Mineralogical Research in Support of Flotation Concentration of Complex Polymetallic Ore

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Introduction

The polyimetallic deposit Draznja is located in the north-eastern part of Kosovo. The deposit and the occurrences of the Pb-Zn-Sb-As-(Ag, Au) mineralisation belong, according to their age, to the same group as the majority of lead-zinc deposits in Kosovo and have similar geological/structural characteristics as well as the similar basic mineral composition. Studies have shown that the Draznja deposit has many genetic and morphological similarities with deposits of the Artana (Novo Brdo) and the Belo Brdo mine.

The mineralized area of the Draznja deposit has a long history of exploration under the Roman, Illyrian and Slavonic civilizations. Numerous prospecting pits, shallow trench excavations and minor underground development have been recorded from a relatively small area. These explorations and possible exploitation activities likely date from the Middle Ages (Ibrahim Salja Ferat, 2013; Slowey, Galen, 2009).

The latest large-scale explorations were carried out by the Lydian company. The exploration included trenching, geochemical and geophysical surveying, trial adits, thus more than eighty drilling holes were drilled for the assessment of mineral resources and for mineral resource classification (Slowey, Galen, 2009). The explorations included trial adits (20 000 m), extensive headings, and mine working. Rich mineral reserves were assessed (Slowey, Galen, 2009). According to the available data, ore reserves of the Draznja deposit are estimated at about 4.7 million tons, with the average content of Pb of 2.44%, Zn of 4.92%, and Ag of 45 g/t.

Abstract

High Sb and As contents in zinc and lead concentrations, have always been obtained by conducting experiments with flotation concentration of complex poly-mineral Pb-Zn-Sb-As-(Ag, Au) ore ground to varied grinding finenesses. Chemical analyses were not sufficient to explain this phenomenon. With the help of detailed mineralogical analyses of the run-of-mine ore, and, the obtained concentrates that followed, the problem has been solved. All ore minerals were identified, the degree of liberation of galena and marmatite measured, and the frequency of occurrences of certain types of binary, ternary and higher locked grains determined.

The measurements of the liberation degree of galena and marmatite (at the fineness of grinding of 83% -0.074 mm), in the obtained concentrates have shown that the increase in a grinding fineness can only partially result in the increase in recovery and provide better concentration results. In addition, the use of new selective low-cost flotation reagents is required to separate hard-to-beneficiate pairs of sulphide minerals with very similar flotation properties.

Keywords: Pb-Zn ore, complex sulphosalts, ore microscopy, mineral liberation, concentration

In past decades the concentration of Zn, Fe and Mn minerals was carried out by flotation concentration, heavy-media separation and magnetic concentration of carbonate minerals of Mn and Fe at the high-intensity magnetic separator, as well as by the combination of these two concentration methods (0.36% Pb, 1.17% Zn, 18.84% Mn, 9.40% Fe) (Urosevic, 1998). Later explorations in deeper parts of the deposit pointed out that mineralisation at the Draznja deposit was represented by sphalerite, galenite and marcasite/pyrite. Some sections comprise massive sulphide, while others are lower grade zones of semi-massive sphalerite/galena or marcasite/ pyrite dominant sulphides (Dvorani et al., 2012). The ore body II in the southern gallery in the structure Çukë – Lajthishtë, contained 3.16% of Pb and 7.31% of Zn. Excavated during large-scale explorations, this ore was periodically transported for processing to the industrial flotation concentration plants in the vicinity (Stari Trg, Belo Brdo). Experiments of flotation concentration and the determination of liberation of minerals, shown in these examinations were carried out on ore samples collected from the test bore holes and mining work. Studies reported in this paper used this polymetallic Pb-Zn-Sb-As-(Ag, Au) ore. The ore is comparatively rich in Zn and Pb, but with high rates of Sb and As. The conventional lead and zinc concentration by flotation produced galena and sphalerite rich concentrate with high recovery, but with excessive As and Sb contents. After chemical analyses, which could not detect the reason for the excessive elements, ore minerals were identified under the ore microscope, their texture characterised, and the liberation of useful minerals assessed.
Materials and experimental methods

Samples. The material for this preliminary investigation was a composite sample, a representative specimen of the mineral deposit from which it was collected – the Dražnja deposit (Çuka e Batllavës, the ore body II, Çukë-Lajthishtë structure). The crude ore was sampled from three locations in a small amount sufficient for microscopy, flotation tests and milling or mineral liberation measurements.

Representative mineral samples for microscopy were taken from the mixed raw material. Preliminary investigation included twelve polished sections for the study on ore microscopy by polarized reflected light to identify structural/textural character of the ore, all ore minerals, structural relationship of the useful minerals, and to predict behaviour of useful minerals in the process of liberation through grinding and concentration. Ore fragments selected for microscopy were rich in massive sulphide minerals, mineralised fragments of volcanic clastics, with nests or stringers of sulphides, or accumulations of manganese minerals, sulphosalt or visible pyrite nests with arsenopyrite.

Chemical composition. The compositions and content of the chemically analysed composite samples (samples K poor and sample T rich) were the following: Pb 2.87%, Zn 6.56%, Ag 17.82 g/t, As 0.58%, Sb 1.24%.

Mineral composition. The determination of sulphide minerals in this ore for the mineralogical study was made on 12 polished sections by ore microscope under reflected polarised light. For the first time all sulphide minerals were identified as well as their structural-textural characteristics relevant for the comminution and mineral processing concentration. According to results of this microscopic examination, it was possible to establish the behaviour of minerals varying in milling properties or to predict the necessary optimal degree of liberation of galena and marmatite, as well as the grinding fineness of this raw material.

Results and discussion
Mineralogical characteristics. Characteristics of samples for microscopic examinations are thin, thread-like, wire, nest-like and partially massive textures. Typical textures of the tested polished ore preparations are grainy, thin needle-like, textures of the solid solution, exsolution textures. In the rich sulphide mineralisation, the following accompanying minerals were identified, according to their distribution: pyrite, galena, marmatite, sulphosalts (jamesonite, boulangerite, and bournonite), arsenopyrite, chalcopyrite, tetrahedrite, tennantite, iron oxides (limonite, goethite), manganese minerals (rhodochrosite, psilomelane, pyrolusite, polianite, braunite (?), etc. The gangue or petrogenic constituents in the mineral are carbonates, limestone, marble, andesite and some volcanoclastic rocks – volcanoclastics. The minerals are affected by intensive silicification and carbonisation, and on the surface of the terrain, minerals of iron cap, gossan respectively.

Flotation studies. Galena and marmatite were conventionally flotation performed (results in Tab. 1). Samples for flotation were prepared from the secondary representative sample of the row ore, and were milled to 65%, and 83% of -0.074 mm. Secondary representative samples of the ground ore, each 1 kg, were milled in a laboratory ball mill (volume 15.18 litres; 56 rpm, 21 grinding balls from 36 mm to 54 mm in diameter and total mass of 8.5 kg). A Denver flotation cell of one litre capacity was used. Flotation tests were conducted using CaO as the pH regulator, potassium amyl xanthate as the PbS/ZnS collector, NaCN+ZnSO$_4$ as the depressant, and dowfroth-200 as the frother. Galena concentrate contained Pb 59.5%, Ag around 390 g/t, Zn 1.83%, but also Sb 25% and As 0.33%. Pri-
Primary concentration recoveries were: lead about 85%, silver around 80% and antimony 84%. Marmatite concentrate, for the grinding fineness of 83% -0.074 mm, contained Zn 56.27%, Pb 1.40%, with Ag 19.45%. It also contained As 0.10% and Sb even 0.71%. The marmatite recovery in the primary concentrate was 86.78%, As 9.71%, Sb 13.88%, and Ag 14.85%. The grinding fineness for the flotation concentration was the same, 83% or 65% -0.074 mm (Tab. 1).

The above properties raise the principal question: what is the reason for the unsatisfactory galena and marmatite concentration from the relatively rich Pb-Zn ore? What is the reason for the elevated Sb and As in galena concentrate and of the same elements in the marmatite concentrate? The chemical analysis does not provide adequate answers. Ore microscopy of the unfragmented (the ore not having been ground) and of concentration products gives the answers. It has been found that the minerals in raw ore has complex structural/textural characteristic, complex polymineral composition of phased genesis, each phase introducing an association of minerals. All this is manifested in a very complex intergrowing betwixt all minerals of this paragenetic association. The most interesting are certainly complex galena and/or marmatite intergrowths with boulangerite, bournonite or jamesonite (or some other sulphosalt) and a frequent intergrowth with affected arsenopyrite, which are mainly polyminerals.

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It is known that, there are certain limitations in sulphide minerals regarding the size of floating particles, thus there are the smallest grains of galena, which can be up to 6 μm, at 8 μm sphalerite, pyrrhotite at 9 μm, and pyrite 20 μm, etc. (Zhang, T. & Qin, W. 2015). According to these studies, it follows that as a particle size increases, the recovery in the flotation of the sulphides will increase as well (Zhao, C., Chen, J., Li Y., He, Q. & Wu, B. 2015; Bairamova, S. T., Bagieva, M. R., Agapashieva, S. M. & M. Aliev, O. M., 2011).

In published papers (Zhang, T. & Qin, W. 2015), there are cited examples of the possibilities of successful flotation, precisely in such polymetallic Pb-Zn-Sb-As ores, with very fine grain jamesonite of 6-26 μm, where ammonium dibutyl dithiophosphate was used as the collector, or flotation was carried out with the previous flocculation of jamesonite particles. There are also, known cases when satisfactory results were achieved with the concentration of jamesonite grains > 38 μm (Month, et al, 2002; Slowey E., G. White, 2009). Other authors have also studied selective concentration of sulphides such as marmatite and jamesonite (Huang, H. & Sun, W. 2010). For jamesonite and marmatite minerals, which have very similar surface properties, namely their floatability is very similar, there is a problem of their selective flotation, for the presence of one mineral seriously affects the others. There is also an opinion that the main task of future research should be focused on finding a new collector with better selectivity and collectability to enable the effective flotation separation of complicated lead-zinc-iron sulphides (Huang, Sun 2010). The larch tannin extract, which was the optimal depressant for jamesonite flotation, was selected and tested in a laboratory and at an industrial scale (Jian-hue C., et al. 2011). It was demonstrated that the addition of larch tannin extract could improve the selective flotation of jamesonite and significantly decrease the amount of NaCN used. Likewise, satisfactory results have been yielded with a new flotation collector – aryl thiolate (2-aminothiophenol) for sulphide mineral flotation. Some authors (Matveyeva et al., 2015) report that the flotation trial results confirmed how expensive plant extracts may act as flotation modifying agents to separate hard-to-beneficiate pairs of sulphide minerals, replacing highly toxic chemical compounds by environmentally safe substances of a plant origin (Matveyeva et al., 2015).

Microscopic examinations of ore minerals and recording of mineral liberation degree Phenomena of such a complex and frequent intergrowth of useful minerals and mineral followers in a given paragenetic association, shown in given photomicrographs required carrying out basic measurements of the degree of liberation of basic useful minerals on samples of galena and marmatite concentrates. Specimens for these tests were briquetted ore concentrate preparation samples of Zn and Pb concentrates obtained at the optimal fineness of grinding (fineness of grinding of 83% and 65%, sieve opening 0.074 mm ), in the best flotation regime conditions and the consumption of flotation reagents respectively. Recordings were carried out by ore polarizing microscope, line-measuring Rosiwal-Shand method, with the help of Shand integration table. Particle counting was performed on an Ernest Leitz integration table, and control counts by an image analyser. Gaudin correction coefficient has been introduced into direct measurements, and final results are given in Tables 2 and 3. The most common types of intergrowth (in both concentrates) and average shares of useful minerals in recorded intergrowth types have been presented, and finally the degree of liberation of PbS of 30.33% and ZnS of 53.82% calculated.

In the galena concentrate, numerous intergrowths of galena were identified, mostly with sulphosalts (boulangerite, jamesonite, and bournonite), then polymetal- lurgical intergrowths of galena with arsenopyrite-pyrite and petrogenic minerals, as well as frequent intergrowths with marmatite which carries the inclusion of jamesonite and other combinations of minerals. The most common types of intergrowths are given in the accompanying series of photomicrographs in Table 4.

Ore preparations of marmatite concentrate were also analysed where a number of aggregates of marmatite crystals with needle-like forms of sulphosalts (jamesonite) were identified, in addition a very frequent occurrence of inclusion (cross-sections of needle-like sulphosalts) in marmatite, polymetallic ingrowths together with the affected arsenopyrite and pyrite, namely petrogenic minerals, likewise ingrowths of marmatite with galena, which is always accompanied by sulphosalts. Typical examples of intergrown marmatite grains were given in a series of photomicrographs (Table 4).

It can be concluded that additional liberation, first of galena, of the higher grinding fineness, would not lead to the significant improvement of results, namely with marmatite – greater liberation would not be useful. Likewise it should be emphasised that the present arsenopyrite is, for the most part, tiny crystalline, structurally - affected, as older, in grains of useful minerals, with the very rare phenomenon of free outer surfaces with which the contact of flotation reagents would be possible.

It was discovered, by microscopic studies, which could not be determined by chemical analyses alone, that the high content of Sb and the unacceptable content of As in the lead concentrate were caused by
the complexity of the intergrowth of galena, mostly with boulangerite and jamesonite but with other sulphosalts as well. These complex sulphosalts, among other things, have similar characteristics of surfaces, thus showing similar characteristics in flotation concentration. In addition to the fact that they are intergrown with galena in a complex way, i.e. they are not optimally liberated, they are both found in the lead concentrate. It is the same with arsenic high content, whose origin is partially from sulphosalts, and partially from very fine-grained affected arsenopyrite, whether it was an intergrowth with galena or marmatite.

The analysis of results of all measured intergrown grains, in which, besides galena, some of the sulphosalts also occur (with the types of PbS + boulangerite; PbS + jamesonite; PbS + sulpho salts; PbS + sulpho salts + SiO₂), have pointed out that the galena occurs in intergrown grains by a total of 28.62%. Summarily observed, statistically, the average share of mineral sulphosalts in those intergrowths ranges from 30 to 60% (Table 2).

Consequently, the causes for the occurrence of the increased content of Sb and As in concentrates of lead and zinc were identified by the analysis of the degree of mineral liberation in the function of grinding fineness,
i.e. the study of structural and textural characteristics of this ore. The complex outgrowths of the written graph-
ic structure, or the structure of the dissolution of solid
solutions, as well as other types, are classified in this
ore, type 1c, 1d, 3b (according to Amstutz-u, 1960), or
according to geometric classification (J. R. Craig and
D. J. Vaughan, 1981) in the category of a raw mineral
material whose minerals are relatively difficult to lib-
erate or their complete liberation is either very difficult
or impossible.

Measurements have also shown, that despite the
high fineness of grinding of 83% -0.074 mm, the degree
of liberation from galena for the size category +0.066
mm is 30.33%, in the size range of -0.066 +0.038 mm
amounts to 58.00%, while for the smallest size cate-
gory -0.038 +0.000 mm it was only 72.16%. The mass
rate of size fractions was 32.11%; 27.01% and 40.88%,
respectively.

The degree of marmatite liberation from zinc con-
centrate, at the same fineness of grinding, was much
higher and amounted 53.82%. The rate of middling par-
ticles of marmatite grains with sulphosalts and galena
(with types: marmatite +jamesonite, marmatite+ sulph-
atesalts, marmatite+sulphatesalts+SiO$_2$, marmatite+-
sulphatesalts+ arsenopyrite/pyrite, as well as marmat-
ite+galenite), amounts totally 22.00%. At the same
time, the share of intergrown grains in which marmat-
ite is intergrown with minerals that carry As, is only
4.12% (types of locked particles: ZnS+FeAsS, ZnS+Fe-
AsS/FeS, ZnS+SiO$_2$+FeAsS/FeS$_2$). The total degree of
the marmatite intergrowth is 46.15%.

Conclusions

• The mineral raw material of the Draznja de-
pot in Kosovo is categorised as a rich Pb-Zn-Ag ore,
based on large-scale geological explorations and nu-
merous mining operations. Ore microscopic studies,
revealed that it is the case of the complex paragenetic
association of minerals, i.e. a polymetallic Pb-Zn-Sb-
As-(Ag, Au) ore, which contains the following compo-
ents 0.60-0.74% As, 1.24 to 2.23% Sb, Cu from 0.14
to 0.23%, 2.25 to 7.48% Pb, 4.14-11.76%, 12.72-22.00
g/t Ag, or <0.40 g/t Au.

• Galena and marmatite concentrates, with the
high content of useful minerals, as well as very
satisfactory recovery were obtained by conventional
flotation concentration. However, it was found by a
chemical analysis that these concentrates still con-
tain high content of Sb and As. This could not be
resolved even with the change of the regime of used
reagents.

• Chemical analyses alone could not solve the
problem. Then polished sections of the concentration
products were studied. They indicated that the cause of
high Sb and of excessive As in lead concentrate was the
complex interlocking of galena with boulangerite and
jamesonite. These complex sulphosalts, among oth-
er things, have similar behaviour during the flotation
concentration, and in spite of their interlocking with
galena, and therefore inadequate liberation, sulphosalts
remain in the lead concentrate. The same applies to the
elevated arsenic, which is derived partly from sulpho-
salts and partly from the fine-grained interlocked arse-
nopyrite whether in intergrowths with galena or with
marmatite, or occasionally tetrahedrite.

• It was determined by microscopic methods and
measurements of the degree of liberation that it is
possible, by changing the grinding fineness of mineral
raw materials, i.e. better liberation of minerals, to get,
slightly, better galena concentrate, but not much bet-
ter marmatite concentrate. That is owing to structural
properties of the mineral raw material, i.e. the com-
p lex intergrowth of galena, especially marmatite with
sulphosalt minerals and arsenopyrite. The satisfactory
quality of the concentrate can be achieved by new flo-
tation reagents with better selectivity for the separation
of particular sulphosalt minerals from galena and mar-
matite.

• The quality of the marmatite concentrate can-
not be improved significantly even with the increasing
fineness of grinding, or better marmatite liberation
(needle -like intergrowth, jamesonite inclusion in mar-
matite).

• In order to separate marmatite and galena
concentrates successfully from the run- of-mine ore
containing jamesonite and boulangerite, flotation ex-
periments are planned on the basis of the results of the
mineralogical analysis (determining of the structure,
identification of all ore minerals, the predictions of lib-
eration of minerals and determination of the degree of
liberation with the milled ore).
Słowa kluczowe: ruda Pb-Zn, złożone sole siarkowe, badania mikroskopowe, uwolnienie mineralów, koncentracja