on the MnKα, FKα and CKα peaks. The working distance for X-ray was 15 mm. The SEM-EDS analyses were done on the unpolished surfaces. The quantitive mineralogy of the samples was determined by X-ray diffractometry XRD. A Philips PW3710 X-ray diffractometer was used with Cu-Kα 1.54060 Å radiation generated at 40 kV and 30 mA. The sample was scanned at a rate of 1.2° per minute, over the range of 2–70° (2θ). The diffraction pattern were identified and quantified using X'Pert HighScore Plus 4.8 software and the data from the PAN-ICSD database. Interpretation of all results with adequate software support was performed at University "Goce Delcev" in Stip.

3. General features of the old Bor tailing dam

"Old" Bor flotation tailing have been disposed in the Bor River valley from 1933 to 1987. During the exploitation period tailing was divided into two fields separated by the dumps of sand cyclones. The "Old" Bor Tailing pond consist of Field 1 (smallest) and Field 2 (largest), see Figure 1.

Figure 1. Schematic positions of Bor (Serbia) of tailing dams with an accent to old Bor tailing dam and its drillhole sampling ([6], modified)

The fields together contain 27 million tonnes of tailing [4], [5], [7], [6]. In the past, a dam breakthrough has occurred, indicating instability of the tailing surface and dams. Chemical analyzes of individual and composite well tests were performed by IRM Bor - Laboratory for Chemical and Technical Control, and SGS Bor. Under laboratory conditions, chemical analyzes were performed on Cu and Au. During this period, the total number of samples taken from 13 wells was 470 (Table 1).

Table 1. Mean gold and copper contents per well from the old Bor tailing dam

	Medium content	
Well mark	Au (g/t)	Cu (%)
B-13/2	0,410	0,180
B-15/2	0,470	0,260
B-26/2	0,360	0,220
B-31/2	0,270	0,200
B-35/2	0,350	0,210

Wells drilled in the SATREPS project were analyzed in Canada using a mass spectrometer on 36 elements. Mean contents of Cu, Au, and Ag, by wells, are shown in Table 2.

Table 2. Mean drill hole contents of gold, silver and copper based on individual sample analyses

Well mark	Medium content		
	Au (g/t)	Ag (g/t)	Cu (%)
OT/1-01	0,454	1,844	0,279
OT/1-02	0,481	2,153	0,266

OT/1-03	0,446	1,771	0,285
OT/1-04	0,213	0,961	0,174
OT/1-05	0,333	1,232	0,266
OT/1-06	0,421	5,073	0,360
OT/2-01	0,302	1,676	0,201
OT/2-02	0,244	1,021	0,186

In the technogenic reservoir „Old" Bor's tailing, useful components are gold, silver, and copper. The calculated geological reserves are shown in Table 3.

Table 3. Total reserves by the vertical profile method

Q (t)	**Au (g/t)**	**Au (kg)**	**Ag (g/t)**	**Ag (kg)**	**Cu (%)**	**Cu (t)**
22.322.350	0,530	11.822,88	2,826	63.089,84	0,230	51.302,73

The data from the table for the quantities of copper, gold and silver in the old tailings of the Bor mining complex show that according to the current stock exchange prices of the aforementioned 3 metals the value of these tailings is around one billion and three hundred million dollars, normally these are resource values that need further to be calculated with the possibilities for their extraction and degree of utilization, of course with adequate technological solutions. The conclusion remains that the tailings are technogenous deposits of modern interest.

4. Scanning electron microscope (SEM) analyses

After the microscopic study of the polished sections, a total of 6 samples with details of ore grains were analyzed on the Scanning Electron Microscope in the laboratories of the Faculty of Natural and Technical Sciences at University "Goce Delcev" in Stip. The selection of the individual details that were dealt with for SEM analysis was based on the variety of ore minerals, their compactness, their representative morphological forms and of course their position which enables reliable diagnostics under SEM.

Based on the above criteria we selected globular pyrite and magnetite, relict chalcopyrite, standard magnetite, standard pyrite, molybdenite, bornite and individual grains of native gold as well. Analyzes have shown that the analyzed ore minerals confirm the positive identification under the optical microscope and gave the mineral compositions with some influence on the associated trace minerals standard for minerals of this type.

The associated trace elements found in pyrite, chalcopyrite, magnetite, molybdenite, bornite and native gold are in direct correlation with the standard values offered by the SEM in the process of analysis. Depending on the detection limit of the applied SEM we allow for some error in the percentage representation of some trace elements, however, given the overall analysis and composition of the major elements in the studied minerals, one can rightly conclude that these errors are small and in no way affect the correct provision of the minerals tested. Such ratios can be seen in the attached material (microphotographs and tables with compositions of the studied minerals) separately for each studied mineral. At the same time, from the attached material can see the locations of the analysis carried out through the designated points/spectrums documented by a separate SEM microphotograph, while the obtained composition from the analysis are given in separate tables. Complete analyses of several pyrite, several chalcopyrite, magnetite, molybdenite, bornite and native gold have been performed on this principle, and the study results are given for each analyzed mineral separately. This mineral composition strongly reflects findings of numerous former researchers, just to name few of them [8], [9], [10], [11], [12], [7] etc.

Chalcopyrite determined during our SEM study showed the following composition ranges: 32.54-35.73 % S, 29.78-32.13 % Fe, 33.24-36.33 % Cu as well as with some admixtures of antimony and tin (0.1 % Sb and 0.1 % Sn) and silver 0.3-0.5 % Ag (Table 4, 5, 6, 7 and 8; Figure 2, 3, 4, 5 and 6).

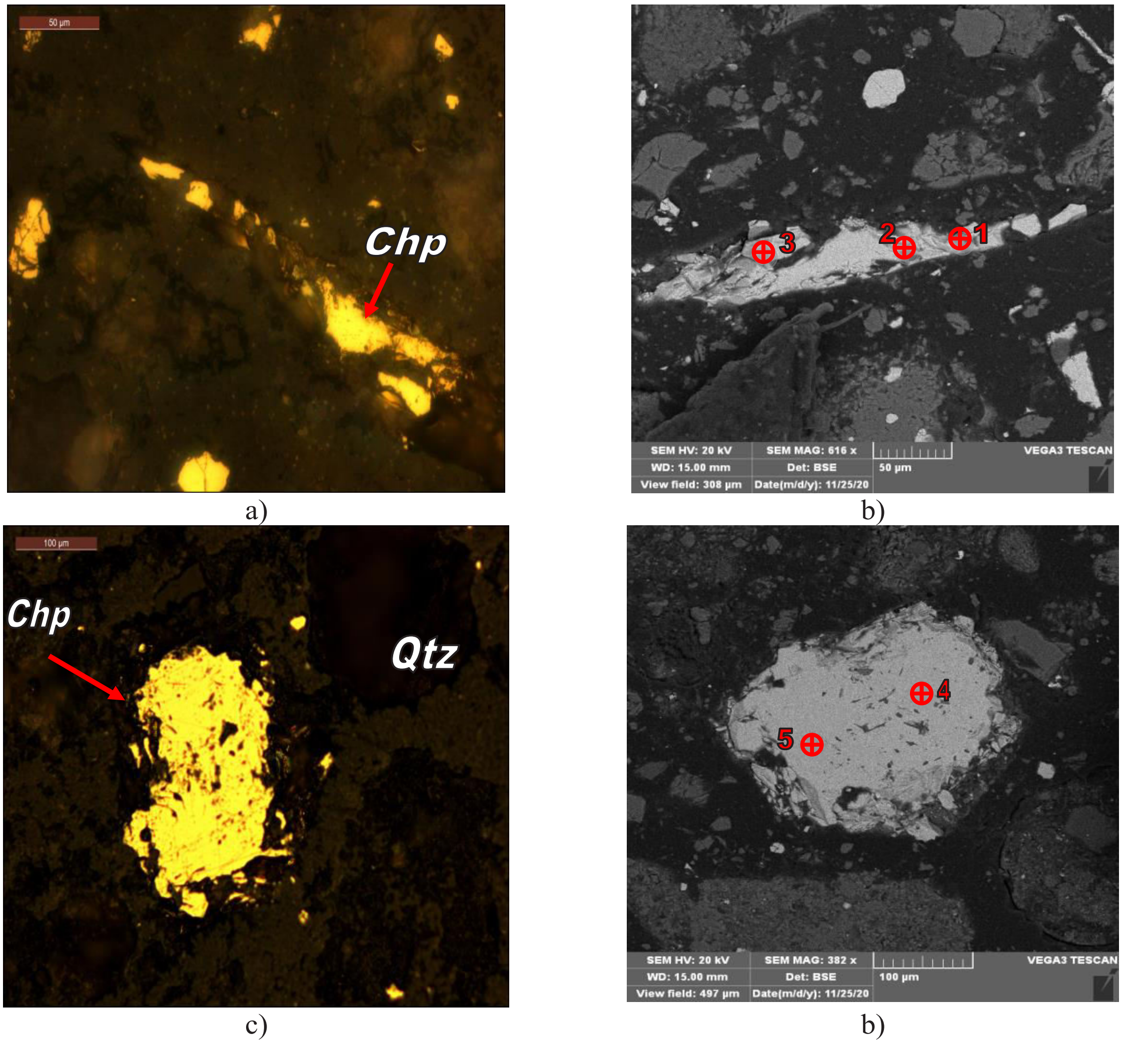


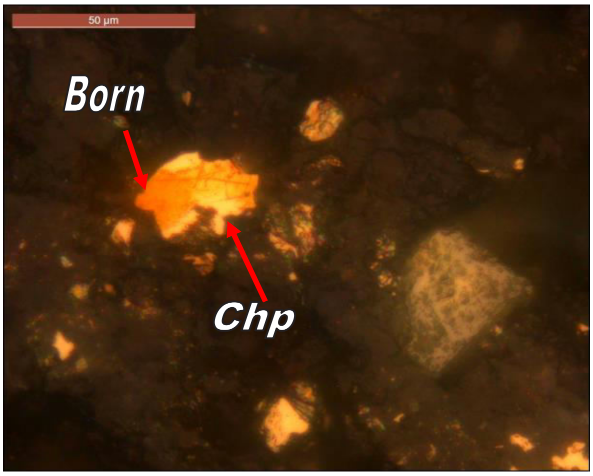
Figure 2. a) Single coarse rod-like chalcopyrite aggregate, cataclized and intensively corroded. Magnif. x400, crossed nichols (polarized optical microscope); b) SEM analyses points ; c) Large, cataclized and corroded ellipsoid chalcopyrite aggregate, but pure and mostly compact. The corossions are by quartz. Magnif. x200, crossed nichols (Polarized optical microscope); d) SEM analyses points

These values of the major elements in chalcopyrite are slightly different (in average just in parts of percent) than the reference values of 34.94 % S, 30.43 % Fe and 34.63 % Cu [13].

Table 4. SEM analysis results of chalcopyrite mineral grains from the Bor tailing (%wt)

	S (%)	Fe (%)	Cu (%)	Sb (%)	Sn (%)	Ag (%)	Au (%)	Total
Spectr. 1	34.78	30.21	35.01	-	-	-	-	100
Spectr. 2	35.73	31.03	33.24	-	-	-	-	100
Spectr. 3	35.04	30.56	34.40	-	-	-	-	100
Spectr. 4	34.13	30.04	35.78	-	-	0.05	-	100
Spectr. 5	34.89	30.47	34.61	-	-	0.03	-	100

Bornite compositions determined during our SEM study showed the following elemental concentration ranges: 23.69-25.43 % S, 11.40-13.01 % Fe, 61.99-64.01 % Cu as well as with some admixtures of antimony and tin (0.2-0.4 % Sb and 0.2-0.3 % Sn), lead 0.11-0.12 % Pb and zinc 0.05-0.15 % Zn (Table 5 and 8; Figure 3 and 6).



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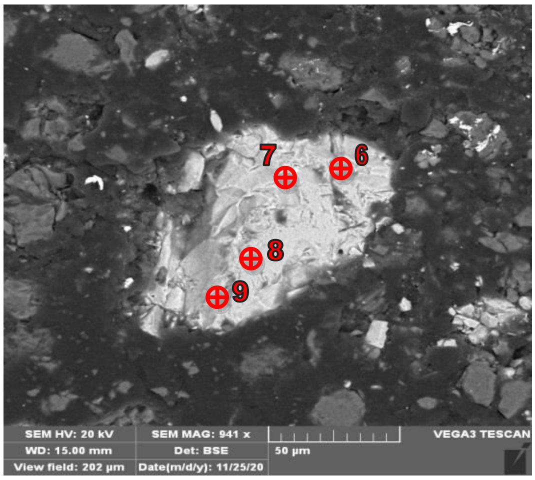

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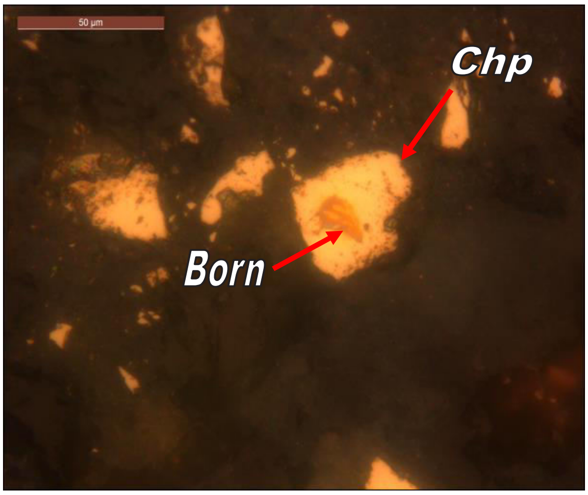

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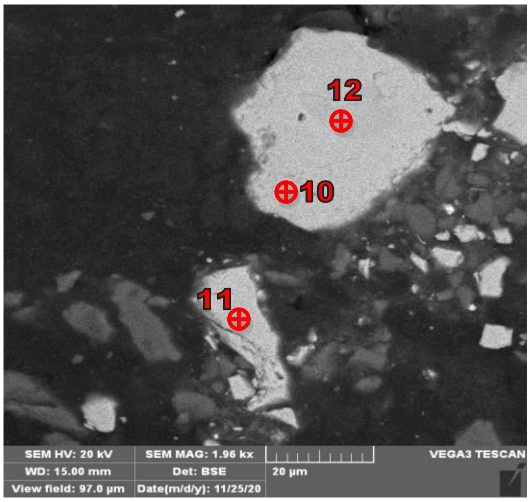


d)

Figure 3. a) Illustration of small (30 µm) chalcopyrite-bornite aggregate, which is compact but cataclized and corroded at the periphery of the grain associated with hypidiomorph magnetite aggregate that is box-like corroded and relic. Magnif. x630, crossed nichols (polarized optical microscope); b) SEM analyses points; c) Single, large and lamellar magnetite, mostly massive, but cataclized and corroded. Magnif. x200, crossed nichols (polarized optical microscope); d) SEM analyses points

Comparison of obtained data with reference data [14], in average, has shown only part of percent discrepancies between the values.

Table 5. SEM analysis results of bornite and chalcopyrite from the Bor tailing (%wt)

	S (%)	**Fe (%)**	**Cu (%)**	**Sb (%)**	**Sn (%)**	**Pb (%)**	**Au (%)**	**Total**
Spectr. 6	25.43	11.4	62.99	0.04	0.03	0.11	-	100
Spectr. 7	24.32	12.3	63.22	0.02	0.02	0.12	-	100
Spectr. 8	35.04	30.56	34.40	-	-	-	-	100
Spectr. 9	35.24	31.01	33.74	0.01	0.01	-	-	100
Spectr. 10	33.34	30.33	36.33	-	-	-	-	100

Spectr. 11	33.58	31.21	35.21	-	-	-	-	100
Spectr. 12	24.11	11.88	64.01	-	-	-	-	100

Chalcopyrite is the most common and the most important ore mineral in regards to copper mineralization of this particular deposit. Within the analyzed mineral aggregates (Figure 3) we have determined that we are dealing with chalcopyrite-bornite intergrowths, which formed as typical textures of decomposition of bornite solid solution and replacement of bornite by chalcopyrite [15]. The most probably, their precipitation simultaneously started and the deposition of chalcopyrite continued after the deposition of bornite. Such distinctive chalcopyrite-bornite association very likely suggests decomposition and replacement processes that could indicate the vicinity of a porphyry-copper system [16], [15].

Numerous magnetite mineral grains determined during our SEM study showed the following composition ranges: iron 70.78-71.81 % Fe and oxygen 28.12-29.15 % O, as well as some admixtures of chromium 0.02-0.07 % Cr (Table 6; Figure 4). These values of the major elements in magnetite, in average, are slightly different (less than a percent) than the reference values [17].

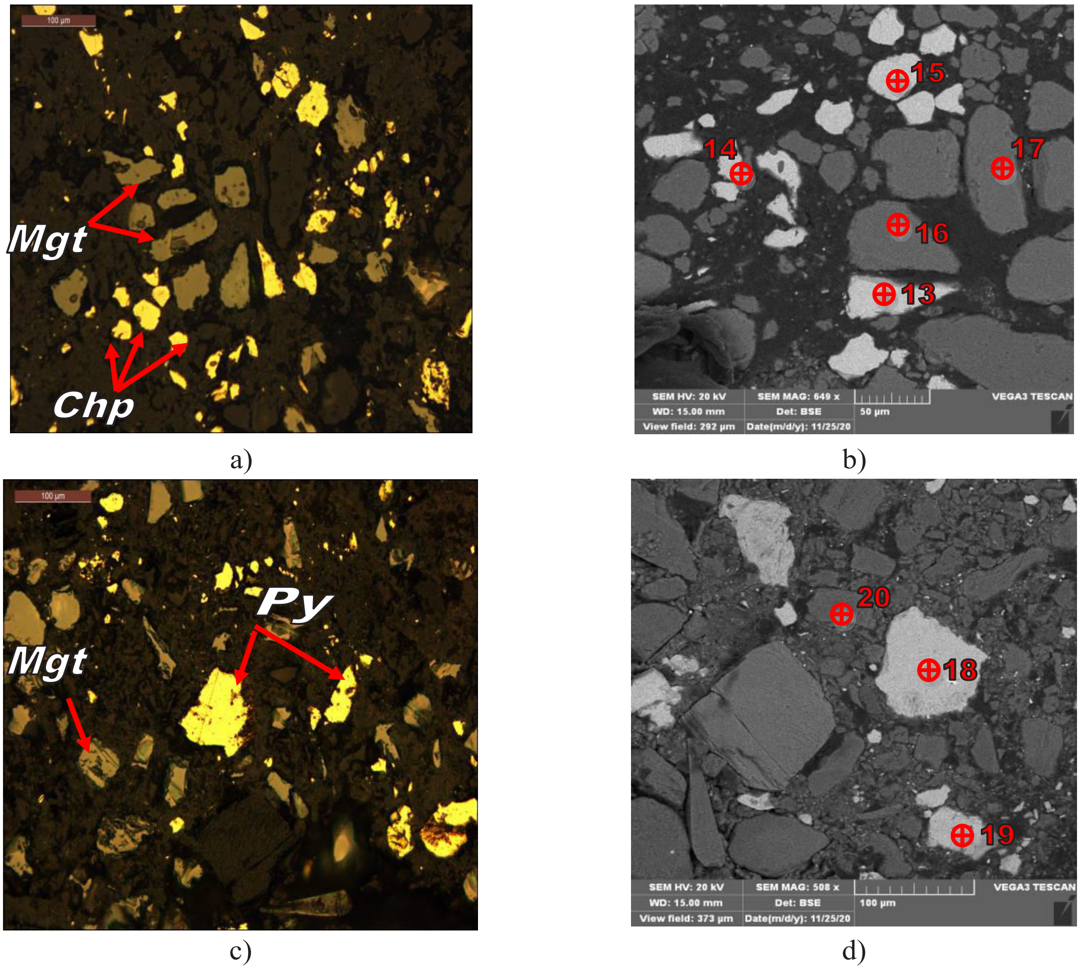


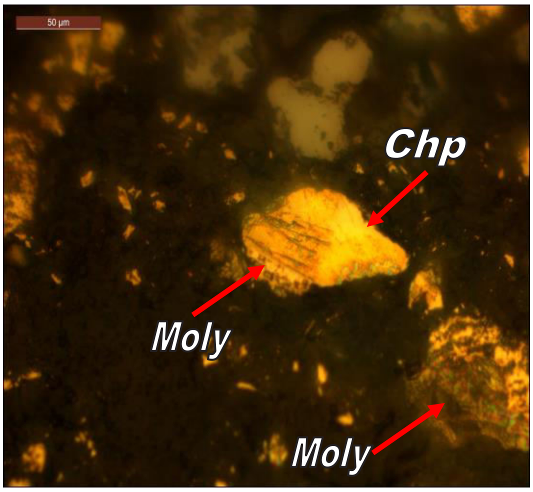
Figure 4. a) Illustration of circular concentric magnetite and chalcopyrite nail-like aggregates followed by smaller chalcopyrite aggregates. Magnif. x200, crossed nichols (polarized optical microscope); b) SEM analyses points; c) Illustration of coarse pyrite grain (around 100 µm), compact, but on the side cataclized and corroded. Magnif. x200, crossed nichols (Polarized optical microscope); d) SEM analyses points

Pyrite mineral compositions determined during our SEM study showed the following elemental concentration ranges: 53.09-54.03 % S, 45.48-46.66 % Fe as well as with some admixtures of copper and zinc (0.07-0.13 % Cu and 0.03-0.05 % Zn), see Table 6 and Figure 4. Comparison of obtained data with reference data [18], in average, has shown only part of percent discrepancies between the values.

Table 6. SEM analysis results of chalcopyrite and magnetite as well as pyrite and magnetite from the Bor tailing (%wt)

	S (%)	**Fe (%)**	**Cu (%)**	**Cr (%)**	**Mn (%)**	**O (%)**	**Zn (%)**	**Total**
Spectr. 13	34.66	30.33	35.01	-	-	-	-	100
Spectr. 14	34.59	30.49	34.92	-	-	-	-	100
Spectr. 15	34.77	31.22	34.01	-	-	-	-	100
Spectr. 16	-	71.09	-	0.02	-	28.89	-	100
Spectr. 17	-	70.78	-	0.07	-	29.15	-	100
Spectr. 18	54.03	45.58	0.13	-	0.23	-	0.03	100
Spectr. 19	53.09	46.66	0.07	-	0.13	-	0.05	100
Spectr. 20	-	71.81	-	0.07	-	28.12	-	100

Several molybdenite mineral grains determined during our SEM study showed the following composition ranges: 37.28-38.46 % S, 58.11-62.41 % Mo as well as with some admixtures of copper and zinc (0.21-2.11 % Cu and 0.04-0.21 % Zn) and iron 0.03-1.12 % Fe (Table 7; Figure 5).



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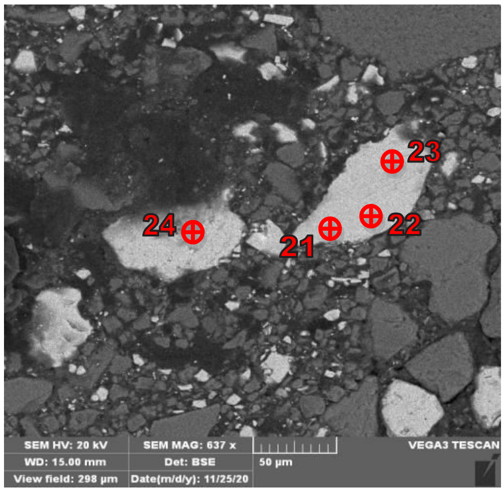

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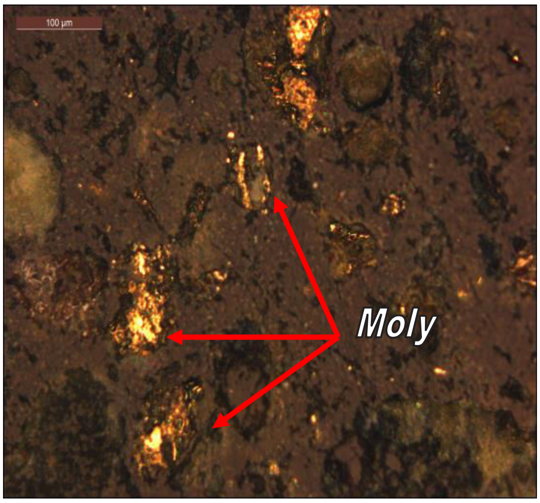

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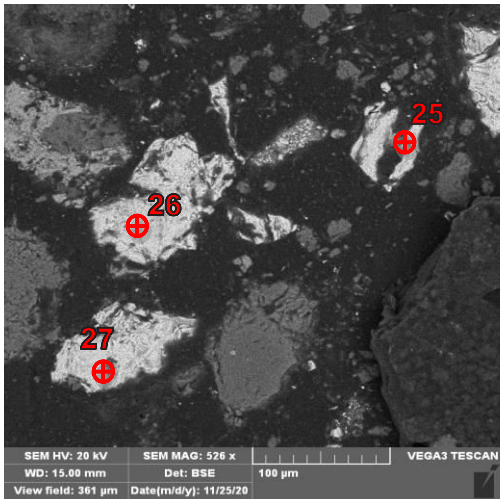


d)

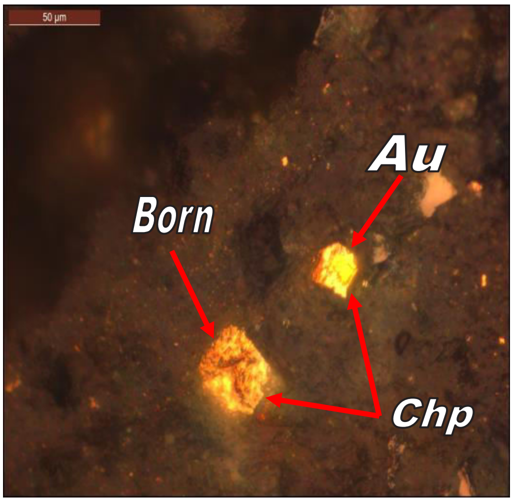
Figure 5. a) Relatively large multi-phase chalcopyrite-molybdeniteggregate interstitially affected by corrosion. In addition to the molybdenite-chalcopyrite contact, molybdenite rods are clearly visible in the compact chalcopyrite aggregate. Magnif. x400, crossed nichols (polarazing optical microscope); b) SEM analyses points; c) Serie of irregular grain- and rod-like molybdenite aggregates strongly cataclized and corroded. Magnif. x200, crossed nichols (Polarized optical microscope); d) SEM analyses points

The major elements in molybdenite, in average, for the molybdenum less than a percent compatibility with the reference values [19] was confirmed, although for the sulfur there is a discrepancy of approximately 2.5% due to admixtures such are copper, zinc and iron, which consumed the "missing" sulfur.

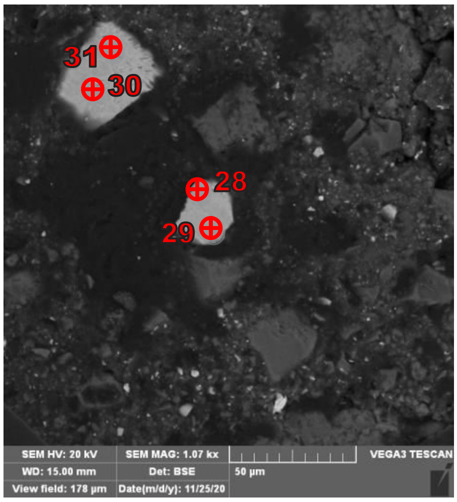
Table 7. SEM analysis results of chalcopyrite and molybdenite from the Bor tailing (%wt)

	S (%)	**Fe (%)**	**Cu (%)**	**Mo (%)**	**Sn (%)**	**Zn (%)**	**Total**
Spectr. 21	34.33	29.78	35.89	-	-	-	100
Spectr. 22	33.46	31.21	35.21	-	-	0.12	100
Spectr. 23	38.45	1.12	2.11	58.11	-	0.21	100
Spectr. 24	37.81	0.05	1.03	60.96	-	0.15	100
Spectr. 25	38.46	0.21	1.09	60.13	-	0.11	100
Spectr. 26	37.28	0.03	0.23	62.41	0.01	0.04	100
Spectr. 27	38.38	0.33	0.21	60.95	-	0.13	100

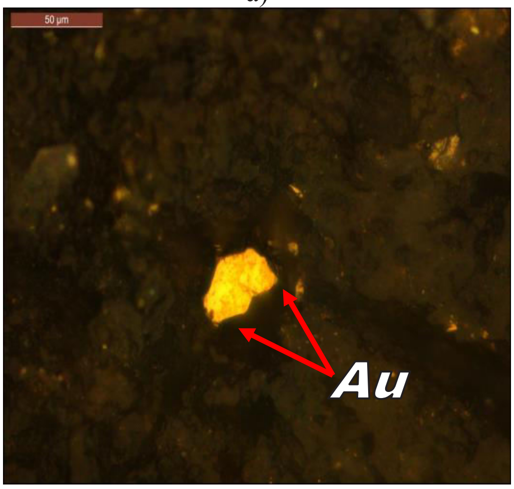
Rare native gold grains, freestanding or associated with chalcopyrite, determined during our SEM study showed the following composition ranges: 95.03-99.46 % Au, as well as with some admixtures of copper 0.09-3.32 % Cu, sulfur 0.11-1.13 % S, iron 0.06-0.52 % Cu and zinc up to 0.31 % Zn (Table 8; Figure 6).



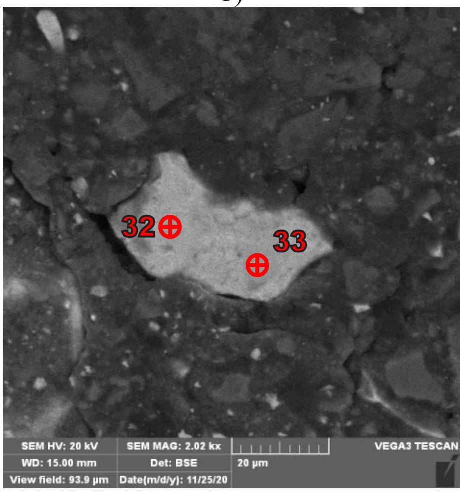
a)



b)



a)



b)

Figure 6. Illustration of two individual two-phase chalcopyrite aggregates, the coarser one is relic chalcopyrite with grape-like deposition of bornite while the finer one encloses native gold (both aggregates are <30µm). Magnif. x400, crossed nichols (Polarized optical microscope); b) SEM analyses points; c) Double plate-like aggregates (flakes) of native gold?. Magnif. x400, crossed nichols (Polarized optical microscope); d) SEM analyses points

These elemental concentrations within the native gold are compatible with the similar deposits in the region [20].

Table 8. SEM anal ysis results of chalcopyrite, bornite and native gold flake from the Bor tailing (%wt)

	S (%)	Fe (%)	Cu (%)	Sb (%)	Sn (%)	Zn (%)	Au (%)	Total
Spectr. 28	32.54	32.13	34.81	-	0.52	-	-	100
Spectr. 29	1.13	0.52	3.32	-	-	-	95.03	100
Spectr. 30	23.69	13.01	63.25	-	-	0.05	-	100
Spectr. 31	24.98	12.88	61.99	-	-	0.15	-	100
Spectr. 32	0.51	0.06	0.09	-	-	-	99.34	100
Spectr. 33	0.11	0.09	0.12	-	-	0.31	99.46	100

Analytically determined mineral composition where the main components are magnetite, pyrite, chalcopyrite, bornite, molybdenite etc., with the most extensive being pyrite and chalcopyrite strongly reflects the mineral composition of porphyry copper mineralization complex within the Bor Mine [21]

5. Quantitative analysis of samples from the Bor mine's tailing dam

According to the project proposal activities within the mineralogical analysis of the material from the Bor tailing dam a quantification was foreseen, which we realized on a number of selected samples. In order to cover evenly all parts of the research area of the Bor tailing dam we decided to take one trial from each drill hole (4 in total), but from different levels in all 4 drill holes, with a certain equilibrium representation at all depths, and however, to meet the optimum quantification minimum. For these needs, a total of 6 samples from the following levels were taken:

- T1 from B-1 (depth 8.0 m to 9.0 m)
- T2 from B-1 (depth 20.0 m to 21.0 m)
- T3 from B-2 (depth 4.0 m to 5.0 m)
- T4 from B-2 (depth 18.5 m to 19.5 m)
- T5 from B-3 (depth 26.0 m to 27.0 m)
- T6 from B-4 (depth 20.0 m to 21.0 m)

From selected materials were prepared polished sections where an optical microscope determined the presence of ore minerals from the Bor ore paragenesis, where had been determined presence of pyrite, chalcopyrite, magnetite and some less abundant mineral phases.

Then the samples with the required amount of material were sent for quantitative analysis to the laboratories of the Faculty of Natural Sciences and Engineering at the University of Ljubljana, Slovenia. Even before the samples have been analyzed, we have been told by the XRD operators' that the quantification of the material will be done within the sensitivity of the method, ie, the determination of those mineral phases whose total participation in the analyzed material is below 1% will be aggravated (Table 9).

Table 9. Quantitative XRD mineralogical analysis of samples from the Bor tailing dam (in %wt) without amorphous phase

Dataset Name	Scan Number	Quartz low [%]	Pyrite [%]	Alunite [%]	Nacrite 2M2 [%]	Hornbl. Mg [%]	Anorthite [%]	Microcline ordered [%]	Greigite [%]	Total
T1 (B-1 8-9 m)	1	82.4	17	0	0.5	0	0	0	0.1	100
T2 (B-1 20-21m)	2	69.2	29.9	0	0.3	0.5	0	0	0.2	100.1
T3 (B-2 4-5 m)	3	84.7	8.8	3.6	2.1	0.1	0.3	0	0.4	100
T4 (B-2 18.5-19.5m)	4	41.2	9.9	0.9	0	12	24.6	10.6	0.6	99.8
T5 (B-3 26-27m)	5	73.6	23.5	2.6	0	0	0	0	0.3	100
T6 (B-4 20-21 m)	6	74.3	8.3	8.5	7.7	0.7	0	0	0.5	100

From the results, enclosed within this review, it could be seen that the reliability of the provision was in favor of the petrogenic minerals (unprocessed minerals), which was a great opportunity for us as we had no other treatment for them, while the ore minerals were found in contents below 1% and their quantification cannot reliably confirm their intensity.

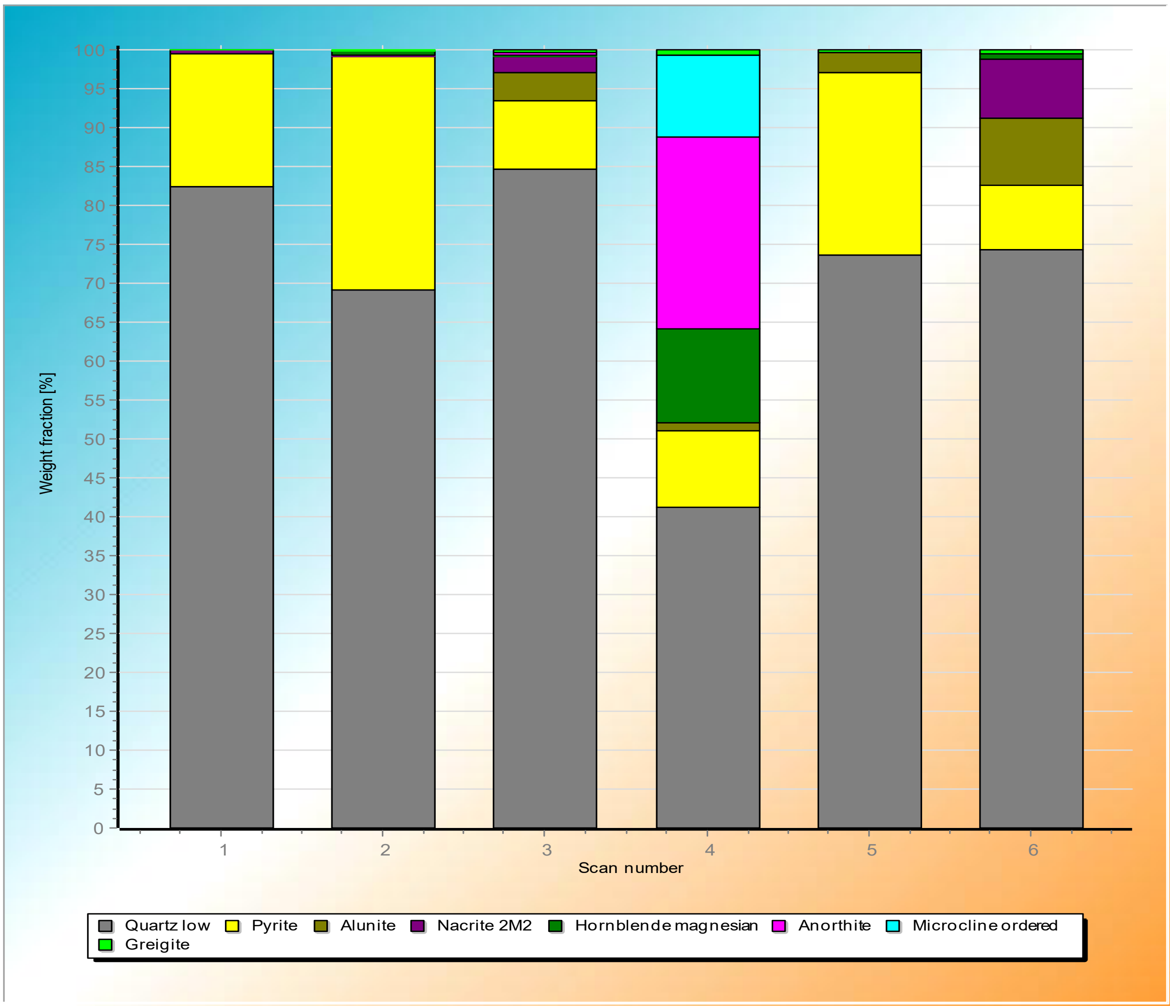


Figure 7. Frequency graph of major minerals in samples from the Bor tailing dam (XRD analysis)

However, the quantification of ore minerals (pyrite) is also present in the review through tailings analysis of tailings.

Conclusion

From the available data presented in the framework of this paper we can conclude that the treated old tailings within the Bor mine complex belong to the group of technogenous deposits with remarkable economic value. The total amount of copper metal of 51 000 t, of gold 11 800 kg and silver of 63 000 kg, as well as the series of rare and scattered elements confirm the economic value. The established mineral composition, which is dominated by chalcopyrite, only confirms the possibility of extraction first of copper, and then of other metals with the help of modern technological solutions such as leaching. The results of the quantification of the material from the old tailings in Bor indicate the fact that the dominant presence of silica, feldspar and amphibole has a positive impact on increasing the economic value of the tailings in terms of using that tailings as building materials.

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