Посебноизданиена
Geologica Macedonica,
Nō.5

МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО - Скопје, 1952

ЧЕТВРТИ КОНГРЕС
на
Геолозите на Република Северна Македонија

ЗБОРНИК НА ТРУДОВИ

Главни и одговорни уредници:
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Охрид, 2021

Посебно издание на
Geologica Macedonica,
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Струга, 2021

Издава: Македонско геолошко друштво – Скопје, 1952

Организатор на Конгресот
Македонско геолошко друштво Скопје 1952

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3-EG-01

SOME GEOCHEMICAL AND MINERALOGICAL FEATURES OF SAMPLES FROM OLD BOR'S TAILING DAM

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A b s t r a c t: The paper presents the results of the latest tests of tailings from the old tailings in the Bor mine complex. A package of 31 elements was geochemically analyzed, in which with increased elemental contents are characterized the elements typical for the Bor ores such as copper (0.25–0.45% Cu), chromium (0.0047–0.1343% Cr), arsenic (0.0031–0.0127% As), selenium (0.30–4.77% Se), silver (0.15–2.87% Ag) and gold (0.08–0.65% Au). Mineralogical study have shown the standardization of several minerals such as pyrite, bornite, chalcopyrite, magnetite and natural gold, which compositions have been confirmed by SEM–Scanning Electron Microscope. Quantitative mineral analysis gave the composition of the main constituents in the tailings dominated by quartz up to a maximum of 60.6%, amorphous mass up to 58.1%, ore minerals dominated by pyrite up to 20.4% followed by albite, microcline, hornblende and others.

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

НЕКОИ ГЕОХЕМИСКИ И МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА ПРИМЕРОЦИ ОД СТАРОТО БОРСКО ХИДРОЈАЛОВИШТЕ

А п с т р а к т: Трудот ги презентира резултатите од најновите тестирања на хидројаловина од старите хидројаловишта во рудниот комплекс Бор. Геохемиски беше анализиран пакет од 31 елемент, во кој со зголемена елементарни содржини се карактеризираат елементите типични за Борските руди, како што се бакар (0,25-0,45% Cu), хром (0,0047-0,1343% Cr), арсен (0,0031–) 0,0127% како), селен (0,30-4,77% Se), сребро (0,15-2,87% Ag) и злато (0,08-0,65% Au). Минералошките проучувања покажаа неколку стандардни минерали како што се пирит, борнит, халкопирит, магнетит и самородно злато, чии состави се потврдени со Скенинг Електронски Микроскоп-СЕМ. Квантитативната анализа на минералите го даде составот на главните состојки во јаловината во која доминира кварц до максимум 60,6%, аморфна маса до 58,1%, а од рудни минерали доминира пирит до 20,4% проследени со албит, микроклин, хорнбленд и други.

Клучни зборови: Рудник Бор, рудни минерали, хидројаловиште, геохемија, квантификација и минералошка анализа

INTRODUCTION

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) (Figure 1). Large quantities of processed material are actually stored in those tailings and their quantities are expressed in millions of tons. Namely, there had been deposited 22 322 350 t of material with 0.530 g/t Au, 2.83 g/t Ag and 0.230% Cu (Jovanović and Maksimović, 2018). 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 Balkans 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 where 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 (technogenous deposits) as it was shown by the latest studies (Serafimovski, 2019; Tasev and Serafimovski, 2020). The positive influences of the technogenous deposits are noted in the work of (Tasev and Serafimovski, 2020), as well as in the works of (Maksimović, 2014; Jovanović and Maksimović, 2018) and others. According to the above, in this paper are presented data from the geochemical and 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.

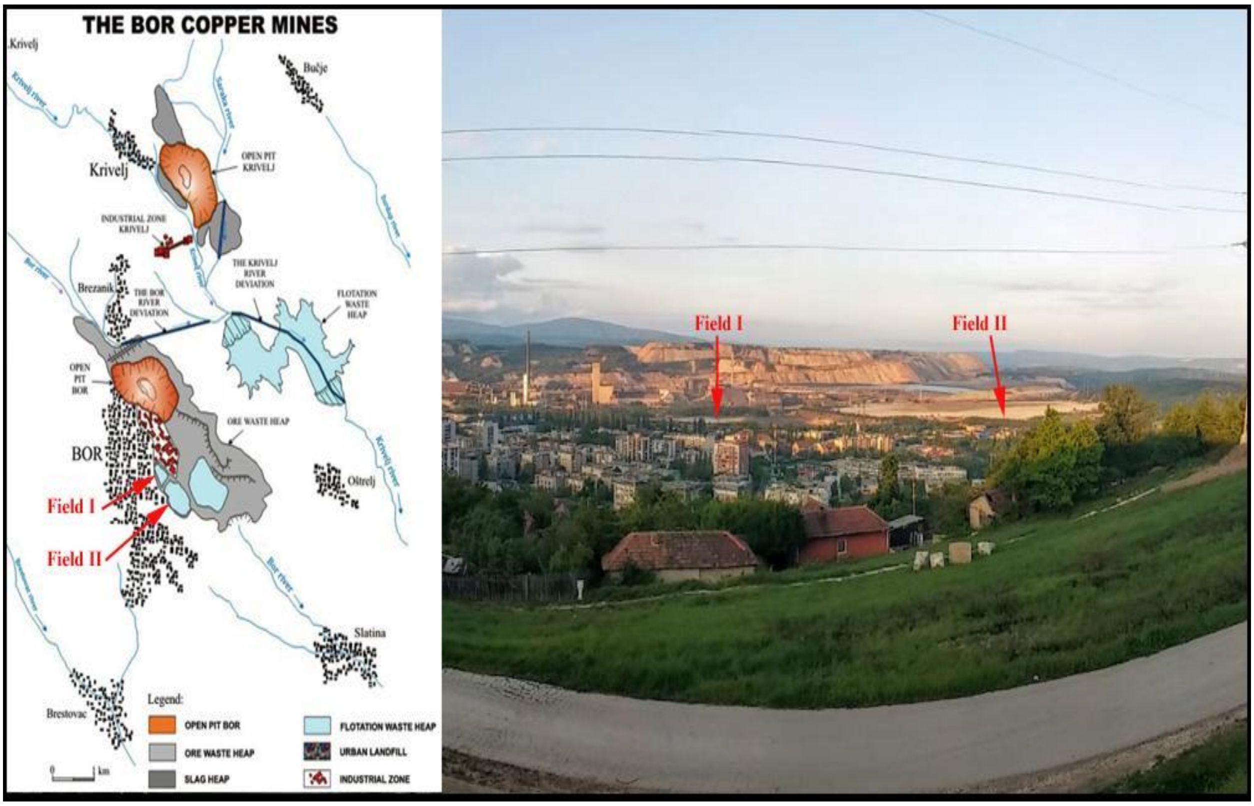

Fig. 1. Schematic positions of Bor (Serbia) of tailing dams with an accent to old Bor tailing dam and its drillhole sampling (Stanojlović et. 2014, modified)

METHODS OF INVESTIGATION

The current paper is based on 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. Quantification of samples was performed at the XRD laboratory of the Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia. Prepared polished sections were previewed on the polarizing optical microscope Zeiss Axiolab Pol in reflected light mode at the Faculty of Natural and Technical Sciences, University "Goce Delčev" University in Štip. The chemical compositions of the major mineral phases were determined by scanning electron microscope (SEM) VEGA3 LMU and INCA Energy 250 Microanalysis System (EDS/EDX), located at the "Goce Delčev" University in Štip. For SEM, the VegaTC software was used. Geochemical analysis of adequate tailing samples was performed using the Inductive Coupled Plasma–Optical Emission Spectrometry located at University "Goce Delčev" in Štip. The sampled tailing fields 1 and 2 together contain 27 million tonnes of tailing (Maksimović, 2014; Jovanović and Maksimović, 2018; Stanković et al., 2018; Ristović, 2020).

GEOCHEMICAL FEATURES

Some of the latest geochemical analyzes of individual and composite drill–holes 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 that period, the total number of samples taken from 13 drill–holes was 470.

Copper flotation tailing from the old copper flotation tailings RTB Bor, Serbia until recently was classified as mining waste (Gardić et al., 2015). Disposal of this kind of waste without prior treatment has a negative impact on the environment (quality of surrounding soil, groundwater, surface water and air). However, if we keep in mind aforementioned quantities of material and concentration of certain metals (Cu, Ag, Au….) and their respective metal exchange prices we may easily conclude that there could be induced high economic interest. Chemical composition of copper flotation tailings is shown in the Table 1.

T a b l e 1

Chemical composition of copper flotation tailings

Parameter	Measure unit	Content	Analitical method
Cu	%	0.2	AAS
Fe	%	4.11	AAS
Fe_3O_4	%	0.06	A– Fe_3O_4
Cu_{ox}	%	0.112	AAS
S	%	5.08	S
SO_4^{2-}	%	7.21	NTU
Al_2O_3	%	14.89	PT
SiO_2	%	62.83	G
MgO	%	0.16	AAS
As	%	0.0082	ICP–OES
Pb	%	<0.03	AAS
Zn	%	0.0030	AAS
Hg	g/t	0.1	AAS
Mn	%	0.005	AAS
Cr	%	0.16	ICP–OES
Cd	%	<0.0025	AAS
Ag	g/t	0.9	FA/AAS
Au	g/t	0.1	FA/AAS

With our latest geochemical analyses of samples from drill–holes from the old tailings in the Bor mine complex, a total of 6 composite samples were analyzed with the ICP–AES method on a program package of 31 elements. The obtained results are shown in Table 2.

From the attached Table 2 can be seen that the obtained results are statistically processed and grouped as minimum, maximum, average, standard deviation and median values. The interpretation showed that with increased and interesting contents are characterized the elements that are characteristic for the ores from the Bor mineralized complex whose post–flotation treatment has been identified in the old tailings. It is about the increased contents of copper, arsenic, silver, selenium, gold and for a special note are the increased contents of chromium which are not characteristic for this type of ores. In the framework of the geochemical treatment of elements from the old Bor tailings, in addition to the presentation of the historical data from the studied Bor tailings (given in Table 1), we decided to give comparative data to the tests performed by Outotec (Lippo, 2021) which are presented in Table 3. The attached Table 3 shows that colleagues from Finland conducted separate and aggregate tests on similar materials from the old Boris tailings. The attached data show that in almost all classes the copper content is increased and maximum values are seen in the classes + 75µm, + 45µm, + 20µm and –20µm. Such values coincide with the results obtained from our studies and previous studies by Gardić et al. (2015).

MINERALOGICAL FEATURES

Mineralogical features of the old tailings in the Bor mine complex have not been studied in detail until recently (Antonijević et al., 2008; Serafimovski et al. 2021). Our latest microscopic study of polished sections showed standard ore minerals from the Bor' ore complex, which are dominated by chalcopyrite and bornite (Figure 2), always followed by pyrite, magnetite, maghemite and commonly in association with molybdenite.

The microphotographs show illustrative samples of the most important minerals identified in the materials from the old Bor tailings (Figure 2). After the microscopic study of the polished sections, a total of 5 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 Štip. 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. Analyzes have shown that the analyzed ore minerals confirm the positive identification under the optical microscope, such as the most common pyrite, chalcopyrite, bornite, magnetite and native gold, and gave the mineral compositions with some influence on the associated trace minerals standard for minerals of this type (Table 4).

T a b l e 2

Results from geochemical analysis of drill hole samples from the old Bor's tailing dam (ppm)

	Min	Max	Average	Std. dev.	Median
Al	17010.35	59045.47	30026.44	16662.63	23311.80
Ca	2366.69	18200.00	5520.78	6228.342	3065.59
Mg	584.00	10500.00	2355.83	3991.087	733.00
Na	1258.62	14893.49	3762.08	5457.241	1595.00
K	1556.21	18023.29	6563.15	6447.615	4709.59
Ti	774.20	2218.06	1186.23	532.1721	1077.16
Fe	27181.96	128795.25	76241.72	41251.77	72534.44
P	252.77	454.47	333.30	69.49695	317.53
Mn	26.30	748.53	152.32	292.1234	34.43
Sr	625.57	662.24	645.60	14.85163	645.10
Ba	111.99	3055.32	1428.91	1288.074	1216.12
Zn	19.43	31.69	25.26	5.595234	24.90
Pb	26.87	76.36	53.35	17.20426	53.27
Cr	47.09	1343.96	382.75	479.2266	252.17
Co	4.00	21.62	13.25	7.156132	11.98
Ni	16.19	28.83	22.65	4.180157	22.79
Cu	2542.99	4244.70	3016.99	691.823	2656.72
As	31.68	127.26	81.22	34.25719	84.01
Li	11.10	29.20	16.80	6.477714	15.99
B	17.70	35.27	26.27	5.766051	26.47
V	21.75	150.28	64.88	47.02375	52.93
Mo	1.49	16.52	6.22	5.220865	4.92
S	27035.23	116845.11	68792.51	39332.04	57673.36
Be	0.50	0.62	0.57	0.042757	0.58
Ga	4.96	10.79	7.48	2.346748	6.98
Ge	0.25	3.13	1.57	1.187415	1.45
Sn	2.80	5.99	3.94	1.351648	3.25
Se	0.30	4.77	2.21	1.549224	1.81
Ag	0.15	2.87	1.42	1.004596	1.50
Au	0.08	0.65	0.31	0.222658	0.29
Tl	0.68	2.58	1.51	0.81933	1.13

Table 3

Chemical and geochemical sieve analyses of samples from drill holes from the Bor's tailing dam

Size fraction		+212 μm	+150 μm	+106 μm	+75 μm	+45 μm	+20 μm	–20 μm	Calc bulk	M9383
Weight (g)		37.35	45.08	48.22	42.49	68.06	97.49	254.56	593.25	Bulk (2)
(%)		6.30	7.60	8.13	7.16	11.47	16.43	42.91	100	100
Cu (%)	P1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.007	0.111
	P2	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.05	0.011	0.022
	P3	0.05	0.05	0.05	0.06	0.07	0.05	0.05	0.052	0.053
	P4	0.03	0.03	0.04	0.06	0.09	0.07	0.03	0.045	0.036
	Sum	0.106	0.075	0.093	0.120	0.155	0.115	0.094	0.115	0.222
	TOT	0.132	0.103	0.123	0.156	0.173	0.145	0.152	0.146	0.241
Fe (%)	P1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	P2	0.89	0.59	0.69	0.79	0.41	0.26	0.73	0.62	0.702
	P3	0.20	0.13	0.12	0.20	0.14	0.13	0.62	0.35	0.36
	P4	3.01	3.09	5.59	9.56	14.70	10.90	4.90	7.14	6.64
	Sum	4.11	3.81	6.40	10.55	15.25	11.28	6.25	8.11	
	TOT	**4.45**	**4.01**	**4.80**	**11.00**	**13.90**	**11.10**	**6.34**	**7.90**	**7.71**

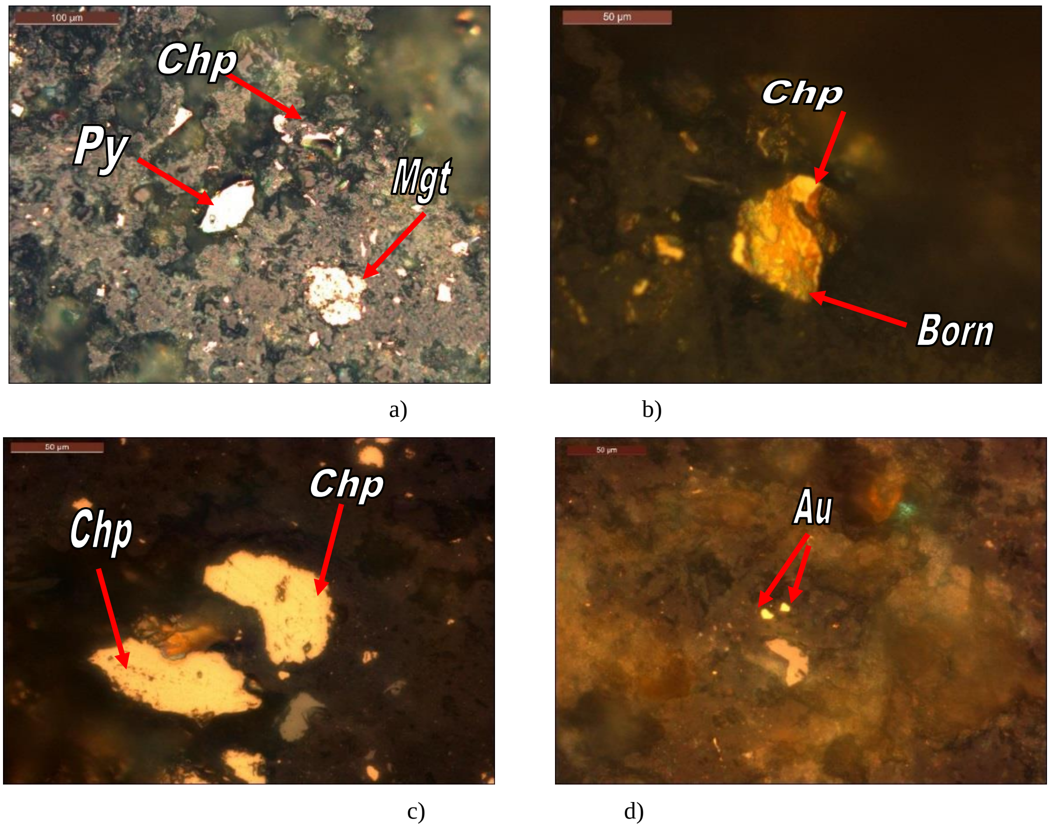

Fig. 2. Representative microphotographs of the most important ore minerals from the old Bor's tailing dam
a) Single aggregate of compact pyrite, sponge–like and partly corroded magnetite and intensively corroded and relic chalcopyrite aggregate (magnif. ×200, crossed nichols); **b)** Two phase chalcopyrite–bornite aggregate mimetically intergrown and plus interstice corossion of bornite over chalcopyrite (magnif. ×400, crossed nichols); **c)** Dual chalcopyrite aggregate. Compact in shape of half arc and relatively pure without corossion traces (magnif. ×630, crossed nichols; **d)** Illustration of two relic native gold grains within oxidized–silicified matrix (magnif. x400, crossed nichols)

Table 4

Scanning–electron microscope analyses of the most common ore minerals from the Bor's old tailing dam (%)

	S	Fe	Cu	Sb	Sn	Te	Cr	O	Ag	Au	Total
Pyrite	52.89	46.51	0.07	–	0.35	–	0.18	–	–	–	100
Magnetite	–	70.69	0.85	–	–	–	0.02	28.44	–	–	100
Bornite	25.43	11.4	62.99	0.04	0.03	0.11	–	–	–	–	100
Chalcopyrite	33.13	30.04	35.13	–	–	0.90	–	–	0.05	0.75	100
Native gold	–	–	1.10	–	–	1.25	–	–	2.60	95.05	100

The attached Table 4 shows that the obtained elemental compositions of the most common minerals in the tailings from the old Bor deposits are quite standard and mostly close to the theoretical values (Palache et al., 1944; Deer et al., 1962; Okrusch and Matthes, 2005; Robb, 2005; Pačevski et al., 2012; Jelenković et al., 2016 and Stefanova et al., 2018). Normally, there are certain specifics that characterize Bor complex ores, and they refer mainly to the elements of impurities, such as the increased presence of copper in pyrite, then the almost regular presence of gold and silver in chalcopyrite, occurrences of tellurium in bornite and chalcopyrite etc.

Quantitative analysis of samples from the Bor mine's tailing dam was realized on a number of selected samples (T1–T6). 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 5).

Table 5

Quantitative XRD mineralogical analysis of samples from the Bor tailing dam (in %wt) with amorphous phase (%)

Dataset Name	Quartz low	Pyrite	Alunite	Nacrite	Hornbl Mg	Anorthite	Microcline ordered	Greigite	Amorphous fraction / %	Total
T1 (B–1 8–9 m)	60.6	12.5	0	0.3	0	0	0	0.1	26.5	100
T2 (B–1 20–21m)	47.1	20.4	0	0.2	0.3	0	0	0.1	31.9	100
T3 (B–2 4–5 m)	48.4	5	2	1.2	0.1	0.2	0	0.2	42.8	99.9
T4 (B–2 18.5–19.5 m)	17.3	4.1	0.4	0	5	10.3	4.5	0.3	58.1	100
T5 (B–3 26–27m)	51.7	16.5	1.8	0	0	0	0	0.2	29.8	100
T6 (B–4 20–21 m)	39.7	4.4	4.6	4.1	0.4	0	0	0.3	46.6	100.1

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

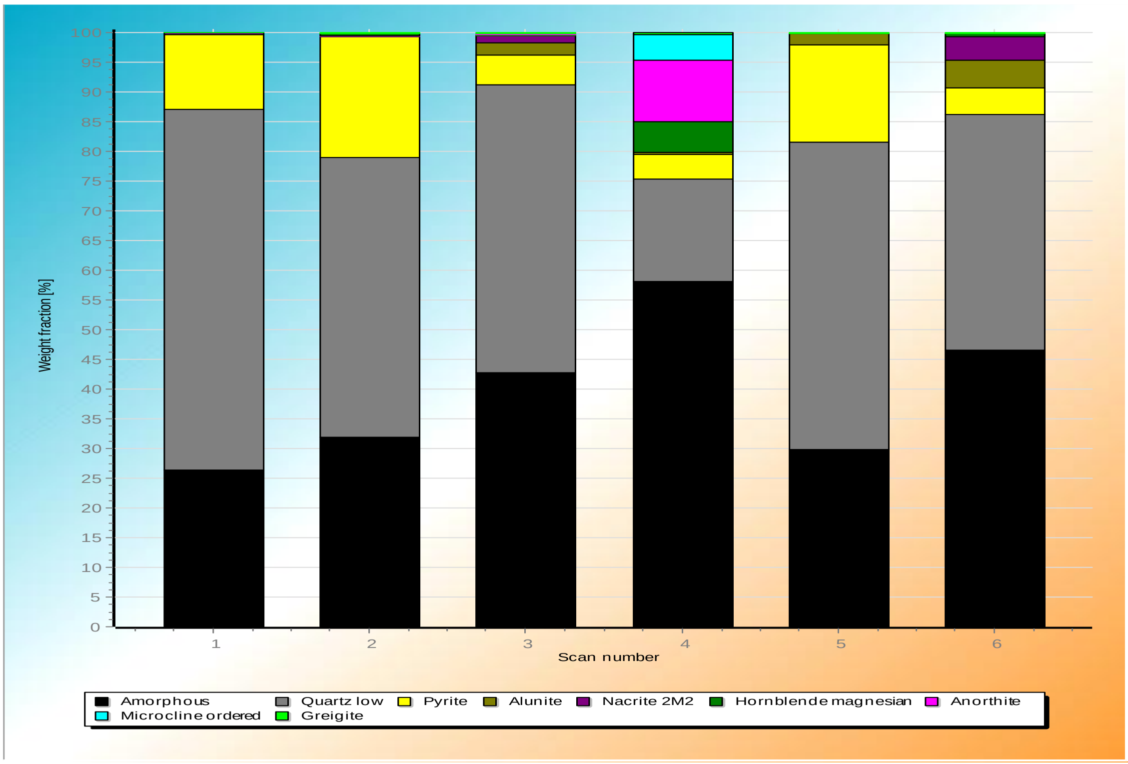

Fig. 3. Frequency graph of major minerals and amorphous phase in samples from the Bor tailing dam (XRD analysis)

CONCLUSION

The realized mineralogical and geochemical studies and the conducted quantification of the treated materials from the old Borski tailings showed that the tailings may be of interest for possible further valorization of certain elements in the first place copper, gold, silver, selenium and possibly even tellurium. The geochemical specialization of all studies conducted so far, including the latest ones, indicates the fact that there is a possibility of special interest for further research of these old tailings. Mineralogical tests confirm a simple mineral composition dominated by chalcopyrite. Quantitative parameters reflect the composition of the complete tailings standard for Bor mine ore types.

Acknowledgement: This work was financially supported by the EIT Raw materials project no. KAVA 18248, RIS–CuRE (Zero waste recovery of copper tailings in the ESEE region).

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