Mineralogy of ore dressing products from Banská Hodruša Au (Ag, Pb, Cu) epithermal deposit

Martin Chovan¹, Ivan Jágerský², Vivien Delaney³, Peter Žitňan², Alexander Kubač⁴, Peter Bačík¹, Danka Troppová⁵ & Tomáš Mikuš⁵

¹Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia; chovan@fns.uniba.sk

²Slovenská Banská Ltd., 966 61 Hodruša-Hámre, Slovakia

³SGS Canada Inc., P.O. Box 4300, 185 Concession Street, Lakefield, Ontario, Canada

⁴Department of Economic Geology, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia ⁵Earth Science Institute of Slovak Academy of Sciences, Ďumbierska 1, 974 01 Banská Bystrica, Slovakia

AGEOS Mineralógia produktov úpravy rúd epitermálneho Au (Ag, Pb, Cu) ložiska Banská Hodruša

Abstract: Gold–sulphide ore from epithermal vein deposit Banská Hodruša consists of gold, electrum, galena, sphalerite, chalcopyrite, and pyrite. Minor amounts of tellurides are present in the form of hessite, petzite and other rare Au sulphides and tellurides. Pyrite as a common product of hydrothermal alteration occurs mainly in the wall rock. Gangue minerals are represented by abundant quartz and adularia, clay minerals and carbonates. A combination of classical mineralogical methods – optical microscopy, electron microprobe, scanning electron microscopy, powder X-ray diffraction, automated mineralogy methods – QUEMSCAN RMS, TMS, PMA, and chemical analysis were used to determine composition of the head sample and individual ore dressing products, such as mineral jig concentrate, flotation concentrate and waste. The information about mineral composition of head sample, distribution of minerals in ore dressing products, their chemical composition and optimal grain size (P_{85-88} of 74 µm) has been determined. The concentrate contains approx. 15 % of gangue minerals and approximately 2.5 % of the waste consists of sulphides. The mineral associations and mineral intergrowns has been studied. Gold is liberated well, with more than 70 % of gold being liberated and amenable to flotation, the rest associated with complex mineral assemblages (18 %), silicates and carbonates (9 %) and sulphides (~3 %). Liberation of sulphides is better than 83 %. The ore has excellent metallurgical properties, maximum achievable gold recovery by flotation is 96–98 %. Results of the study provided information to optimize ore dressing processes, particularly quality of milling, effectiveness of flotation process and gravity circuit.

Key words: epithermal mineralization, flotation, gold recovery, grain size, association, liberation

1. INTRODUCTION

The village of Banská Hodruša was one of the centres of intensive historical mining of silver and gold epithermal ores. Currently, only the deep, subhorizontal stockwork hosted by andesites (Koděra et al., 2005; Maťo et al., 1996; Šály et al. 2008) is being mined for Au, to a lesser extent for Ag, Pb, and Cu by the company Slovenská Banská, Ltd. This precious-metal bearing stockwork is cut by quartz-diorite sills and displaced by steep quartz-carbonate veins that were exploited for Ag, Pb, Zn, Cu ore in the past. The mining operations at this deposit commenced in 1994 and the deposit produced 8 tonnes of Au so far. Since the early 1990's, mining has shifted to the eastern part of the deposit with ores rich in electrum and galena, sphalerite and chalcopyrite as the main sulphide minerals (Kubač et al., 2014; Chovan et al., 2016).

Mining in Hodruša-Hámre dates back at least to 14th century, historically targeting silver ores processed in water-powered stamp batteries. Silver ore was exploited until 1952 when silver mines were abandoned and mining continued with exploitation of sulphide copper ores in the Rozália Mine. Soon after the political changes in 1989, the mining of copper was found to be uneconomic and the closure of the mine was planned. Rich Au-Ag ores, discovered in the last phases of the shutdown of the Rozália Mine, are sustaining the mining there since 1994.

In 1929–1931, the first flotation plant for processing of silver ores was built in Hodruša, one of the first of its kind in former Czechoslovakia. The processing plant underwent several reconstructions since 1994. Since that time, processing targeted Au, Ag, Pb and Cu as the economically most important metals. The ore dressing process has been continuously adjusted to the new type of ore and the last large reconstruction, including a complete renewal of the flotation circuit, took place in 2011-2012. A jig concentrator was introduced into the circuit to recover part of the coarse-grained gold, rest of the gold was collected by flotation. Later, the jig concentrator became obsolete owing to rigorous milling and proper homogenization of the head sample, leaving only the flotation units for ore extraction. The performance of a set of modern semi-automatic flotation cells was optimized during semitechnological tests of the plant. Full optimization, however, could be achieved during the routine operation of the

flotation cells, with a large body of information about mineralogical composition of the ores, their textures, and the behavior of gold as the most important ore constituent in the ore dressing process. Mineralogical research was performed with modern research methods including automatized mineralogy (Adams, 2016; Goodall & Scales, 2007; Zhou, 2004; Králová & Dosbaba, 2014) and was focused on three major factors influencing recovery, that is, grain size, association and liberation. These studies also addressed the question of the distribution of minerals in the concentrates and in the waste (flotation tailings).

The distribution and occurrence of gold and other minerals in concentrates and waste was studied by Chovan et al. (2014, 2016), a team of mineralogists and geoscientists from the Faculty of Natural Sciences, Comenius University in Bratislava and the Earth Science Institute of the Slovak Academy of Sciences. During their work campaigns between November 2013–April 2014 and December 2014–May 2015, they contributed significantly to the successful solution of this complicated problem.

Several recent case studies document the advantages of automated mineralogy data collection for mineral processing, including grinding and flotation (Gu et al., 2014). In order to apply such advanced methods to the ores and ore processing in Hodruša, SGS Minerals Services Lakefield (Canada) were contracted in autumn 2015 to investigate and quantify a number of parameters on a bulk ore sample accumulated between July and September 2015. The aim of the study was to confirm and optimize processing parameters via a detailed quantitative mineralogical study (Delaney & Zhou, 2016).

The objective of this paper is to briefly summarize results of the studies (Chovan et al. 2014, 2016; Delaney & Zhou, 2016) and their practical application. The mineralogical study of ore dressing products defined properties and mineral distribution in concentrates and waste in different size fractions.

METHODS AND MATERIALS

Samples for this study were collective samples of the mineral jig (gravity) concentrate (labelled S), flotation concentrate (labelled K), and waste (labelled B), collected on a monthly basis since November 2013 until April 2014. The mineral jig concentrate was collected only in November 2013 as it was not in operation afterwards. Weight of each sample was approximately 1.5 kg. The samples were submitted to the Department of Mineralogy and Petrology at the Comenius University in Bratislava.

The processing plant of Slovenská Banská, Ltd, is crushing and milling the ore to a final grain size of ~70 μ m size. Grain size analysis was carried out by a combination of sieve analysis and hydrometer test. The following sieve mesh sizes were used: 63, 71, 80, 90, 100, 250, 500, and 1000 μ m. Different grain size fractions, some of them further processed by gravity separation methods, were inspected in a binocular microscope Olympus.

Bulk sample for powder X-ray diffraction (pXRD) semiquantitative analysis was prepared from homogenized and pulverized samples. One gram of pulverized sample was homogenized with 0.25 g of an internal standard (99.9 % Al₂O₃, American Elements). Unoriented samples were analyzed with a Philips PW1710 diffractometer (Cu Ka = 1.54060 Å, accelerating voltage 35 kV, beam current 20 mA, step 0.02° 2θ, step time 2 s per one step, graphite monochromator, Geological Institute of the Slovak Academy of Sciences in Bratislava). The range of the measurement was 4-65° 20. Quantitative pXRD analysis was also performed on the BRUKER D8 Advance diffractometer (Laboratory of X-ray diffraction SOLIPHA, Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University in Bratislava) under the following conditions: Bragg-Brentano geometry, Cu Ka radiation, $\lambda = 1.5406$ Å, Ni K_{β} filters, accelerating voltage 40 kV and beam current 40 mA. The step size was $0.01^{\circ} 2\theta$, counting time 1 s per step, and measurement range from 2 to $65^{\circ} 2\theta$. Measured data was evaluated with DIFFRAC^{plus} EVA and quantitative analysis by Rietveld method was made with the DIFFRAC^{plus} TOPAS software. Selected data sets were re-analyzed by the X'pert High Score Plus software.

Polished sections were studied in reflected (RPL) and transmitted (TPL) polarized light with a Leica optical microscope. Selected polished sections were analyzed with the electron microprobes (EMP) Cameca SX-100 (State Geological Institute of Dionýz Štúr in Bratislava) and Jeol JXA 8530FE (Earth Science Institute of Slovak Academy of Sciences in Banská Bystrica). The instruments were used to acquire semi-quantitative energydispersive (EDS) analyses, quantitative wavelength-dispersive (WDS) analyses, and back-scattered electron (BSE) images. For the WDS analyses, these analytical conditions were used: native gold, tellurides, sulphides, and sulphosalts-accelerating voltage 25 kV, current 15 nA, beam diameter 1–3 µm, ZAF correction, Ag (La) PETL – hAg, S (Ka) PETL – pyrite, Cu (Ka) LIFL – chalcopyrite, As (La) TAP – GaAs, Se (La) TAP – Bi₂Se₃, Au (Ma) PETH – Au, Te (La) PETH – CdTe, Sb (La) PETH – stibnite, Hg (Ma) PETJ – cinnabar, Bi (Ma) PETJ – bismuthine, Fe (Ka) LIFL – hematite, Pb (Ma) PETH – galena.

Gold and sulphides were only minor minerals in most of the samples. Therefore, heavy minerals were concentrated by gravity separation (Earth Science Institute of Slovak Academy of Sciences). After the initial sieving, the separation comprised sluicing, elutriation and panning of fine-grained (< 80μ m) fractions. Some samples were concentrated using heavy liquids.

Chemical composition of the samples (49 elements analyzed) was determined by a suite of methods based on fire assay and inductively-coupled plasma (ICP) spectrometers (ALS Chemex laboratories in Rosia Montana, Romania). Sample preparation was conducted using the PUL-31 method (250 g sample split pulverized to $D_{85} > 0.075$ mm). Au and Ag assay was carried out by the Au-GRA-21 method (fire assay with gravimetric finish) from 30 g of sample. Other elements were assayed by the ME-MS-61method (four acid digestion with ICP/AES or ICP/MS finish). Au, Ag, Pb, Cu, Zn assays of the concentrates acquired internally by Slovenská Banská, Ltd., were also used for the purpose of this study.

Modal mineralogy, degree of liberation, and association of the key sulphide and iron oxide minerals for the as-received samples were determined by Quantitative Evaluation of Materials by Rapid Mineral Scan (QEM-RMS) (SGS Minerals Services facility in Lakefield, Canada). The output is designed to provide simple bulk modal mineralogy using QEMSCAN Particle Mineral Analysis (PMA) measurement and XRD analysis. The abundance and the average grain size of gold were determined by QEMSCAM Trace Mineral Search (TMS) in all the super panning products. A gold deportment study was conducted on the sample. The procedure included pre-concentration by gravity through heavy liquid separation (HLS) and super panning (SP). Optical microscopy, SEM-EDS analysis, and QEMSCAN methods were conducted on the representative concentrate samples for gold mineral scanning, identification, grain size measurement, and association characteristics. Chemical assays were also used to determine the distribution of gold in the pre-concentration fractions.

3. RESULTS

3.1. Grain size

Using the sieve analysis, crushed and milled ore was divided into three grain size groups > 100 μ m (coarse-grained), 63–100 μ m (medium-grained), and < 63 μ m (fine-grained).







This basic classification is applied to ore dressing products from November 2013 (S,K,B-11) and January 2015 (K,B-1) (Fig. 1). The mineral jig concentrate (November 2013, Fig. 1A) is mostly coarse-grained (more than 60 % in the fraction $100-250 \mu m$), but also with abundant fine-grained fraction (24 % in the fraction < 63 mm). The flotation concentrate (sample K-11) and waste (sample B-11) are predominantly fine-grained (70-80% in the < 63 μ m fraction), with only 10–20 % of the material being coarser than 100 µm. After the implementation of rigorous milling and proper homogenization of the head sample, the jig concentrator was not used anymore. The samples which underwent better milling and homogenization (e.g., our January 2015 samples) do indeed contain no coarse fraction (> $250 \,\mu m$, Fig. 1B). More than 70 % of material in these samples (both concentrate and waste) is fine-grained (< 63 µm), similar as in the November 2013 samples.

Gravity pre-concentration (laboratory of Earth Science Institute of Slovak Academy of Sciences) revealed that most of the material (74.5 %) in flotation concentrate samples (K-2/2015) is concentrated in the float fraction, abundance of middlings containing mostly sulphides is 23 %. High-density fraction represents only 2.1 % but, as expected, concentrates most of

> gold. Slurry contains 98 % of low density fraction and only 0.6 % of the high density fraction that contains sulphides and occasionally also native gold.

> The coarse fraction (> 100 μ m, Fig. 2A) is dominated by quartz in all ore dressing products as well as by high abundance of pyrite in the mineral jig concentrate, partially also in the flotation concentrate. The medium fraction (63–100 µm, Fig. 2B) has comparable mineral composition for the mineral jig and flotation concentrates. The waste samples contain mostly quartz and more adularia, sheet silicates (illite, dickite, clinochlore), and calcite than the concentrates. Sulphide content in the waste is very low. The finest size fraction < 63 µm (Fig. 2C) has similar distribution of minerals in mineral jig and flotation concentrates; sulphide content is higher in both. The flotation concentrate contains much more sulphides than gangue minerals. Mineral composition of the flotation waste is similar for fineand medium-grained fractions.

> Grain size distribution of gold in the head samples was monitored in the laboratories of SGS Mineral Services (Fig. 3). Much of the gold (33 %) is coarse, > 100 mm, and would have been captured in the jig concentrate, if the jig was still in operation (Fig. 1A). Only 24 % of gold were found in the 63–100 mm fraction and 44 % in the fine-grained (< 63 mm)

fraction. This gold could be recovered in the flotation concentrate.

3.2. Distribution of minerals in ore dressing products

In the ores, gold is associated with galena, chalcopyrite, and sphalerite, less with pyrite. Gangue minerals are quartz, carbonates, with less adularia and clay minerals (Fig. 4A). Some parts of the deposit contain quartz-gold ores with little sulphides (Fig. 4B), in other parts of the deposit, gold is typically associated

with carbonates. The material delivered to the processing plant contains both ores and hydrothermally altered country rocks with dominant quartz, adularia, clay minerals, and pyrite (Kubač et al., 2014). Mineral composition of the ore is reflected in the chemical analyses (Delaney & Zhou, 2016). The dominant components are SiO₂ and Al₂O₃ from quartz and aluminum silicates (adularia, clay minerals) (Tab. 1). The assays show high K₂O (from adularia and illite) and low Na₂O (plagioclase essentially removed during alteration). High Fe (measured as Fe₂O₃total) can be ascribed to pervasive pyritization of the wall rock, high CaO, MnO, and MgO to carbonates in the ore. MgO and Fe may be also present

 Tab. 1. Whole rock analysis by ICP on the head

 sample.

| oxides | wt % | | |
|--------------------------------|--------|--|--|
| SiO ₂ | 71.4 | | |
| Al ₂ O ₃ | 11.4 | | |
| Fe ₂ O ₃ | 5.31 | | |
| MgO | 1.56 | | |
| CaO | 1.78 | | |
| K ₂ O | 5.13 | | |
| TiO ₂ | 0.48 | | |
| MnO | 0.38 | | |
| Cr ₂ O ₃ | < 0.02 | | |
| V ₂ O ₅ | < 0.02 | | |
| Na ₂ O | < 0.2 | | |
| P ₂ O ₅ | 0.073 | | |
| elements | wt % | | |
| Fe | 3.52 | | |
| Pb | 0.71 | | |
| As | 0.016 | | |
| S | 2.88 | | |
| | g/t | | |
| Au | 26 | | |
| Ag | < 10 | | |

in chlorites, elevated TiO_2 is related to rutile or other Ti oxides in altered wall rock. Elevated concentration of Fe, Zn, Pb, and Cu correspond well to the presence of sulphide minerals in the extracted ore.

The QEM-RMS method was used to determine mineral composition of the head sample (Fig. 5). The most abundant minerals are quartz and feldspars (K-feldspar is much more common than plagioclase) and clay minerals, carbonate content is low. The least common gangue mineral whose abundance exceeds 0.5 % is rutile. These mineral proportions in the head sample



Fig. 2. Mineral abundance in ore dressing products (semiquantitative X-ray analysis): A - > 100 µm size fraction; B - 63–100 µm size fraction; C - < 63 µm size fraction.



< 10 to > 105 µm classes.

Tab. 2. Element analysis on the head sample.

| Elements | g/t | Elements | wt% |
|----------|--------|------------------------------|-------|
| Au | 18.7 | Cu | 0.17 |
| Pt | < 0.02 | Fe | 3.32 |
| Pd | < 0.02 | Pb | 0.71 |
| Ag | 16.3 | Zn | 1 |
| As | < 30 | CO3 | 2.16 |
| Ва | 745 | s | 3.12 |
| Ве | 1.12 | S= | 2.79 |
| Bi | < 20 | AI | 5.66 |
| Cd | 54 | Ca | 1.17 |
| Со | 11 | К | 3.95 |
| Cr | 72 | Mg | 0.854 |
| Li | 26 | Mn | 0.258 |
| Мо | < 7 | Na | 0.145 |
| Ni | < 20 | Ti | 0.267 |
| Р | 318 | | |
| Sb | < 20 | _ | |
| Se | < 30 | _ | |
| Sn | < 30 | _ | |
| Sr | 89.1 | _ | |
| TI | < 30 | _ | |
| U | < 20 | _ | |
| v | 72 | _ | |
| γ | 11.2 | S=: Pulp-sulphur as sulphide | |

CD Kfs Otz Ani Sp 100m JEOL 3/9/2016



Fig. 4. Gold in primary ore: A – gold intergrowths with carbonates, quartz and K-feldspar (adularia) and together intersect sphalerite and galena; B – gold forming impregnations and filling of quartz and carbonate druses. BSE image.

correspond well to the mineral proportions in the extracted ore. The most common sulphide is pyrite (4.58 %), followed by sphalerite (1.68 %), galena (0.96 %), and chalcopyrite (0.5 %). Pyrite and rutile are relatively scarce in the ores but very common in hydrothermally altered rocks. Chemical analyses of head samples gave average concentrations of 18.7 ppm for Au and 16.3 ppm for Ag (Tab. 2).

Quantitative pXRD analysis determined mineral distribution in the individual ore dressing stages. Distribution of gangue minerals in the head sample (Fig. 5) and the waste (Fig. 6B) is similar. Feldspars are dominantly represented by adularia, less by plagioclase, carbonates are represented by calcite, less by dolomite. Clay minerals are mostly illite, with less dickite; kaolinite is rare, chlorites (clinochlore) are common. High proportion of gangue is present in the mineral jig concentrate, but their content is lower. In contrary, carbonate and sulphide content is higher (Fig. 6C). The percentage of gangue in the flotation concentrate (Fig. 6A) is much lower, but the percentage of sulphides significantly increases. High pyrite content is related to the pyrite impregnation in hydrothermally altered host rocks. Other sulphides are major constituents of the ore and their quantitative distribution is from the most to least abundant: sphalerite, galena, chalcopyrite. Similar mineral distribution was identified in the flotation concentrate samples and waste (samples from December 2014 to May 2015). Sulphide content in concentrates of all twelve studied samples is between 63-90 %, sulphide content



Fig. 5. Summary of Bulk Mineralogy by QEM-RMS of head sample (technological sample, autumn 2015).



Fig. 6. Mineral distribution in ore dressing products (semiquantitative X-ray analysis), average from 11/2013 to 04/2014 (6 months): A – flotation concentrate; B – flotation waste; C – mineral jig concentrate.

in the waste is 0.8–3 %. Average data for 8 samples (excluding extreme values) are shown in Fig. 7.

Mineral distribution in the ore dressing products reflects the goal of maximal gold recovery. In intergrowths with quartz and sulphides, gold is found in the coarse fraction in the mineral jig concentrate. The intergrowths of gold with sulphides are concentrated in the fine-grained fraction. Mineral jig concentrate has also higher content of carbonates and adularia which are commonly intergrown with gold.

3.3. Mineral and chemical composition of ore dressing products

Bulk rock assay of the technological sample (head sample sent to the SGS Minerals Services Lakefield in Canada) (Tabs. 1, 2) confirmed overall low sulphide content in the ore, increased Zn, Pb, Cu grades, and significant enrichment in gold and silver. High content of Al and K and elevated content of Ca, Mg, Mn correspond to the presence of the identified gangue minerals. The analyzed elements in the multielement assays (49 elements) of dressing products on monthly basis (November and December 2013, January-March 2014), were divided to several groups based on mineralogy. First group contains elements of precious-metal minerals, that is, Au, Ag, Te, Se, Cu, Pb, Zn and Fe represent the major sulphides and As, Cd, Sb, Bi, In, Mo are trace elements of the major sulphides or major constituents of rare ore minerals (Mo, Bi). Al, K, Na, Ti, Mg belong to the major silicate and oxide gangue minerals and Ca, Mn, Mg are major constituents of carbonates. Some other elements (Si, Mg, Fe, Mn, Ag) are present in minerals from several groups. Si occurs in all sillicates and quartz, Mg in chlorites and carbonates, Fe in pyrite, chlorites, carbonates, Mn in carbonates and rhodonite, and Ag in native gold, Ag tellurides and sulphosalts.

The proportions of Au and Ag in the first group of elements (Au, Ag, Te, Se) is variable, possibly caused by variable fineness of electrum and fraction of silver bound in tellurides (Fig. 8A). Flotation concentrate has the highest Ag, Te and Se contents and high Au content. Mineral jig concentrate has the highest Au content, with diminished content of Ag, Te, and all other major elements including Pb (Fig. 8B). The Au-Ag correlation is low ($r^2 = 0.269$) (Fig. 9A). High correlations were detected (Fig. 9B–D) for the element pairs Ag-Te ($r^2 = 0.939$), Ag-Pb ($r^2 = 0.980$), and Te-Pb ($r^2 = 0.972$). They can be explained by the prevalence of hessite (Ag₂Te) over other Au-Ag tellurides and the close spatial association of the tellurides and galena. The Ag tellurides often occur as inclusions in galena and remain locked there in the ore dressing process.



Fig. 7. Percentage of sulphides and gangue minerals in concentrates and waste in eight samples from 2014–2015.

The highest content of metals of the major sulphides (Cu, Pb, Zn, and Fe) was detected in the flotation concentrate, the lowest in the waste (Fig. 8B). Among the four elements, Fe is the one with the highest concentration in all ore dressing products, followed by comparable content of Pb and Zn and lower Cu content. Vast majority of Fe in the chemical assays is related to pyrite, Pb and Zn can be ascribed to galena and sphalerite, respectively. Cu is related to chalcopyrite and its low concentration was





also indicated by microscopic evaluation and pXRD analyses. The latter method tends to overestimate the abundance of chalcopyrite in the samples. The relative proportions of the four elements in the S, K, and B samples are similar.

Flotation concentrate has usually low concentration of all elements of rock-forming minerals (Al, K, Na, Ti). Higher content of these elements was identified in the mineral jig concentrate and the highest concentration is typical for the waste (Fig. 8C). Al and K show very similar distribution pattern in the studied samples. They occur both in illite, muscovite, and adularia, additional sources of Al are kaolinite and dickite. Na content related to rare plagioclase and Ti content related to rutile are very low, but their relative enrichment in the waste is clearly discernible.

Ca, Mn and Mg occur in low concentrations, with Ca having the highest concentrations (Fig. 8D). They are mainly bound to carbonates (calcite, dolomite, and rodochrosite). Mn is the main constituent of the inosilicate rhodonite, which was identified in the ore, but the pXRD analysis did not identify rhodonite in the ore dressing products. The content of all three elements is increasing from the flotation concentrate to the gravity concentrate and waste. Mn may be an exception and be enriched in the concentrates because of common intergrowths of Mn carbonates, sulphides, and gold. Ca in the waste is related to calcite and dolomite and Mg to clinochlore and dolomite.

Among the trace elements As, Cd, Sb, In, Mo, Bi (Fig. 8E), high correlation was calculated for Cd-Zn, implying the usual Cd-Zn substitution in sphalerite. Somewhat weaker correlation for As-Fe (r^2 =0.769) can be explained by heterogeneous As distribution in pyrite. Pyrite in altered rocks contains As whereas pyrite in the hydrothermal veins does not. Minor proportion of As is related to the sporadic polybasite-pearceite. The highest correlation among the trace elements was observed for Bi-Ag (r^2 = 0.954) in the concentrate samples. These elements can be bound to very rare Bi, Ag, (Cu) sulphosalts (mainly matildite). These sulphosalts, together with minerals of the polybasite-pearceite group, were identified in younger mineralized structures that cut the Au mineralization. Ores delivered to the processing plant may occasionally contain also material from these younger structures.

3.4. Minerals and their intergrowths

A detailed study of gold minerals requires preconcentration of ore dressing products by separation in heavy liquids in the laboratories of SGS Minerals Services Lakefield and at the Slovak Academy of Sciences. Heavy liquid separation (HLS) enriched the samples in Au, Fe, Pb, As, and S. After HLS, ~89 % of gold and 7 % of the mass of the sample occur in the sink fraction.

Among the concentrates studied here, the mineral jig concentrate contains the highest fraction of coarse gold, with wirelike and dendritic morphology (Fig. 10A). This is primary gold intergrown with galena, other sulphides as well as gangue

minerals. Most of gold in the mineral jig concentrate is found in the grain size fraction $150-300 \,\mu\text{m}$ (Fig. 10B-F). The coarse fraction may contain gold integrown with prevailing sulphides and gangue minerals. Much gold is present also in the fine fraction (< $80 \,\mu\text{m}$).

The coarse fraction of the flotation concentrate contains relatively little gold. In this concentrate, gold is mostly found in the < 80 μ m fraction, either free or as intergrowths with other minerals. Common flake-like morphology is likely caused by milling and grinding; dendritic aggregates of gold are less frequent (Fig. 11A). Similar morphology is observed for gold in the finest fraction (< 40 μ m) (Fig. 11B). We were able to liberate fine-grained gold (~ 40 μ m in size) by dissolution in HNO₃.

There are fine (~ 80 μ m) but very rare gold aggregates (Fig. 11C) in the waste. This gold forms fine intergrowths with sulphides in association with galena, to a lesser extent with pyrite, sphalerite and chalcopyrite, or occurs free with signs of milling. Gold of this type was identified also in 40–80 μ m size fraction (Fig. 11D).

An extraordinary high Au content in the flotation waste (up to 6 g/t Au) in January 2014 was an incentive to carry out a detailed study of the waste. Samples B2 and B4 were identified as those with particularly high Au content. Gold was found in > 100 μ m size fraction obtained by panning and heavy liquid separation in the laboratory and its presence confirmed by examination of these samples in BSE images. Most of the gold is very fine (up to 5 μ m, Fig. 12A,B) but intergrown with larger grains of quartz, rhodonite and carbonates. The finely disseminated gold in the



Fig. 9. A – negative correlation between Au and Ag; B – high positive correlation between Ag and Te; C – Pb and Ag; D – Pb and Te in ore dressing products (K – diamond, S – quadrate; B – triangle – 11/2013–03/2014).

gangue minerals is common in these samples and is responsible for the high Au content in the waste. We observed also much larger grains (hundreds of μ m) with gold impregnations (Fig. 12C, D). Most of the exposed surface of these grains comprises gangue minerals which do not respond well in the flotation process. Rigorous milling and technically best achievable homogeneity of the fine fraction are required to resolve these technological problems. The finest gold fraction, even if liberated by milling, cannot be recovered mechanically. Chemical treatment, i.e., leaching would be necessary to collect this gold.

Quantitative assessment (QEMSCAN) of gold and base-metal minerals was carried out on a head sample from autumn 2015. This sample was further processed in the laboratories of SGS Minerals Services Lakefieldin Canada and then examined. A summary of the findings relating to pyrite and galena as possible gold carriers, is presented in the following paragraphs.

The total abundance of pyrite is 4.5 % (Fig. 5). Approximately 89 % of the pyrite present in the sample is free (i.e., > 95 area % of the particle is pyrite) or liberated (i.e., > 80 area % of the particle is pyrite). Approximately 3 % of the pyrite is associated with quartz and/or feldspar, and 5 % is in complex mineral assemblages, and trace amounts (< 1 %) occur with other sulphides, clays, and carbonates. The total abundance of galena is approximately 1 % in composite 1 (Fig. 5). Approximately 84 % of the galena present in the sample is free (i.e., > 95 area % of the particle is galena) or liberated (i.e., > 80 area % of the particle is galena). Approximately 5.8 % of the galena is associated with pyrite, 5 % with complex mineral assemblages, ~ 3 % with quartz and



Fig. 10. A – free gold from mineral jig concentrate S 04/2014, 300–500 μm grain size fraction; B–F – intergrowths of gold with sulphides and gangue minerals in mineral jig concentrate S-12/2013; B – intergrowth of tiny gold, galena, and chalcopyrite, RPL; D – BSE; E – gold intergrowths with sphalerite, galena, chalcopyrite, and K-feldspar, surrounded by galena and pyrite, RPL; F – BSE.

feldspar, 2 % with sphalerite, and trace amounts (< 1 %) with clays and/or other minerals. Degree of liberation of the four sulphides (pyrite, sphalerite, galena, and chalcopyrite) found in composite 1 is summarized in Fig. 13. For all four minerals, liberation is \geq 83 %. Therefore, it is assumed that the sulphides are amenable to flotation. Binary middling particles between the sulphides and gold grains are of minor amounts. However, some of the complex gold particles consist of both non-sulphide and

sulphide minerals. It is possible that such particles might also be recovered with flotation. Furthermore, any sub-microscopic gold will be recovered along with the sulphides.

Native gold (averages Au 85 %, Ag 15 %) and electrum (25 % < Ag < 50 %) are the main gold minerals in the sample and account for ~ 92 % of the total mass of the gold minerals. Gold-silver tellurides, including petzite and hessite, account for about 8 %. A few aggregates, identified with the QEMSCAN as an AgAuS



Fig. 11. A – liberated gold and intergrowth of gold with galena, K-04/2014, 40–80 μm grain size fraction; B – tiny gold aggregates from K 04/2014 in < 40 μm grain size fraction, RPL; C – liberated gold and intergrowths with sulphides (galena, pyrite) in waste B-04/2014, size fraction >80 μm, RPL; D – intergrowth of gold with galena B-04/2014, size fraction 40–80 μm, RPL.

mineral, were not further studied. They may also represent fine native gold or electrum associated with sulphides (Fig. 14).

The gold mineral occurrences are grouped into three association categories: (1) Liberated: A gold grain with no other mineral attached and/or a binary particle with ≥ 80 % of gold surface area exposure to the epoxy medium. (2) Exposed or associated as middlings (midds): A gold grain containing < 80 % of surface area exposure to the epoxy medium and occurs adjacent to another mineral. The gold grains are very well liberated and exposed. (3) Locked: A gold grain totally enclosed in another mineral or particle, with 0 % exposure to the epoxy medium in a two-dimensional plane. Locked gold may occur as inclusions that are completely encapsulated in a host mineral, as inclusions in a porous or framboidal permeable host mineral, in interstitial spaces between mineral grains and at borders of mineral grains, enclosed in fractures and micro-fractures, as veinlets and micro-veinlets in the host minerals. The analysis shows that approximately 71 % of gold minerals are free or liberated; 18 % are contained in complex particles, 6 % associated with quartz and feldspar, 2 % with micas and clays, 1 % with galena, the rest of $(\sim 2\%)$ is associated with iron sulphides, sphalerite, silver minerals, carbonates, and other minerals.

Spot WDS electron microprobe analyses (150 analyses) gave average chemical composition of gold in the primary ore as 86 wt % of Au and 16 wt % of Ag. Electrum (25 % < Ag < 50 %) with average Ag content of 26 wt %. is less frequent. Hessite (nominally Ag₂Te) (Fig. 15A,B) contains 63.36 wt % Ag, 36.44 wt % Te, 0.09 wt % S, and 0.51 wt % Au (average of 57 analyses). Petzite (Ag₃AuTe₂) is rare and contains 40.44 wt % Ag, 23–26 wt.% Au, 30.4–33.6 wt.% Te (43 analyses). The AgAuS phase identified by QEMSCAN most likely corresponds to uytenbogaardtite (Ag₃AuS₂) or to a mixture of AuAgSTe minerals (Fig. 15C). WDS analyses identified additional rare minerals calaverite (AuTe₂), krennerite (Au₃AgTe₈), sylvanite (AuAgTe₄), and unnamed AuAgTeS phase (Chovan et al., 2016).

3.5. Modifications of the processing operation

The concentrates produced in the past contained appreciable percentage of gangue minerals. To suppress the gangue minerals, the volume of air flow into the flotation cells was diminished and the froth volume lowered. These measures caused lower volume of pregnant foam in the scavenger tanks and extended flotation time in this technological nod. Despite the expectations, these





Fig. 12. Gold in samples of flotation waste, January 2014: A – impregnations of ore minerals – galena, gold, sphalerite, and hessite in quartz, BSE; B – impregnations of tiny gold grains in quartz and rhodonite, bigger gold aggregate in the lower part of picture, BSE; C – approx. 600 µm big grain, intergrowth of carbonate and quartz with galena, sphalerite, and gold, RPL; D – detailed view of C, BSE.

measures did not affect overall gold recovery, even though the last flotation cell contained higher volume of sulphides in waste. High degree of liberation of gold from its hosts is responsible for the unchanged recovery despite the changes in the technological process.

A placement of the mineral jig (gravity nod) before the flotation nod also did not improve Au recovery. This problem arose because the position of the mineral jig in the circuit was not optimal as no effective control of mineral jig mass recovery was possible. Therefore, another way to improve the gold recovery must have been sought.

The results and suggestions of the mineralogical studies (Chovan et al. 2014, 2015) led to implementation of changes of milling to minimize the coarse $(100-500 \,\mu\text{m})$ fraction. This fraction represented more than 65 % in the mineral



Fig. 13. Liberation (free and liberated) of galena, pyrite, sphalerite, and chalcopyrite



Fig. 14. Main gold minerals abundance

jig concentrate. After the removal of the mineral jig from the processing circuit, the coarse (> 100 μ m) fraction was reduced to ~ 13 % (Fig. 1). Thereby, the process suppressed the very large particles which were responsible for lower gold recovery.

Improved quality of milling resulted in better homogeneity of the mill feed. Gold recovery in the gravity concentrate was 28–47 % (Fig. 16) and improvement or decline of recovery in the gravity nod had no impact on the overall recovery. The content of sulphides in the waste does not significantly correlate with gold recovery. This is another proof that gold is well liberated and recovered mostly as free grains. The overall recovery corresponds well to the Au content in the head sample.



Fig. 15. A – intergrowth galena, gold and tellurides – hessite and petzite, S-12/2013, BSE; B – hessite and petzite intergrown with gold S12/2013, BSE; C – intergrowth of gold with calaverite/krennerite, uytenbogaardtite and unnamed AuAgTeS mineral, K-2/2015, BSE.





The most important pre-requisite of high gold recovery is the optimization of the milling process to achieve homogeneous particle size distribution and high degree of liberation. Technical and organizational measures resulted in stabilization of milling and separation in the range P_{85-88} of 74 µm, meaning that more than 80 % of the grains are smaller than 74 µm. Currently, this is the best achievable result.

Gold is activated in our technological process by the addition of sodium metabisulfite to the flotation froth (Chryssoulis et al., 2003), resulting in rapid improvement of gold recovery to approx. 95 %.

In order to confirm this flotation reagent regime, Canadian SGS laboratory was contracted to perform a flotation test program with objective to confirm and optimize flotation performance. A series of 9 flotation testworks performed in various milling size (P_{85} of 100 µm, P_{85} of 75 µm, P_{85} of 63 µm) confirmed that the current flotation regime can achieve 96–98 % gold recovery. The test work program confirmed the assumption that the best results can be achieved with the finest milling P_{85} of 63 µm. Mineralogical studies recommended to introduce gravitational separation as a technological step before flotation.

The recommendations provided by SGS Canada and the results of mineralogical and chemical monitoring of ore dressing products will be applied to introduce changes to the milling steps. One primary mill will be added and secondary milling will be divided among two separate mills. At the same time, a mineral jig will be installed into the primary circuit. This measure should result in increase of milling size to 95 % – 74 μ m and optimize gravity circuit to weight recovery to < 1 %.

4. CONCLUSIONS

The ore is polymetallic with elevated content of precious metals.

Economically important minerals are: native gold, electrum, hessite, petzite, galena, sphalerite, chalcopyrite. They are carriers of Au, Ag, Pb, Zn, and Cu in the concentrate. Other significant elements in the ore are Te, Cd, and S.

The following minerals are not utilized: pyrite, quartz, Kfeldspar, clay minerals (illite, dickite, kaolinite, chlorites), Ca-Mn-Mg-Fe carbonates.

Pyrite and Cd-rich sphalerite are depressed in flotation. The content of potentially toxic elements (As from pyrite, Cd from sphalerite) in the ore and waste is low.

Ore textures are suitable for processing, liberation of the minerals contained in the ore is high. Particle size has a fundamental impact on liberation and Au recovery.

Sulphide content in waste has no influence on Au recovery.

Certain types of ore contain very fine-grained gold associated with gangue minerals, mainly as impregnations in quartz and adularia that are refractory to flotation.

The flotation process can be optimized to achieve 96–98 % gold recovery.

Very high recovery of gold (99 %) could be achieved by hydrometallurgical leaching.

Gravity separation in a mineral jig in the secondary mill circuit did not have significant impact on overall Au recovery and was temporary abandoned. We are seeking utilization of the mineral jig in the primary mill circuit, secondary milling is going to be conducted in two separate ball mills.

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