Characterization of polymetallic ore and flotation concentrate from the Mária Mine (Rožňava, Spiš-Gemer Ore Mts., Eastern Slovakia)

Slavomír Hredzák¹, Marek Matík¹, Ol'ga Šestinová¹, Daniel Kupka¹, Jozef Hančuľák¹, Anton Zubrik¹, Ingrid Znamenáčková¹, Silvia Dolinská¹, Martin Sisol², Michal Marcin²

¹Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, SK-04001 Košice, Slovakia
²Institute of Earth Resources, Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Košice, Letna 9, SK-04200, Košice, Slovakia

hredzak@saske.sk

Abstract. The contribution deal with the study on composition of tetrahedrite-bearing siderite ore from Maria Mine nearby Rožňava and of tetrahedrite concentrate prepared from this ore by froth flotation. The Rožňava ore field consists of two main vein systems, namely Mária and Strieborná (Argenteous/Silvery) ones, respectively. The both vein systems are situated in the Early Paleozoic Gelnica Group of the Gemeric Superunit, in Bystrý Potok Formation (Upper Silurian) and in the Drnava Formation (Early Devonian). The filling of vein systems is formed mainly by siderite, quartz, tetrahedrite, pyrite, arsenopyrite, chalcopyrite, ankerite, albite, pyrrhotite, marcasite, less tourmaline, sercite, chloride, apatite, magnetite, etc. The rock surroundings is represented by quartzy metapsammite, sericitic-quartzite and sericitic-graphitic phyllites (Jakubiak, 2008, Blišťan, 2009, Varga, 2013, Mikuš, 2018). Thus, metal ore as a feed to froth flotation and obtained concentrate were subjected to grain size analysis. The grain size fractions were assayed using GA, AAS, MS-ICP and CHNS. Mineral composition of samples was studied using XRD. So, polymetal ore contains 18.99 % SiO₂, 37.01 % FeO, 1.84 % MnO, 7.36 % C, 2.36 % Cu, 1.70 % Sb, 0.15 % As, 2.32 % S, 770 ppm Ag and 216 ppm Hg. Tetrahedrite concentrate containing 25.59 % Cu, 19.68 % Sb, 1.19 % As, 20.08 % S, 0.57 % Ag, 1.20 % Hg, 1 % SiO₂, 16.16 % FeO, 0.48 % MnO and 2.17 % C at a mass yield of 4 % was prepared. XRD study showed that siderite occurs as a dominant mineral in metal ore. Quartz, tetrahedrite and sercite are presented as accompanying minerals. Accessories are represented by chlorite, probably clinochlore. As to flotation concentrate, tetrahedrite is dominant mineral, which accompanied by siderite. Accessories can be represented by chalcopyrite, arsenopyrite, sercite, pyrite, quartz and chloride.

1. Introduction
The area of the Spiš Gemer Ore Mts. is known by intensive mining activity in the past. The siderite-sulphidic veins were exploited to obtain metals such as iron, copper, antimony, mercury, manganese gold, silver, nickel, cobalt, etc. The first written documents about mining and ore processing in the surroundings of Rožňava are coming from as far back as the 11th century. The mining of precious and nonferrous metal ores was dominant during the 11th-14th centuries and from 17th century the mining and processing of iron ores began. The Golden age of Rožňava mining can be dated at the turn of the 16th century, when new technologies were introduced to mining entrepreneurship. Similarly, a modernization of iron production in this region started in the second half of the 19th century. Finally, the period after WW2 until 1990 was further boom age of Rožňava mining.
but after 1993 mining activities in the vicinity of Rožňava were finished (excepting only siderite ore mining and processing facility in Nižná Slaná, which was closed in 2008) [1].

Thus, from 1990s mining activities were reduced not only in Slovakia, but generally in whole Europe mainly due environmental movement and naive views. This fact resulted in an identification of EU’s unwilling overdependence on raw materials import, which causes vulnerability the EU’s economy or more precisely industry. So, up to now 4 editions of List of Critical Raw Materials were published, last in 2020 [2]. There are also other significant documents e.g. “A New Industrial Strategy for Europe” [3] and “The European Green Deal” [4] from which also implies higher demand for metals. Thus, low-carbon technologies require key six metals, namely Li, Co, Cu, Ni, Mn and REE [5], and their enhanced consumption is expected [6], e.g. IEA reported that electrical car needs about 6 times more minerals (total ca 207 kg, graphite 66.3 kg, Cu 53.2 kg, Ni 39.9 kg, Mn 24.5 kg, Co 13.3 kg, Li 8.9 kg....total 207 kg), than conventional car (Cu 22.3 kg, Mn 11.2 kg....total 33.9 kg, in both cases steel and aluminium is not considered). Similarly, as to power generation plants, Solar PV, Onshore wind and Offshore wind need 5.9, 8.7 and 13.2 times more minerals comparing to natural gas (kg per MW), e.g. Cu consumptions are 1100 for natural gas, 1150 for coal, 1473 for nuclear, 2822 for solar PV, 2900 for Offshore wind and 8000 for Offshore wind, respectively (all values in kg per MW) [6].

Based on above mentioned some Slovak deposits of critical (within the meaning of the EU list) and other significant minerals/metals were revaluated as it is reported in [7]. Currently, only one metal deposit is exploited in Slovakia, namely Banská Hodruša. The vein with precious metals mineralization occurs in the surroundings of pyroxenitic andesite, typical association is as follows: quartz, rhodonite, rhodochrosite/Mn-calcite, Fe-dolomite, siderite, pyrite, galena, sphalerite, chalcopyrite, further tetrahedrite, polybasite, hessite, electrum, and gold of fineness 806-878 [8]. The ore contains 12.3 g/t (6.5-14.8 g/t) Au, 7.5 g/t (5-8.7 g/t) Ag, 0.2 % Pb and 0.044 % Cu. The concentrate at mass yield of 2.465 % runs 480 g/t (135–323 g/t) Ag, 8.1 % (3.1–9.6 %) Pb and 1.9 % (0.6–2.4 %) Cu [9].

Finally, the Strieborná (Argenteous/Silvery) vein system seems to be perspective as to winning some critical or strategic metals. The vein filling is represented by siderite and quartz-pyrrhotite association. Siderite forms 65–70 % of vein stuff, furthermore quartz, tetrahedrite, pyrite, arsenopyrite and chalcopyrite are of significant abundance as aggregates, nests and grains. Tourmaline, apatite, rutile, gersdorffite, magnetite occur as minor minerals. Eventually, accessories are represented by ullmannite, bismuthinite, horobetsuite, native bismuth, galena, sphalerite, jamesonite, boulangerite, stibnite and native silver [10-14]. An overview of geological examination results (prospecting drifts, cross-cuts, excavations, underground prospecting wells) are reported in [15]. Thus, 3,302,179 tons of economic reserves with quality 33 % Fe, 0.816 % Cu, 0.527 % Sb, 0.010 % Hg and 173.8 g/t Ag are referred [15]. After [3] an amount of geological reserves is 4,211,000 tons, economic reserves are 3,495,000 tons of quality 33.64 % Fe, 0.961 % Cu and 204.5 g/t Ag.

As a matter of course, it is not expected that Slovakia will be a key player regarding critical minerals, but some at least small contribution to improvement of unfavourable balance of metal trade in the EU can be made.

So within the frame of current research, the samples of tetrahedrite-bearing siderite ore and tetrahedrite flotation concentrate prepared from the ore at mass yield of 3.94 % were studied with the aim to determine mineralogical composition, grain size distribution and chemical composition in dependence on grain size [16].

2. Material and methods
The samples of tetrahedrite-bearing siderite ore and tetrahedrite flotation concentrate were subjected to grain size analysis by dry way using multi-deck oscillating screen TE-III (Chirana, Slovakia) equipped by sieves of required mesh size. The products of screening have been weighted due to determination
of mass yields, further quartered and ground in vibrating mill VM-1 (KSMH Hranice, Czech Republic), output grain size of 0.020–0.150 mm to obtain specimens for analyses. Thus, on the basis of mass yields and contents of assayed chemical components, the quality of ore and concentrate as well as recoveries of observed components into grain size fractions were determined.

X-ray fluorescence method was applied for preliminary assessment of samples. It was carried out by means of a table XRF spectrometer Spectro Xpos model XEPO3 (Spectro Analytical Instruments, GmbH, Germany) at following conditions: HOPG-crystal, X-ray tube VF50 Pd with Be window, maximum power 50 W and voltage 50 kV, resolution 145 eV on Kα Mo line, the measuring range 11Na–92U. The pressed tablets with diameter 32 mm consisting of 5 g sample under 100 μm and 1 g powder CEREOX BM-0002-1 were prepared for analyses.

Loss on ignition (LOI) at 900 ºC and SiO₂ content were assayed gravimetrically (GA). Mg, Ca, Mn, Al, Fe, K and Na have been analyzed by atomic absorption spectroscopy using the device Varian AA240FS, (Australia). Ti, Cr, Zn a Mn were assayed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using the device Agilent 7700 (Agilent Technologies, Inc. Wilmington, USA) for detection of elements in the range 2–260 μμ, possibility of ultratrace analysis with sensitivity in ppt unit.

The analyses of Hg content were performed using the device Tri-Cell DMA 80 (Direct Mercury Analyzer, Milestone, Inc. USA.), which operates on the basis of combination of thermal decomposition, amalgamation and AAS. The atomic absorption is measured at 253.65 nm by silicon UV detector. The limit of detection is 0.0015 ng of Hg.

Carbon, hydrogen, nitrogen and sulfur were determined using a CHNS Vario MACRO Cube analyzer (Elementar Analyse systeme GmbH, Hanau, Germany) equipped with a thermal conductivity detector. Helium (purity 99.995 %, intake pressure 2 bar) was chosen as a carrier gas in all analyses. The purity of oxygen for combustion was 99.995 % with intake pressure of 2 bar. The combustion tube was set at 1150ºC, the reduction tube at 850ºC. The sulfanilamide (C = 41.81 %, N = 16.26 %, H = 4.65 %, S = 18.62 %) was used as the CHNS standard.

X-ray powder diffraction study was performed using D8 Advance diffractometer (Bruker, Germany), working with Cu Kα1 radiation at voltage 40 kV and current 40 mA. The data were collected over the angular range 5° < 2θ < 80° with measuring steps 0.03° and a counting time 5s. Measured diffractograms were processed using programs Diffracplus Basic and Excel. The databases such as webmineral, handbook of mineralogy and the Arizona bookcase were also used at mineral phases identification [17,18]. Abbreviations of minerals were used after [19,20].

Optical observations were performed by monocular microscope Levenhuk (magnification max. 30x). Documentation of lump ore was performed by mobile phone Sony Xperia. The cleaning of surface grains was performed using the ultrasound vessel K6 (Kraintek, Slovakia) output 200 W, frequency 38 kHz.

3. Results and discussion

3.1. Tetrahedrite-bearing Siderite Ore

The results of chemical analyses are introduced in Table 1. The recoveries of observed chemical components into grain size fractions are summarized in Table 2.

As to grain size, the most copper-rich are finer classes below 0.5 mm, or more precisely below 0.25 mm. The most silver-rich class is under 0.1 mm. A content of Fe corresponds with C, Mn and less with Mg. So the highest content of these elements are in class 0.71-1 mm. This fact points to bond of Mn and Mg in siderite.
Table 1. Chemical composition of ore as dependence of grain size

| Grain size [mm] | Yield [%] | LOI [%] | SiO₂ [%] | FeO [%] | Cu [%] | Sb [%] | Ag [%] | MnO [%] | Zn [%] | As [%] | CaO [%] | MgO [%] |
|-----------------|-----------|---------|----------|---------|--------|--------|--------|---------|--------|-------|---------|---------|
| +2.00           | 1.89      | 22.37   | 24.88    | 34.92   | 1.36   | 1.048  | 0.074  | 1.77    | 0.037  | 0.104 | 0.23    | 2.99    |
| 1.00 - 2.00     | 18.28     | 24.14   | 18.98    | 37.57   | 1.75   | 1.367  | 0.038  | 1.90    | 0.039  | 0.121 | 0.19    | 3.13    |
| 0.71 - 1.00     | 11.67     | 24.50   | 16.88    | 38.33   | 2.26   | 1.898  | 0.075  | 1.96    | 0.059  | 0.117 | 0.32    | 3.12    |
| 0.50 - 0.71     | 10.26     | 23.60   | 19.69    | 36.67   | 1.98   | 1.562  | 0.062  | 1.89    | 0.045  | 0.096 | 0.24    | 3.05    |
| 0.25 - 0.50     | 20.05     | 23.97   | 18.48    | 37.37   | 2.34   | 1.992  | 0.090  | 1.82    | 0.057  | 0.156 | 0.36    | 2.99    |
| 0.10 - 0.25     | 18.26     | 23.73   | 17.62    | 37.31   | 2.81   | 1.800  | 0.061  | 1.87    | 0.080  | 0.184 | 0.50    | 2.91    |
| - 0.10          | 19.58     | 22.50   | 21.10    | 35.45   | 2.91   | 1.650  | 0.124  | 1.70    | 0.087  | 0.196 | 0.48    | 2.67    |

feed 100.00 23.66 37.01 3.26 1.73 0.077 1.84 0.062 0.151 0.36 2.26

Table 2. Recoveries of observed chemical components into grain size fractions

| Grain size [mm] | Yield [%] | LOI [%] | SiO₂ [%] | FeO [%] | Cu [%] | Sb [%] | Ag [%] | MnO [%] | Zn [%] | As [%] | CaO [%] | MgO [%] |
|-----------------|-----------|---------|----------|---------|--------|--------|--------|---------|--------|-------|---------|---------|
| +2.00           | 1.89      | 1.78    | 2.47     | 1.78    | 1.09   | 1.16   | 1.82   | 1.81    | 1.12   | 1.30  | 1.21    | 1.91    |
| 1.00 - 2.00     | 18.28     | 18.65   | 18.27    | 18.55   | 13.53  | 14.67  | 9.03   | 18.85   | 11.42  | 14.66 | 9.69    | 19.33   |
| 0.71 - 1.00     | 11.67     | 12.09   | 10.38    | 12.09   | 11.16  | 13.01  | 11.38  | 12.42   | 11.04  | 9.05  | 10.42   | 12.31   |
| 0.50 - 0.71     | 10.26     | 10.23   | 10.64    | 10.16   | 8.59   | 9.41   | 8.27   | 10.52   | 7.40   | 6.53  | 6.87    | 10.57   |
| 0.25 - 0.50     | 20.05     | 20.31   | 19.51    | 20.24   | 19.84  | 23.45  | 19.80  | 18.31   | 20.73  | 20.13 | 20.25   | 17.97   |
| 0.10 - 0.25     | 18.28     | 18.33   | 16.96    | 18.42   | 21.72  | 19.32  | 14.49  | 18.55   | 23.43  | 22.29 | 25.49   | 17.97   |
| - 0.10          | 19.58     | 18.61   | 21.76    | 18.75   | 24.09  | 18.97  | 31.56  | 18.06   | 27.29  | 25.43 | 26.20   | 17.66   |

feed 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00

| Grain size [mm] | Yield [%] | LOI [%] | SiO₂ [%] | FeO [%] | Cu [%] | Sb [%] | Ag [%] | MnO [%] | Zn [%] | As [%] | CaO [%] | MgO [%] |
|-----------------|-----------|---------|----------|---------|--------|--------|--------|---------|--------|-------|---------|---------|
| +2.00           | 1.89      | 2.06    | 2.03     | 0.77    | 0.37   | 2.25   | 1.18   | 1.89    | 1.82   | 2.26  | 2.05    | 1.31    |
| 1.00 - 2.00     | 18.28     | 16.10   | 17.46    | 7.51    | 36.88  | 20.02  | 13.88  | 15.43   | 18.28  | 18.92 | 18.23   | 23.47   |
| 0.71 - 1.00     | 11.67     | 8.81    | 11.85    | 9.36    | 5.76   | 11.16  | 6.86   | 9.62    | 11.67  | 12.16 | 11.06   | 11.53   |
| 0.50 - 0.71     | 10.26     | 9.03    | 11.02    | 6.62    | 17.99  | 10.42  | 4.78   | 8.92    | 10.26  | 10.35 | 7.42    | 11.14   |
| 0.25 - 0.50     | 20.05     | 12.61   | 19.15    | 16.47   | 5.64   | 19.96  | 19.49  | 18.22   | 20.05  | 20.39 | 16.50   | 21.78   |
| 0.10 - 0.25     | 18.28     | 16.10   | 17.46    | 20.12   | 31.46  | 17.10  | 29.24  | 20.38   | 18.28  | 18.42 | 12.31   | 21.09   |
| - 0.10          | 19.58     | 35.30   | 21.03    | 39.16   | 1.90   | 19.10  | 24.58  | 25.93   | 19.58  | 17.94 | 32.22   | 17.40   |

feed 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00
Taking into consideration chemical composition the sample contains ca 71 % of siderite and about 7 % of tetrahedrite. Generally, the both siderite and tetrahedrite are not stoichiometric after their formulas. For instance siderites of the Spiš-Gemer Ore Mts. commonly contains in their lattice admixtures of Mn, Mg and Ca and their formula would be written for instance as: Fe$_{0.78}$Mg$_{0.16}$Ca$_{0.01}$Mn$_{0.05}$CO$_3$, but not simply FeCO$_3$ [21].

The lump ore were study with the aim to verify ore composition and macro-intergrowth. Detection of secondary minerals is also important. Due to small amount they can not be detected in powder form using XRD study but their occurrence can significantly influence the separation process, especially flotation. Similarly, some primary minerals can be “caught” only visually. Thus, pieces of lump ore are described below in Figures 1 and 2, respectively.

![Figure 1. A piece of tetrahedrite (dark grey) covered by secondary covellite (on left, above all blue but also blue-yellow-red islands/films), left from centre light grey quartz (scale at bottom in mm).](image1)

![Figure 2. A piece of ore, siderite, upper left secondary covellite on primary chalcopyrite and tetrahedrite, and Fe oxyhydroxides from weathered siderite (scale at bottom in mm).](image2)

The optical study of ore fraction +2 mm was carried out using monocular. The grains have a size of 2–3 mm. The selected grains are documented in Figures 3 and 4, respectively.

![Figure 3. A grain of tetrahedrite above quartz](image3)

![Figure 4. A rhombohedron of siderite on top left and quartz on top right](image4)

Similarly, specimens of finer grain sizes are introduced in Figures 5, and also in Figure 6 after ultrasound (US) cleaning of grains surface.
Figure 5. Specimens of ore, grain size 0.71-1.0 mm (A, B) and 1.0-2.0 mm (C, D), tetrahedrite – dark grey grains of metallic luster, siderite - brown grains strongly covered by brown ochre, occasionally rhombohedron is visible (centre of A), quartz - white irregular grains, rare chalcopyrite grain (right of centre in D).

Figure 6. Specimens of grain size fraction 0.71-1.0 after US treatment also smaller grains occur due to comminution during US cleaning, tetrahedrite – dark grey grains of metallic luster, siderite - brown grains, quartz - white irregular grains, rare chalcopyrite grain (left of centre in A).
The XRD pattern of tetrahedrite-bearing siderite ore is illustrated in Figure 7. Siderite occurs as dominant mineral in this sample. Quartz, tetrahedrite and sericite are presented as accompanying minerals. Accessories are represented by chlorite, probably clinochlore.

Figure 7. XRD pattern of Tetrahedrite-Bearing Siderite Ore:
Sdr – Siderite, Td – Tetrahedrite, Qtz – Quartz, Ser – Sericite, Chl – Chlorite

3.2. Tetrahedrite concentrate

The results of tetrahedrite concentrate chemical analyses are introduced in Table 3, the recoveries of observed chemical components into grain size fractions are summarized in Table 4.

Table 3. Chemical composition of tetrahedrite concentrate as a dependence of grain size

| grain size [μm] | yield [%] | LOI [%] | SiO₂ [%] | FeO [%] | Cu [%] | Sb [%] | Ag [%] | MnO [%] | Zn [%] | As [%] | CaO [%] | MgO [%] |
|----------------|-----------|---------|----------|---------|-------|-------|-------|--------|-------|--------|--------|--------|
| +150           | 3.39      | 17.76   | 1.47     | 11.05   | 30.44 | 22.20 | 0.44  | 0.08   | 0.72  | 2.35   | 0.07   | 0.18   |
| 100 - 150      | 6.63      | 18.08   | 1.05     | 11.21   | 29.82 | 22.21 | 0.47  | 0.10   | 0.74  | 2.25   | 0.08   | 0.20   |
| 71 - 100       | 8.54      | 18.58   | 0.45     | 11.62   | 30.31 | 22.21 | 0.55  | 0.14   | 0.75  | 2.03   | 0.11   | 0.27   |
| 40 - 71        | 13.70     | 16.41   | 0.95     | 12.61   | 28.00 | 21.10 | 0.63  | 0.22   | 0.74  | 1.49   | 0.15   | 0.41   |
| - 40           | 67.75     | 14.01   | 1.05     | 18.19   | 23.85 | 18.70 | 0.57  | 0.63   | 0.61  | 0.86   | 0.27   | 1.09   |
| feed           | 100.00    | 15.13   | 1.00     | 16.16   | 25.59 | 19.68 | 0.57  | 0.48   | 0.65  | 1.19   | 0.22   | 0.84   |

| grain size [μm] | yield [%] | K₂O [%] | Na₂O [%] | Pb [ppm] | Hg [ppm] | Al₂O₃ [ppm] | Co [ppm] | Ni [ppm] | Cd [ppm] | C [%] | H [%] | N [%] | S [%] |
|----------------|-----------|---------|----------|---------|---------|-------------|--------|--------|--------|-------|-------|-------|-------|
| +150           | 3.39      | 0.61    | 0.12     | 0.02   | 1.405   | 298.54      | 100.00 | 311.00 | 14.00  | 0.530 | 0.144 | 0.154 | 23.84 |
| 100 - 150      | 6.63      | 0.16    | 0.11     | 0.03   | 1.405   | 192.73      | 87.00  | 280.00 | 12.00  | 0.698 | 0.154 | 0.113 | 24.05 |
| 71 - 100       | 8.54      | 0.11    | 0.07     | 0.06   | 1.345   | 234.30      | 77.00  | 259.00 | 13.00  | 0.884 | 0.141 | 0.124 | 23.73 |
| 40 - 71        | 13.70     | 0.13    | 0.08     | 0.08   | 1.267   | 282.48      | 54.20  | 205.80 | 11.20  | 1.223 | 0.123 | 0.133 | 22.89 |
| - 40           | 67.75     | 0.52    | 0.08     | 0.17   | 1.144   | 1117.64     | 13.50  | 96.70  | 7.70   | 2.750 | 0.154 | 0.148 | 18.48 |
| feed           | 100.00    | 0.41    | 0.08     | 0.13   | 1.204   | 838.75      | 32.30  | 144.91 | 9.13   | 2.170 | 0.148 | 0.141 | 20.08 |
Table 4. Recoveries of observed chemical components into grain size fractions

| grain size [μm] | yield [%] | LOI [%] | SiO₂ [%] | FeO [%] | Cu [%] | Sb [%] | Ag [%] | MnO [%] | Zn [%] | As [%] | CaO [%] | MgO [%] |
|----------------|-----------|----------|----------|---------|--------|--------|--------|---------|--------|--------|---------|---------|
| +150           | 3.39      | 3.98     | 4.98     | 2.32    | 4.03   | 3.82   | 2.64   | 0.55    | 3.74   | 6.70   | 1.08    | 0.74    |
| 100 - 150      | 6.63      | 7.92     | 6.96     | 4.60    | 7.72   | 7.48   | 5.51   | 1.43    | 7.52   | 12.54  | 2.54    | 1.57    |
| 71 - 100       | 8.54      | 10.49    | 3.85     | 6.14    | 10.12  | 9.64   | 8.31   | 2.53    | 9.82   | 14.59  | 4.37    | 2.70    |
| 40 - 71        | 13.70     | 14.86    | 13.02    | 10.69   | 14.99  | 14.69  | 15.26  | 6.26    | 15.54  | 17.17  | 9.64    | 6.76    |
| -40            | 67.75     | 62.75    | 71.19    | 76.26   | 63.14  | 64.37  | 68.29  | 89.24   | 63.37  | 49.01  | 82.36   | 88.24   |
| feed           | 100.00    | 100.00   | 100.00   | 100.00  | 100.00 | 100.00 | 100.00 | 100.00  | 100.00 | 100.00 | 100.00  | 100.00  |

As to grain size the most copper-rich and antimony-rich classes are coarser, namely +71 μm. On the contrary the most iron-rich class is the finest, i.e. below 40 μm. This finest class also achieved the highest mass yield, which strongly influenced the values of recovery. Thus, all important chemical components, such as Fe, Cu, Sb and Ag attained the recovery into this class more then 63 %.

Coming from chemical composition of tetrahedrite concentrate contains about 71 % of tetrahedrite (ca 64 % of own tetrahedrite Cu₁₂Sb₄S₁₃ and ca 7 % of tennantite Cu₁₂As₄S₁₃ constituents, small part of As is bonded in arsenopyrite) and about 20 % of siderite.

The XRD pattern of tetrahedrite concentrate is presented in Figure 8. Thus, tetrahedrite is dominant mineral in sample, which is accompanied by siderite. Accessories are represented by chalcopyrite, sericite, arsenopyrite, pyrite, quartz and chlorite.

![Figure 8. XRD pattern of Tetrahedrite Concentrate: Td – Tetrahedrite, Sdr – Siderite, Cep – Chalcopyrite, Apy - arsenopyrite, Py – Pyrite, Ser – Sericite, Chl – Chlorite](image-url)
4. Conclusions
On the basis of preformed research it was shown that ore is formed by siderite as a dominant mineral. Quartz, tetrahedrite and sericite are presented as accompanying minerals. Accessories are represented by chlorite, probably clinochlore. Mineral (siderite) grains are strongly covered by ochres. Chromatic colours are also visible on tetrahedrite grains.

Naturally, tetrahedrite concentrate is composed from tetrahedrite as dominant mineral, which is accompanied by siderite. Accessories are represented by chalcopyrite, sericite, arsenopyrite, pyrite, quartz and chlorite. The concentrate is fine grained, i.e. almost 68 % is under 40 microns. And just this grain size fraction contains the most amount of siderite, which Cu-Sb-Ag contaminates concentrate.

As to targeted metals, namely Cu, Sb and Ag, their enrichment in concentrate comparing to metal content in ore attained 10.8, 11.55 and 7.40, respectively.

Further research will be focused on siderite elimination in concentrate and selective bioleaching of concentrate.

Acknowledgments
This work was supported by the Slovak Scientific Grant Agency for the project VEGA 2/0167/21. This study has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation (Project BioLeach: Innovative Bio-treatment of RM, grant number: 18259).

References
[1] O. Rozložník, “Mineral Raw Materials in the vicinity of Rožňava”, Maj Gemer 2016, 136 p. available at: https://www.majgemer.sk/images/stories/kultura/banici/banictvo/nerastne-suroviny-roznava.pdf
[2] European Commission, “Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability”, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, COM(2020) 474 final, 24 p., Brussels, 3.9.2020.
[3] European Commission, “A New Industrial Strategy for Europe”, Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions, COM(2020) 102 final, 17 p., Brussels, 10.3.2020.
[4] European Commission, “The European Green Deal”, Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions, COM(2019) 640 final, 24 p., Brussels, 11.12.2019.
[5] J. Timperley, “Explainer: These six metals are key to a low-carbon future”, Carbon Brief, Technology, 12 April 2018. Available at: https://www.carbonbrief.org/explainer-these-six-metals-are-key-to-a-low-carbon-future.
[6] International Energy Agency, “The Role of Critical Minerals in Clean Energy Transitions”, World Energy Outlook Special Report, 287 p., IEA, Paris, 2021. Available at: https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions.
[7] P. Baláž, “3. Review of Reserved Deposits of Metals in Slovakia”, Sloval Geol. Mag., vol. 15, No. 2, pp. 31–38, 2015.
[8] V. Nárožný, “The past and future of gold mining in Hodruša-Banská Štiavnica Ore Area”, Conference Proceedings from the International Conference on The present and Future of the Mining and Geology, Proceedings, Wellness Hotel Repíská, Demänovská Dolina, October 5–6, 2017, ed. Mikuláš Beránek, Slovakian Mining Society, Banská Bystrica 2017, pp. 6–11,
2017 (in Slovak).

[9] R. Kaňa, M. Okál, "The development of the production activities of the Slovenská banská, s.r.o. Hodruša-Hámre,” International Conference on Mineral Resources and Environment, Proceedings, Hotel Repiská, Demänovská Dolina, Slovakia, October 7–8, 2010, ed. Mikuláš Beránek, Slovakian Mining Society, Banská Bystrica 2010, pp. 57–59, 2010 (in Slovak).

[10] Z. Jakubiak, “Strieborná vein silver project, Rožňava mining district, Slovak Republic, Latitude 48° 40’ 29˝ N, Longitude 20° 32’ 31˝ E”, Technical report for Global Minerals Limited, Vancouver, British Columbia, Canada - Melbourne, Australia, 82 p., April 2008.

[11] P. Blišťan, P. Grinč, P. Varga, “Reinterpretation of the additional exploitation possibility of the Strieborná žila vein (Rožňava, Slovakia)”, Mineralia Slovaca, vol. 41 pp. 321–330, 2009. (in Slovak).

[12] P. Varga, S. Vargová, E. Vargová, J. Hovanec, J. Daleck, J. Tuček, “Plan of development works and mining of reserved deposit of complex Fe, Cu, Ag ores Rožňava – Strieborná žíla II (silver vein II) by underground way for 2014–2019”, Project on activation of mining production after the law No. 24/2006 on assessment of influence on the environment, 97 pages, 2013. (in Slovak).

[13] T. Mikuš, J. Kondela, S. Jacko, S. Milovská, ”Garavellite and associated sulphosalts from the Strieborná vein in the Rožňava ore field (Western Carpathians)”, Geologica Carpathica, 69, 3, pp. 221–236, June 2018. doi: 10.1515/geoca-2018-0013.

[14] T. Sasvári, L. Maťo, “The characteristics of the Rožňava ore district, in relation to the structural-tectonic analysis and mineralization exemplified by the deposition conditions of the Strieborná vein, Mária mine, Rožňava”, Acta Montanistica Slovaca, Monograph, 1/98, „Rožňava Metal Ore Field“, vol. 3, No. 1, pp. 33–117, 1998 (in Slovak).

[15] I. Mesarčík, M. Jančura, “Geological research and survey on deposits of siderite and complex ores in the ore field - Rožňava an their prognostic evaluation”, Acta Montanistica Slovaca, Monograph, 1/98, „Rožňava Metal Ore Field“, vol. 3, No. 1, pp. 11–25, 1998 (in Slovak).

[16] D. Kupka, S. Hredzák, Z. Bártová, L. Hagarová, A. Luptáková, E. Vargová, M. Matik, A. Zubriš, O. Šestínová, J. Hančuľák, J. Hančuľák, I. Znamenáčková, D. Gešperová, M. Muľová, Z. Szabová, „EITRM106357 WP3.1 - Report on collection of and laboratory works on raw materials samples with spectographic analyzes“, 18259 - BioLeach. BioLeach: Innovative Bio-treatment of RM, Institute of Geotechnics of the SAS, Košice, RIS Task Partner, 08/02/2021.

[17] D. Barthelmy. [Online] 1997-2014 .Available at: www.webmineral.com.

[18] J. W. Anthony, R.A. Bideaux, K. W. Bladh, M. C. Nichols (eds.), “Handbook of Mineralogy”, Mineralogical Society of America, Chantilly, VA 20151-1110, USA. Available at http://www.handbookofmineralogy.org/. 2004-2020.

[19] D. Ozdín, „Minerals abbreviations approved by IMA“, Mineralia Slovaca, vol. 36, pp. 367-370, 2004 (in Slovak).

[20] J. Siivola, R. Schmid, "RB2. List of Mineral Abbreviations", Recommendations by the IUGS Subcommission on the Systematics of Metamorphic Rocks. Recommendations, web version of 01.02.2007. http://www.bgs.ac.uk/scmr/products.html.

[21] S. Hredzák, M. Lovás, M. Matik, J. Briančin, K. Štefušová, J. Vereš, I. Znamenáčková, “Comment to mineralogical-chemical limits of Slovak spathic iron ores as exemplified by upgrading of siderite from the Nížná Slaná deposit”, Situation in ecologically loaded regions of Slovakia and central Europe, Hrádok, 23-24 October 2014, Proceedings, vol. XXIII. Slovak Mining Society, pp. 146-153, 2014 (in Slovak).