GEOCHEMICAL CHARACTERISTICS AND SIGNIFICANCE OF TAILING DUMP FROM POLYMETALLIC Pb - Zn DEPOSIT ZLETOVO (REPUBLIC OF MACEDONIA)

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ABSTRACT

The paper will show the results of the geochemical tests on composite samples and samples taken from boreholes made in the last few years.
Old inactive waste dumps occupy an area of about 0,39 km^2 and contain about 10 million tons of sterile mass, the mean depth of these dumps is 9,2 m. While in recent active dumps are deposited around 4 million tons sterile mass.
The elements show different concentrations in grain - size different parts of the deposited material. Pb, Zn and Mn show maximum concentrations in sandy part and slightly lower in the clay part of the old inactive waste dumps Probistip.
Average content of Pb and Zn in sterile mass deposited in tailing dumps of mine Zletovo is 0,37 % Pb and 0,32 % Zn, so in the not too distant future exploitation could be done the of these valuable components of this removed material with the proper technique.
The concentration of Fe in all composite samples from the boreholes is high, average Fe content is 8.32 % (from 7.09 to 9.54%). The concentration of Mn in sterile mass is also high, ranging in the interval from 3.52 to 5.60%.
Also within the sterile mass deposited in the mine tailing dumps Zletovo some accompanying metals such as Ge, Ga, Cd and In are present, whose application in the course of history was not known so they were not exploited and concentrated in the sterile mass.

KEY WORDS
Polymetallic deposit Zletovo, Tailing dump, Average content, Pb, Zn, Fe, Mn, Heavy metals, Value assessment.

1. INTRODUCTION

The remains of the old mining suggest that the lead ores from Zletovo deposit and its immediate surroundings have been used since the Middle Ages or even earlier. The first

significant research started in 1928 by the English firm Selection mines limited and the deposit was investigated continuously until 1939.
In this period, the deposit was prepared for exploitation with capacity of 120 000 t per year. Modern mining started after the World War II, when the deposit Zletovo was built as modern mine with capacity of 400 000 t per year. The mine is still active and product lead - zinc concentrates.
Ecological problems increased in the last 30 years with the accumulation of tones of tailings in the mine tailing dumps. Big part of these tailings now is a source of drainage waters with low quality. The dumps are located along the river Kiselnica and it is a reason for the high concentration of heavy metals (Pb, Zn, Cd, Mn, Cu, As etc.) in its flow. Because of that, the interest for studying and utilization of the mine waste increased. Knowing the mineral and geochemical composition of the tailing is basic indicator for managing the mine tailing dumps (Zlatev, Mladenova, 2004).
Large quantities of material were deposited in the old inactive tailings Probistip and the newer active dump Ozren in the mine Zletovo. Material was deposited in the old dumps I, II, III, IV and V on the increasing distance from the processing facilities; newer dump (in use since 1975) is on the south.
It is very important that large quantities of lead and zinc are in the mass deposited in the tailing dump of the Zletovo mine, and as a result there can be considered a special type of deposit, so - called technogenic Pb - Zn deposit.
Recent mining hydro - dumps and their immediate environment from chemical and geochemical aspect were studied by Mirchovski et al. (2004) and Spasovski et al. (2007, 2009).

2. DESCRIPTION OF STUDIED AREA

Old inactive tailings Probistip and the newer active tailing Ozren are locate in ore district Kratovo - Zletovo, northeastern Macedonia (Fig. 1).

Figure 1: Position of the surveyed area

Tailings occupy naturally negative relief (Fig. 2). Old inactive waste dumps occupy an area of about 0,39 km^2 and contain about 10,5 million tons of sterile mass, the mean depth of these dumps is 9,2 m. While in recent active dumps are deposited around 4 million tons sterile mass.
In old inactive tailings Probistip and in the newer active tailing Ozren is stored slag which is product of processing of lead - zinc ore from the Zletovo mine.
The slag is transported and deposited as aqueous suspension and in that way, in the recent tailing Ozren, becomes to a natural granulometric separation of the material from the slag. In the part of the tailing Ozren, surface water produced swamp with large quantities of acid mine waste water with volume which is variable depending on the seasone (Fig. 2).

Figure 2: Satellite displaying of mining hydro - dumps formed by Pb - Zn deposit Zletovo

3. RESULTS AND DISCUSSION

Chemical composition of the gangue from the old inactive tailings is shown in table 1 and illustrated on fig. 3, 4 and 5. Fe concentration in all composite samples of boreholes is high. Average content is Fe = 8,26% (from 7,09 to 9,54%). Presence of Fe in the sterile mass is due to the significant Fe minerals in the ore deposit Zletovo (siderite, pyrite, pyrotine, marcasite, magnetite, etc.).
Concentration of Mn in the waste is also high (fig. 5), ranging in the interval from 3,52 to 5,60 %. This is because of the fact that this element has important role in the hydrothermal solutions, and as a result, it contaminated almost all minerals in the mineral paragenesis. Mn is present primarily in sphalerite, galena, pyrite and Mn - siderite.

Table 1: Contents of elements in composite samples of boreholes (%)

Boreholes	Pb	Zn	Mn	Fe	Cu	S	Cd	As	Bi	Ag(g/t)
1	0,53	0,84	3,52	7,09	0,02	4,11	Trace	0,05	0,003	18
2	0,42	0,83	3,69	7,71	0,02	4,38	Trace	0,06	0,004	21
4	0,38	0,94	4,54	8,17	0,04	3,62	Trace	0,06	0,004	14

5	0,52	1,10	5,79	9,54	0,05	3,73	Trace	0,05	0,005	24
6	0,49	1,35	5,60	8,05	0,06	3,32	Trace	0,04	0,006	11
Average content	**0,47**	**1,01**	**4,73**	**8,26**	**0,04**	**3,84**	**Trace**	**0,05**	**0,004**	**17,6**

Pb and Zn have relatively constant concentrations, very high contents are determined only in individual samples (fig. 3, 4). Cd in the sterile mass occurs in traces, its presence there is due to fact that Cd, basically, is concentrated in sphalerite.
Content of Cu in all composite samples from the boreholes is constant, and it is because of the presence of significant copper minerals in the ore from Zletovo mine and presence of Cu as admixture in other ore minerals (sphalerite, pyrite, Mn - siderite etc.).
Content of Ag in all samples is within 11 - 24 g/t (average 17,6 g/t). these values are due to determined presence of various sulphosalts in the ore and also presence of Ag as admixture in the main ore minerals sphalerite and galena.
As is present in all borehole samples with relatively constant contents within 0,04 to 0,06%. Basic mineral is arsenopyrite, which is present in the ore from Zletovo mine. Also tennantite is present. Presence of As is because it occures as trace element in many sulfide minerals.
Bi is found in all composite samples of sterile mass from the old inactive dumps. Basic mineral carrier of Bi is the galena. Also, Bi appears in sphalerite, Mn-siderite and other minerals.
During formation of old inactive dumps Probistip only tailing from mine Zletovo was deposited there. Therefore mining activities and processing facilities directly affect the chemical composition of sterile mass. In addition, major factors affecting the lack of zonality regarding the deployment of useful components in the formation of inactive tailings are:

- First, number of boreholes and their spatial distribution are limiting factors to give a complete overview of the tailing.
- Second, polyphase disposal of the material in old inactive dumps and manner of entry of material from two directions as pulp contributes to mixing and homogenization of sterile mass during its release in hydro - dump.
- Third, the streams in the area contribute to mixing and homogenization of the material at the surface of the dump.

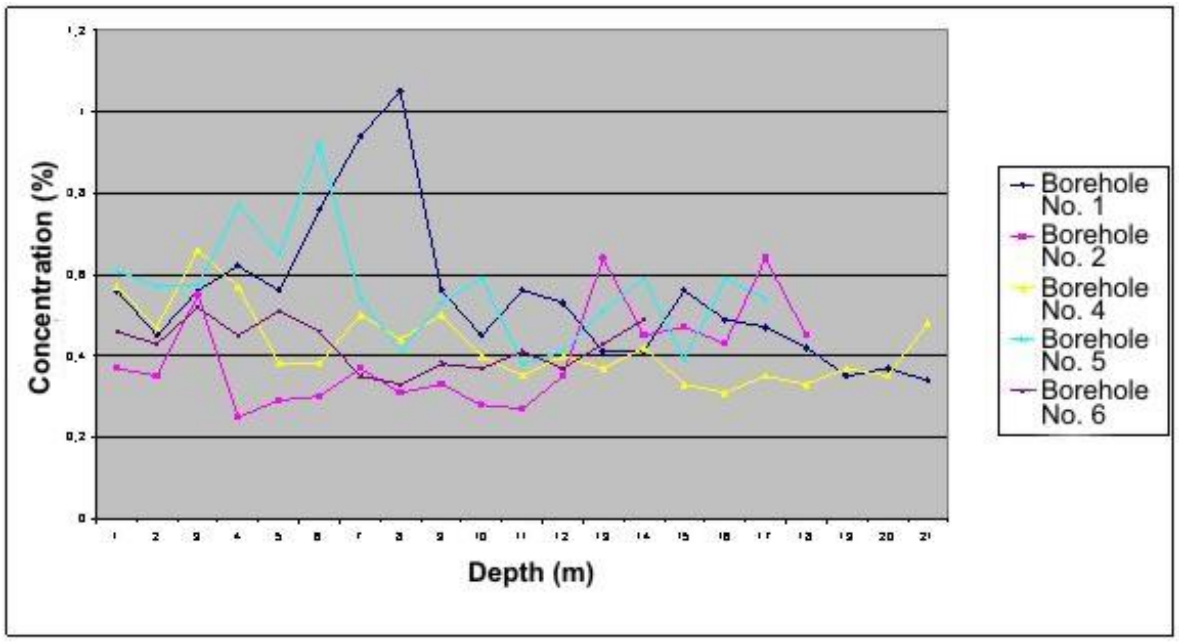

Figure 3: Diagram of lead concentrations in the samples of sterile mass from five boreholes in old inactive dumps

However, some zones can be separated. Moreover, the composition of the ore, probably marks the zone due to particle size and weight difference in present minerals. Lead shows minor enrichment on the depth of 2 to 9 m (fig. 3), and zinc also shows enrichment in the depth (fig. 4), especially in the deepest parts of the dump. It is because during the Second World War, when the site Zletovo was exploited by the Germans, they produced only Pb - concentrate, and Zn went in the waste. Manganese has similar concentrations in all samples (fig. 5).

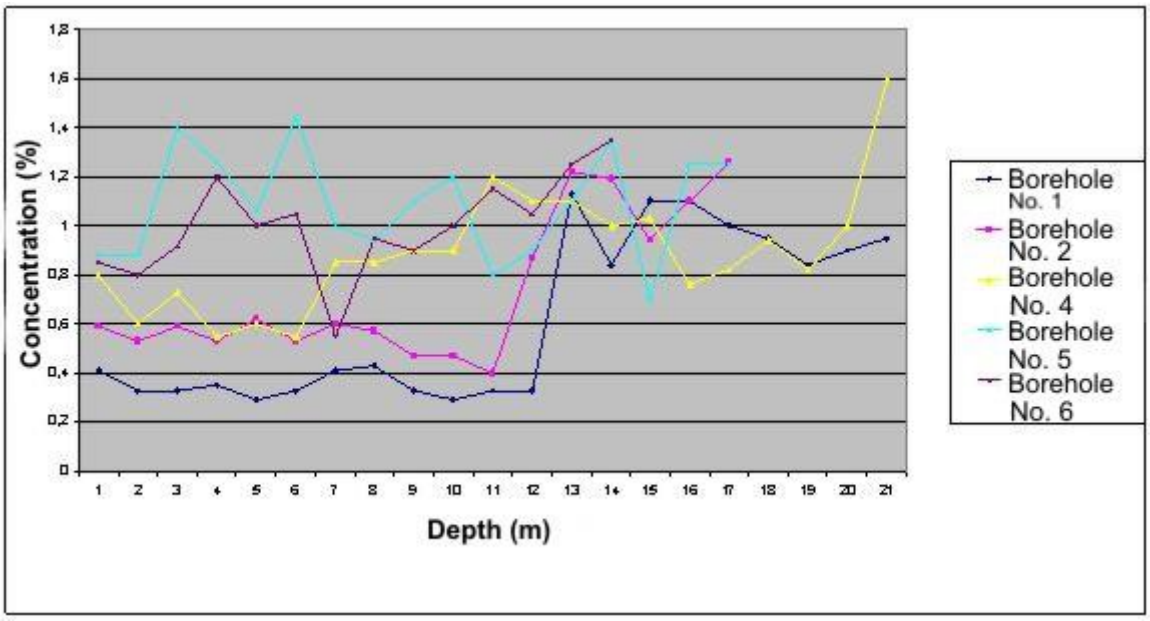

Figure 4: Diagram of zinc concentrations in the samples of sterile mass from five boreholes in old inactive dumps

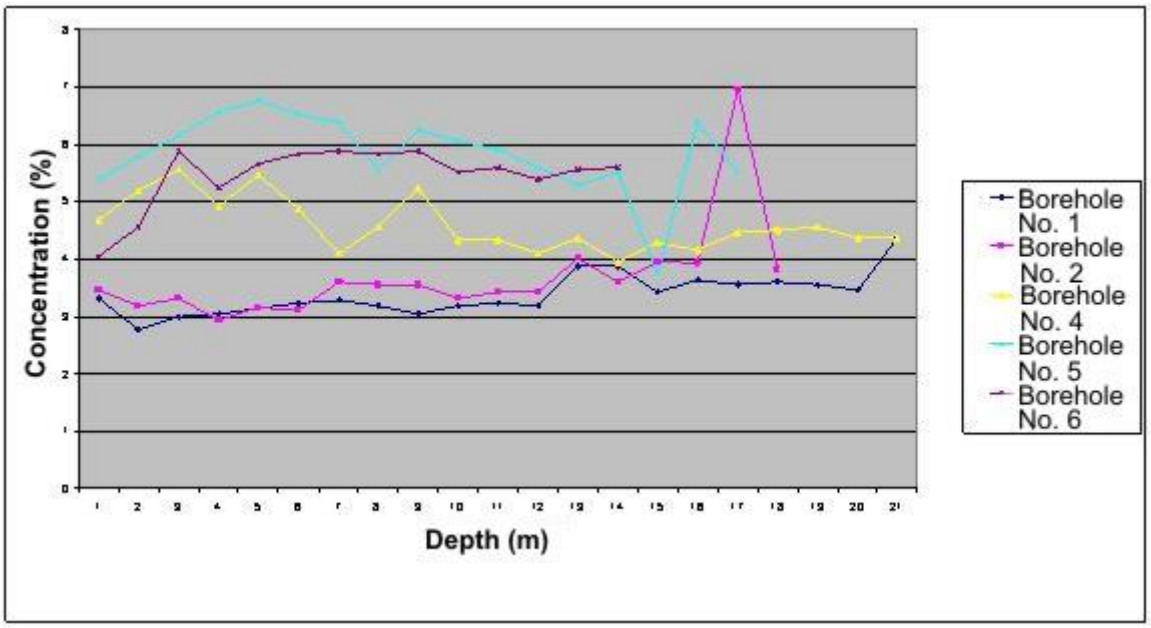

Figure 5: Diagram of manganese concentrations in the samples of sterile mass from five boreholes in old inactive dumps

The elements show different concentrations in granulometric different parts of the deposited material. Pb, Zn and Mn show maximum concentrations in sandy part and slightly lower in the clayey part of the old inactive tailings Probistip.

It can be seen that geochemical data for the old inactive mining tailings Probistip reflect the type of flotation ore and tailing deposited in the time during some sedimentation processes and climatic factors heavy rains like and flows of surface and underground waters.

It can be conclude that over the time in old inactive tailings Probistip was developed oxidation zone of variable thickness. Areas with very thin oxidation zone were likely characterized by the cementation of the pore space with secondary minerals, making the oxidation zone strong and compact; this zone is called the cement zone.

The formation of cement zone results in the generation of gas diffusion barrier, which prevents the infiltration of oxygen and carbon dioxide in depth. This is the reason for reducing oxidation kinetics, resulting in a thin oxidation zone. Past findings suggest that the main parameters that promote the formation of cement zone are combination of high content of sulfides, grains of small size and presence of carbonates.

Experimental tests of the petrogenic minerals that make up the ore shows that minerals placed in the hydro - dumps of the mine Zletovo are very sensitive to air and water - ventilation minerals. Although the development of models for predicted models for the description of the oxidation processes is a separate (specific) for each hydro - dump, some natural factors and laboratory results can help in modeling of these complex processes.

Exposure of surface conditions and decomposition these minerals present in the tailing causes pollution of waters and soils in the region.

Exploitation and flotation of lead - zinc ore is followed with the creation of large amounts of waste rock and dump waste. Wastewater contain metals / contaminants such as Pb, Zn, Cd, Cu, Mn, As and others, depending on the nature of the ore.

4. VALUE ASSESSMENT OF TEHNOGENIC Pb - Zn DEPOSIT RELATED TO TAILING OF HYDRO - DUMP IN THE MINE ZLETOVO

It is important to say that large amounts of lead and zinc are present in the waste deposited in the hydro - dumps of mine Zletovo, and as a result it can be a word of formation of new type of deposit, so - called technogenic Pb - Zn deposit. This shows that such type of deposits refers to dump that is sterile or poorly mineralized rock mass in contact with the mineral deposit or is intercalated in it. Within this waste material is present small content of Pb and Zn (average content of lead and zinc in the sterile mass deposited in the hydro - dump of mine Zletovo is 0.37 % Pb, 0.32 % Zn), so these useful components in the near future, can be exploited with proper technique.
Also, within the sterile mass deposited in the hydro - dumps of mine Zletovo are present some accompanying metals such as Ge, Ga, Cd and In whose application in the course of history was not known so they are not exploited and concentrated in the dump. But, with time and development of industry and technology was established that accompanying components have unique application, so in the future they can be use. However, their complex obtaining, primarily the rare metals (Ge, Ga, Cd and In) in the form of rare - metal ore concentrates rather impedes their industrial applications and increases the cost to obtain.
In the old inactive tailings Probistip were deposited 10 497 900 t sterile mass (table 2), and in the new one 4 000 000 t. The total amount of deposited sterile mass must be reduced for the various dispersing of the dump (water, air, etc.), which are valued at about 500,000 t. So basically, the total amount of dump deposited in the flotation tailings of the Zletovo mine is about 14 million t.

Prices of Pb, Zn, Mn, In, Ge in USD/t for 25.11.2008 were (London Metal Exchange):

Pb → 2 210 USD/t
Zn → 1 891 USD/t
Mn→ 2 060 USD/t
In → 700 USD/kg
Ge → 1 344 USD/kg

Value of technogenic Pb - Zn deposit related to tailing of hydro - dump in mine Zletovo in that moment was:

- Production:

$Pb = C_{Pb} \times E_e \times E_o \times E_m = 0,37 \times 0,92 \times 0,95 \times 0,96 = 0,31\%$
$Zn = C_{Zn} \times E_e \times E_o \times E_m = 0,32 \times 0,90 \times 0,82 \times 0,85 = 0,201\%$

where:
C – average content of useful component
E_e – production due exploitation
E_o – production due enrichment
E_m – production due metallurgy

- Total value of technogenic deposit:

Pb = 2 210 x 0,0031x14 000 000 = 95 914 000 USD
Zn =1 891 x0,00201x14 000 000 = 53 212 740 USD

TOTAL: 149 126 740 USD

It should be noted that this total value of the tailings is not final, since there is increased concentrations of Mn, In, Ge, Ga and other metals which are not taken in consideration in the calculation.

Table 2: Parameters of old inactive dumps

Field	I	II	III	IV	V
L (m)	200	250	300	300	450
S (m)	200	230	200	250	350
P (m^2)	40 000	57 500	60 000	75 000	157 500
H (m)	7	8	10	10	11
V (m^3)	28 000	460 000	600 000	750 000	1 732 500
V_t	2,75	2,75	2,75	2,75	2,75
Q_t (t)	756 000	1 265 000	1 650 000	2 062 500	4 764 400

5. CONCLUSION

Geochemical data for the old inactive mining tailings Probistip reflects the type of flotation ore and sterile mass deposited in the time range under certain sedimentation processes and climatic factors.
Exploitation and flotation of lead - zinc ores are followed with formation of large amounts of waste rocks and sterile mass. Wastewaters contain metals / contaminants such Pb, Zn, Cd, Cu, Mn, As etc. depending of the ore character.
There are 10 497 900 t of sterile mass deposited in the old inactive tailings Probistip and about 4 000 000 t in the new one. The total amount of deposited sterile mass must be reduced for the various dispersing of the dump (water, air, etc.), which are valued at about 500,000 t. So basically, the total amount of dump deposited in the flotation tailings of the Zletovo mine is about 14 million t.
Average content of lead and zinc in the sterile mass deposited in the hydro - dump of mine Zletovo is 0.37 % Pb, 0.32 % Zn.
The total value of the mining hydro - dumps Zletovo is 149 126 740 $. It should be noted that this total value of the tailings is not final, since there is increased concentrations of Mn, In, Ge, Ga and other metals which are not taken in consideration in the calculation.

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