СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 84, кн. 1, 2023, с. 3–9

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 84, part 1, 2023, p. 3–9

Mineral composition of Laky tailings dam, Central Rhodopes, Bulgaria

Tsveta Stanimirova[1], Victoria Vangelova[1], Tanja Stoilkova[1], Dian Vangelov[2*]*

[1] Department of Mineralogy, Petrology and Economic Geology, Faculty of Geology and Geography, University of Sofia "St. Kliment Ohridski", 15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mails: stanimirova@gea.uni-sofia.bg; vpatrick@gea.uni-sofia.bg; tstoilkova@gea.uni-sofia.bg
[2] Department of Geology, Paleontology and Fossil fuels, Faculty of Geology and Geography, University of Sofia "St. Kliment Ohridski", 15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mail: dedo@gea.uni-sofia.bg
** Center of Competence „Clean & Circle"*

Минерален състав на хвостохранилище „Лъки", Централни Родопи, България

Цвета Станимирова[1], Виктория Вангелова[1], Таня Стоилкова[1], Диан Вангелов[2*]*

[1] Софийски Университет „Св. Климент Охридски", Геолого-географски факултет, „Катедра Минералогия, петрология и полезни изкопаеми", 1504 София, България
[2] Софийски Университет „Св. Климент Охридски", Геолого-географски факултет, „Катедра Геология, палеонтология и изкопаеми горива", 1504 София, България
** Център за компетентност „Clean & Circle"*

Резюме. Минералният състав на хвостохранилището на Лъки е представен главно от кварц, калцит, фелдшпати, каолинит, слюда (биотит или серицит) и хлорит. В по-малки количества са представени доломит, амфибол и йохансенит. Наблюдават се също епидот, хипогенен хематит, по-рядко самородно сребро, гранат, родонит и воластонит. Основни рудни минерали са пирит и халкопирит, по-рядко сфалерит и галенит. Разпределението на минералите е сравнително хомогенно в пробите, взети от основния участък, въпреки че се наблюдава стратификация в дълбочина, с редуване на слоеве, богати на сулфиди, и такива, съставени главно от кварц. Всички случаи на обогатяване с тежки минерални фракции са свързани със сезонни процеси и не може да се установи закономерност в минералното разпределение. Резултатите предполагат, че само минералите кварц и фелдшпат могат да представляват интерес за практическа употреба.

Ключови думи: минерален състав, разпределение, Лъки, хвостохранилище.

Abstract. Quartz, calcite, feldspars, kaolinite, mica (biotite or sericite), and chlorite were determined as predominant minerals. Dolomite, amphibole, and johansenite are presented in smaller quantities. Epidote, hypogene hematite, rarely silver nugget, garnet, rhodonite, and wollastonite are also observed. Pyrite and chalcopyrite, less often sphalerite and galena are the main ore minerals. The distribution of minerals is relatively homogeneous in the samples taken from the main area, although stratification is observed in depth, with alternating layers rich in sulfides and those composed mainly of quartz. All cases of enrichment with heavy mineral fractions are associated with washing with seasonal processes and no permanent mineral distribution can be established. The results suggested that only quartz and feldspar minerals could be of interest for practical use.

Keywords: mineral composition, distribution, Laky tailings damp.

Introduction

In 2018, under Project BG05M2OP001-1.002-0019, a Center of Competence "Clean technologies for a sustainable environment – water, waste, energy for a circular economy" (acronym Clean & Circle) was established. One of the Center's tasks is to characterize different types of waste landfills with the aim of their possible inclusion in the processes of the circular economy. During the past period, activities were carried out to characterize the tailings deposits of some mines. In the present work, the data from

https://doi.org/10.52215/rev.bgs.2023.84.1.3

the study of the mineral composition of the tailings depository of the Laky deposit are presented.

The tailings storage facility in Laky (Central Rhodopes) is owned by GORUBSO-Laky, which develops the Govedarnika and Goranska padina lead-zinc deposits. The ore is processed on-site in the flotation factory in the town of Laky, where a Pb-Zn concentrate is obtained. The rest of the non-ore mass with most of the chalcopyrite and pyrite is deposited in the tailings dam located near the city.

The earlier studies (Vangelova et al., 2007; Vangelova, Neikova, 2009) of the hypogene mineralization in the operating mines show that the sulfide minerals in them are carriers of various trace elements, including harmful heavy metals, some of which with high concentrations. Most of these elements along with their carrier minerals end up in the tailings dam, where they accumulate over years.

The purpose of the study is to clarify and characterize the mineral composition of the sediments in the tailings dam.

Materials and methods

Tailings dam “Laky-2 complex” of “LAKY INVEST” JSC consists of two parts – active tailings dam “Laky-2 temporary” of sloped type, located on the right bank of the river Yugovska and Reservoir Lake “Laky-2 dam”. To date, the “Laky-2 complex” tailings dam is only presented by “Laky-2 temporarily” as an operating floating-type tailings storage facility, with full recycling of the clarified waters back into the main flotation cycle at the OF “Laky“. After 2010, the tailings storage facility “Laky-2 dam” (sediment lake) is out of operation, practically completely dried up and unusable. “Laky-2 temporarily” remains as a facility for the temporary storage of tailings by washing with tailings pipes equipped with fittings and washing deviations (washing drains). The washing of tailings is realized in two formed sections (washing cell 1 and dry cell 2), separated with a 15 m wide technological levee (Fig. 1).

During the field investigations, 50 samples were taken from the tailings dam sludge (cell 2). Sampling from the “Laky-2 temporary” tailings storage facility was carried out in two directions: (I) in the NW-SE and W-NE direction. In the NW-SE direction, sampling is done at 50 m along profile lines. The profile lines are parallel to the tailing pipes (east end-side of the tailings) and are spaced: immediately below the pipes (I) and 20 (II), 50 (III), and 70 (IV) m from the pipes. In the NW-SE direction, sampling is in 25 m. There are two profile lines: parallel to the technological levee (1) and parallel to the southern end-side of the tailings (2) (Fig. 2). The examined samples are from fractions with sizes: 0.5–0.25 mm and 0.25–0.1 mm.

The phase composition of all 50 samples was investigated by powder X-ray diffraction (XRD) analysis. The powder XRD patterns were recorded on diffractometer D8 Advance, Bruker. Filtered Co-Kα radiation was used in the range 2Θ 4–80°, step 0.02° 2Θ, and exposure time per step 1.5 s. The specialized software Diffrac.Eva was used for qualitative and semi-quantitative phase composition determination.

The chemical composition of selected samples was carried out with Atomic Absorption Analysis. The study was performed with a Perkin-Elmer 3030 atomic absorption spectrophotometer, flame: air-acetylene.

Some minerals typomorphic to the deposits, as well as the predominant fractions, were digitally photographed with a LEICA EZ4D magnifier at magnification 35.

Results and discussion

Mineral composition

Mineralogical studies of the samples taken from the tailings dam show that, regardless of the fraction

Fig. 1. Laky tailings dam: general view

Фиг. 1. Хвостохранилището в Лъки: общ изглед

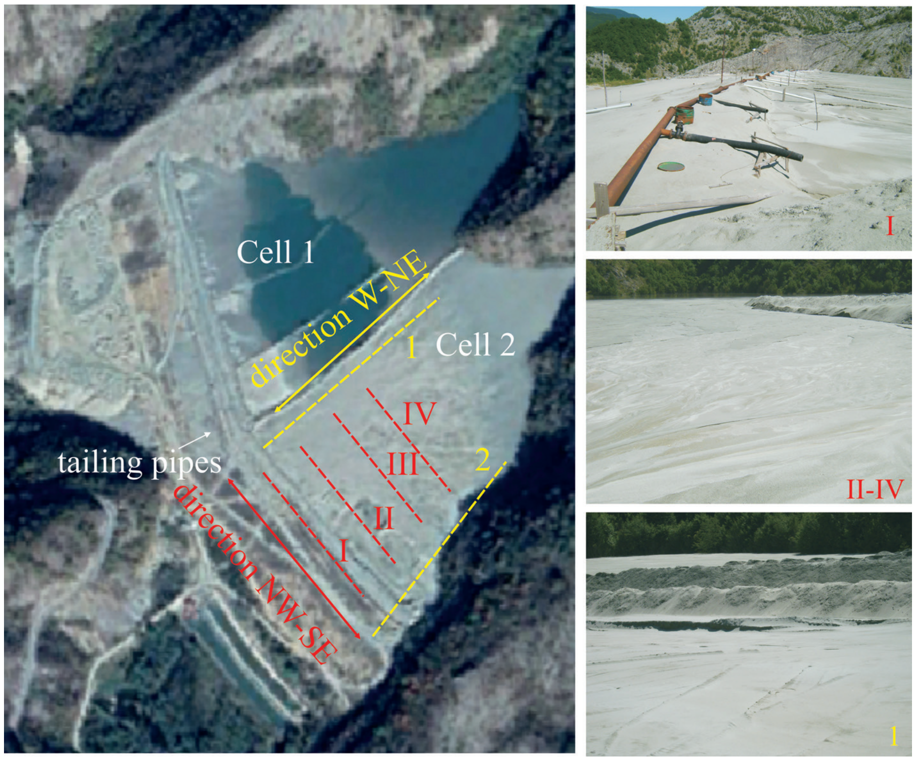


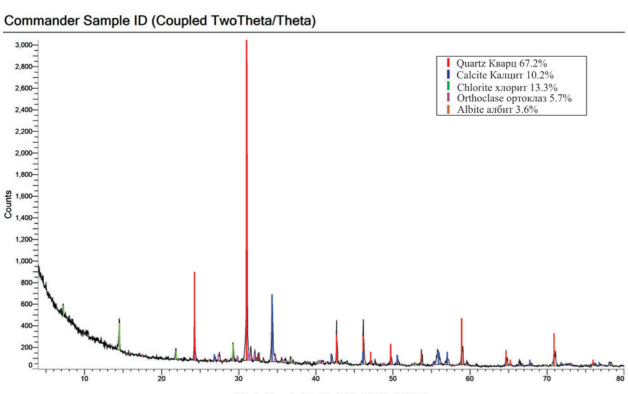
Fig. 2. Laky tailings dam: sampling directions and profiles

Фиг. 2. Хвостохранилището в Лъки: посоки и профили на опробване

size and location of the sediment, its composition is quite similar. According to XRD analyses, quartz, calcite, feldspars, kaolinite, mica (biotite or sericite), chlorite predominate, and dolomite, amphibole, and johansenite are presented in smaller quantities (Fig. 3).

Epidote, hypogene hematite, rarer silver nugget, garnet, rhodonite, wollastonite, johansenite, and ore minerals pyrite, chalcopyrite, galena, and sphalerite are also observed under a magnifying glass in most samples (Fig. 4).

Pyrite and chalcopyrite, less often sphalerite and galena were determined from the ore minerals by XRD. Observations under a magnifying glass show that they are most often intergrowth with quartz (Fig. 5) and less often with carbonates.



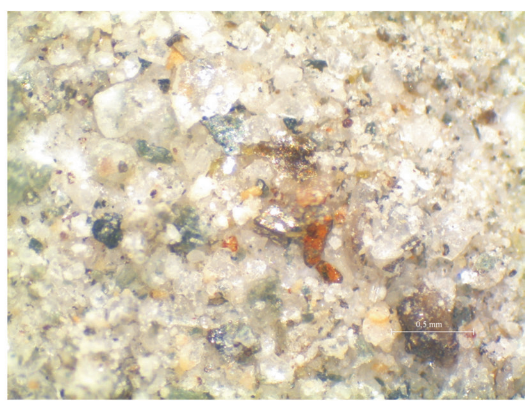


Fig. 3. Mineral composition of tailings dam material – main minerals

Фиг. 3. Минерален състав на материала на хвостохранилището – основни минерали

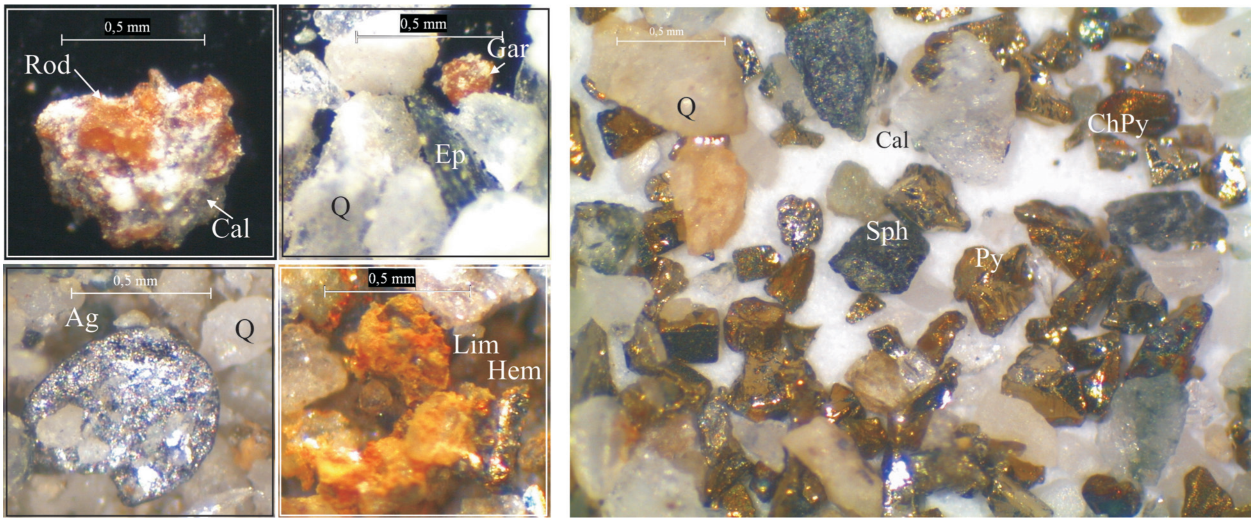


Fig. 4. Mineral composition of tailings dam material – rare minerals (Rod, rhodonite; Cal, calcite; Ag, silver; Gar, garnet; Ep, epidote; Q, quartz; Py, pyrite; ChPy, chalcopyrite; Lim, limonite; Hem, hematite)

Фиг. 4. Минерален състав на материала на хвостохранилището – редки минерали (символи: Rod – родонит; Cal – калцит; Ag – сребро; Gar – гранат; Ep – епидот; Q – кварц; Py – пирит; ChPy – халкопирит; Lim – лимонит; Hem – хематит)

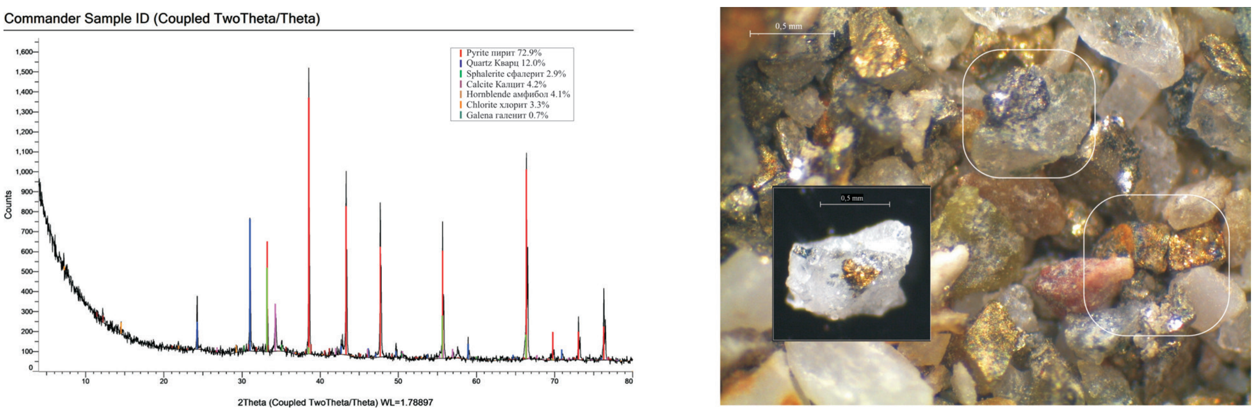


Fig. 5. Mineral composition of tailings dam material – main sulfide minerals; intergrowth of sulfides with quartz

Фиг. 5. Минерален състав на материала на хвостохранилището – основни сулфидни минерали; прорастване на сулфидни минерали с кварц

Main minerals

The predominant mineral is quartz. Its color is quite diverse: both transparent and milky white, as well as yellowish, reddish, and greenish, which is due to micro-inclusions mainly of limonite, hematite, and chlorite. Relatively often, it is fine-grained and associates with the main sulfide minerals: galena, chalcopyrite, and pyrite (Fig. 5), less often sphalerite, whose dimensions usually do not exceed 0.2–0.3 mm. This shows that the complete extraction of the metals by the used flotation technologies is practically impossible and a part of them (along with their trace elements) will always end up in the tailings pond sludge.

Ore minerals

Pyrite is found to be ubiquitous. Depending on the length of the transport, it is observed under a magnifying glass as stronger or slightly broken crystals. It is often oxidized (limonitized or hematitized). Chalcopyrite is also present almost in all samples but in different quantitative ratios. Pyrite and chalcopyrite were found not only in all samples from the tailings pond but also in those taken outside it: from the sand embankment of the levee, from the terrace 50 m below it, and below the retaining wall.

Galena is less common, but this is probably due to its stronger crushing and “pulverization”. Sphalerite was identified in only a few samples, but it is assumed that it is present in a highly fragmented form in all the others given their high zinc contents according to the chemical analyzes (Table 1).

Other minerals

Epidote, biotite, amphibole, and hypogene hematite are also found in almost all samples, but in much smaller quantities. Very rarely spessartine-type gar-

Таблица 1
Атомно-абсорбционни анализи (в ppm) на проби от хвостохранилището в Лъки

Table 1
Atomic absorption analyzes (in ppm) of samples from the Laky tailings dam

№	Fe	Cu	Zn	Pb	Ag	Mn	Cd	Co	Ni	Cr	Li	Rb
Direction NW-SE												
Profile I (under pipes – Eastern end-site)												
1	64195	1397	4109	3391	6	17464	31	47	25	< 2	20	61
2	79941	1517	2325	4516	2	19762	19	69	29	7	19	63
3	81046	1421	3533	3473	7	18294	21	71	34	< 2	20	67
4	66253	1498	4523	3855	4	16642	38	51	27	9	18	66
Profile II (on 20 m E from the pipes)												
1	28118	466	2830	1972	< 1	13825	13	22	28	< 2	27	102
2	31953	287	1802	1768	1	15759	15	21	29	< 2	24	98
3	27884	331	1793	1831	1	14316	13	23	27	2	26	100
4	29913	289	1558	1648	1	12352	11	22	30	3	28	104
Profile III (on 50 m E from the pipes)												
1	17815	306	1149	1228	1	8317	7	23	24	< 2	26	91
2	17194	141	910	913	< 1	8315	5	22	37	11	24	93
3	18777	395	1381	1694	< 1	6974	7	23	26	< 2	23	88
4	19609	237	1009	1417	< 1	7859	8	21	40	8	25	81
Profile IV (on 70 m E from the pipes)												
1	17381	169	802	937	< 1	6975	7	25	28	13	27	99
2	18234	312	1291	895	1	5452	10	22	34	16	25	97
3	22571	155	1611	1706	< 1	5712	9	24	69	52	24	94
4	20318	587	3077	2539	1	6588	14	27	31	37	26	101
Direction W-NE												
Profile 1 (levee)												
1	21437	328	2353	1471	< 1	14194	11	20	23	16	31	89
2	20504	279	2976	911	1	15472	7	22	21	13	23	94
3	22114	271	1956	1097	1	14132	11	21	54	19	27	88
4	19894	409	3374	1258	< 1	15914	15	21	29	< 2	26	91
Profile 2 (Southern end-site)												
1	29852	1238	1274	1602	1	26296	33	24	24	2	24	79
2	34064	1030	978	1264	< 1	25047	25	29	51	< 2	24	84
3	33650	1174	1008	1437	1	25742	19	27	37	2	23	81
4	35109	1349	1283	1775	1	26879	13	31	29	< 2	22	82
Ore fractions												
1	137432	1517	2155	3284	7	14073	16	172	30	< 2	17	53
2	156319	2781	12107	15763	21	12969	75	133	174	29	15	37
3	160146	5466	2637	7482	24	8911	13	166	43	16	12	41
4	211195	2479	2295	5247	11	8671	11	211	394	< 2	10	29
5	145166	5101	11401	12059	< 1	14234	16	123	28	17	31	88

net, wollastonite, and johansenite were found and in some isolated cases native silver is observed.

Mineral distribution

The distribution of minerals is relatively homogeneous in the samples taken from the main area, although stratification is observed in depth, with alternating layers rich in sulfides and those composed mainly of quartz (Fig. 6).

A general enrichment of the heavier mineral fraction, made up of mostly pyrite and chalcopyrite, can be noticed along the end-sides and on the "tongues" upstream (Fig. 7). In the other areas, ore minerals in small amounts occur in all fractions even in the finer-grained and more clayey micronized fractions.

However, all cases of enrichment with heavy mineral fractions are associated with washing with rainwater i.e., the processes are seasonal and ran-

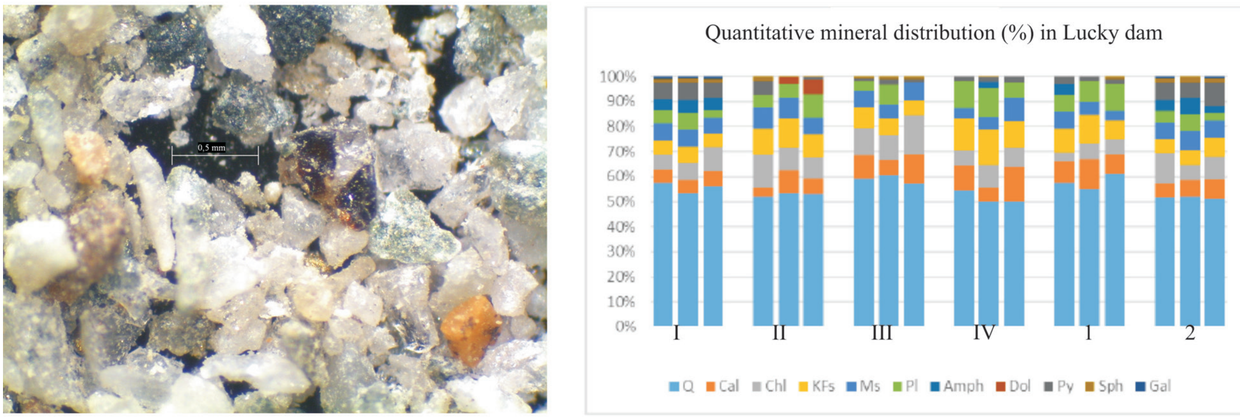


Fig. 6. Tailings dam material: average shaft samples – diagram of quantitative ratio of minerals according to XRD analysis (symbols: Q, quartz; Cal, calcite; Chl, chlorite; Amph, amphibole; KFs, potassium feldspar; Ms, muscovite; Pl, plagioclase; Dol, dolomite; Py, pyrite; Sph, sphalerite; Gal, galena)

Фиг. 6. Материал на хвостохранилище: средни валови проби – диаграма на количественото съотношение на минералите според XRD анализ (символи: Q – кварц, Cal – калцит, Chl – хлорит, Amph – амфибол, KFs – калиев фелдшпат, Ms – мусковит, Pl – плагиоказ, Dol – доломит, Py – пирит, Sph – сфалерит, Gal – галенит)

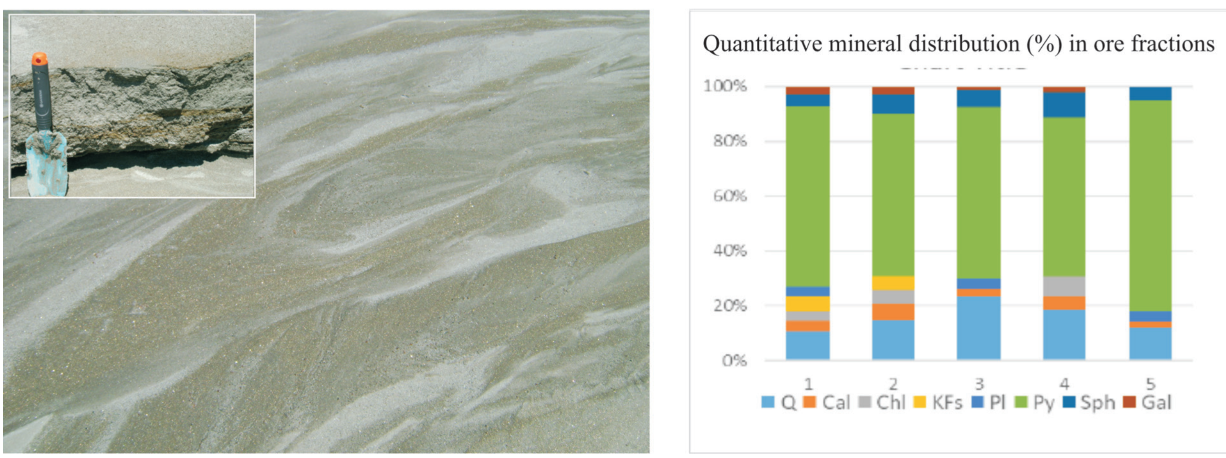


Fig. 7. Tailings dam material: "tongues" upstream and stratification of tailings sediments – diagram of quantitative ratio of minerals according to XRD analysis (symbols: Q; quartz, Cal; calcite, Chl, chlorite; KFs, potassium feldspar; Pl, plagioclase; Py, pyrite; Sph, sphalerite; Gal, galena)

Фиг. 7. Материал на хвостохранилище: руслови „езици" и стратификация на утаения материал – диаграма на количественото съотношение на минералите според XRD анализ (символи: Q – кварц, Cal – калцит, Chl – хлорит, KFs – калиев фелдшпат, Pl – плагиоказ, Py – пирит, Sph – сфалерит, Gal – галенит) dom, and no permanent mineral distribution can be established.

On the other hand, except for sulfide-enriched stratified levels and "tongues" of current, the difference in the composition and granulometry of the sediment in the tailings and outside is not particularly large. From this, it follows that a part of the dry sediment in the tailings pond together with all the minerals present in it (both non-ore and ore) is carried by the wind all over the valley, including near the city of Laky, and is probably absorbed by the soil layer and the vegetation.

Chemical composition

The mineral composition of the tailings samples explains the results obtained from the atomic absorption analyses (Table 1). The high values of Fe content (from 17 194 to 21 1195 ppm) are consistent with the presence of pyrite and chalcopyrite and the rock-forming mafic minerals, skarn silicates, carbonates, and oxidizing (hematite and limonite) phases. The presence of pyrite and chalcopyrite in almost all samples explains the contents of Co (20–211 ppm) and Ni (21–394 ppm) in all analyses, which are their characteristic trace elements. The high concentrations of Mn (from 5452 to 26 879 ppm) are due to both its presence as a trace element in sulfide minerals and widespread manganese silicate and carbonate mineralization in the developed deposits.

Despite the effective technology of extracting the main components Zn and Pb, the chemical analysis shows high concentration values of the two elements Zn 810–4109 ppm, and Pb 895–4516 ppm in the base material of the tailings and Zn up to 12 107 ppm, Pb up to 15 763 ppm in the enriched ore minerals fractions. The most likely reason for the non-recovery of Pb and Zn in flotation is the observed fine intergrowth of their sulfides with quartz (Fig. 5) and less commonly with carbonates. The data from the chemical analyses show that the contents of Ag and Au are insignificant. In 30% of the analyses, its contents are below the detection limit of atomic absorption (below 1 ppm), and in about 40% it is 1 ppm (i.e., at the lower limit of the method). A slightly higher silver content (21–24 ppm) is reported in individual samples enriched in the ore fraction.

Conclusions

The lack of regularity in the spatial enrichment of ore minerals, and the insignificant contents of gold and silver determine that, in the current state of technological processing, the tailings of the Laky deposit cannot be considered a technical (anthropogenic) deposit. Of particular interest for possible applications in the ceramic industry are quartz and feldspars. The presence of micro-inclusions in quartz, mainly of limonite, hematite, and chlorite, on the one hand, is an obstacle to its use, but on the other hand, the methods of synthesis of sulfide glass-ceramics have been published (Rowcliffe et al., 1978; Rawlings et al., 2006; Hayashi et al., 2010).

***Acknowledgments*: The authors thank for the financial support and equipment provided by Project BG05M2OP001- 1.002-0019: "Clean Technologies for a Sustainable Environment – Water, Waste, Energy for a Circular Economy" (Clean & Circle) for the construction and development of a Competence Center, funded by the Science Operational Program and Smart Growth Education, co-financed by the European Union through the European Structural and Investment Funds.**

References

Hayashi, A., K. Minami, M. Tatsumisago. 2010. Development of sulfide glass-ceramic electrolytes for all-solid-state lithium rechargeable batteries. – *J. Solid State Electrochem*, *14*, 1761–1767; https://doi.org/10.1007/s10008-010-1098-5.

Rowcliffe, D. J., R. L. Jones, J. K. Gran. 1978. A notched ring fracture toughness test for ceramics. – In: Bradt, R. C., D. P. H. Hasselman, F. F. Lange (Eds.), *Flaws and Testing. Fracture Mechanics of Ceramics*, 3. Boston, MA, Springer; https://doi.org/10.1007/978-1-4615-7017-2_27.

Rawlings, R. D., J. P. Wu, A. R. Boccaccini. 2006. Glass-ceramics: Their production from wastes – A Review. – *J. Mater. Sci.*, *41*, 733–761; https://doi.org/10.1007/s10853-006-6554-3.

Vangelova, V., Ts. Stanimirova, Ts. Iliev. 2007. New data on the mineralogy and geochemistry of a deposit Goranska padina, Laky ore field. – *Ann. Univ. Sofia "St. Kl. Ohridski", Fac. Géol. et Géogr.*, *100*, 1–Géol., 131–154.

Vangelova, V., E. Nejkova. 2009. Mineralogy and geochemistry of Laky dam sediments (central Rhodopes): environmental effects. – *Ann. Univ. Sofia "St. Kl. Ohridski", Fac. Géol. et Géogr.*, *103*, 1–Géol., 89–112.

Постъпила на 22.11.2022 г., приета за печат на 5.12.2022 г.
Отговорен редактор Йоцо Янев