8^{th} BALKAN MINING CONGRESS

PROCEEDINGS

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THE CONTENT

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SCIENTIFIC EXPERT VALIDATION OF PB-ZN SLAG FROM TOPIONICA – VELES (NORTHERN MACEDONIA), BASED ON PHYSICO-CHEMICAL AND MINERALOGICAL TESTS OF SLAG SAMPLES FROM THE LANDFILL

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Abstract: *Pb-Zn slag from "Topionica"-Veles- North Macedonia, belongs to potentially valuable technogenic raw materials. There are over 2,000,000 tons of this material at the landfill near Topionica-Veles. In ITNMS, a detailed physicochemical characterization was performed on this sample of Pb-Zn slag. These tests were the basis for the validation of this raw material and they determined the parameters that are needed as a basis for further technological tests.*

Key words: VALIDATION, PB-ZN SLAG, VELES SMELTER, NORTH MACEDONIA

INTRODUCTION

Pb-Zn slag from "Topionica"-Veles- North Macedonia, owned by "Keps mont group" Skopje belongs to potentially valuable technogenic raw materials. There are 2,000,000 tons of this man-made raw material at the landfill near Topionica-Veles. Previously performed chemical analyzes showed that the slag is inhomogeneous, with variable metal contents (zinc-Zn about 8%, lead-Pb about 3.6%, and precious metals silver-Ag with a content of about 60ppm). The physical-chemical-mineralogical properties of the slag sample carried out in ITNMS determined the possibilities of its valorization. These tests defined all the parameters that are needed as bases for further technological tests. All planned tests (including technological ones), provided data, based on which procedures and methods should be determined to extract any commercial product from the slag in question using the methods of mineral processing and metallurgy.

EXPERIMENTAL

Materials and methods

The initial sample of Pb-Zn slag, on which physico-chemical and mineralogical tests were performed, mass m=50kg, ggk 5mm, was submitted to ITNMS. On the initial sample of Pb-Zn slag, gross moisture, hygroscopic moisture, and granulometric composition were determined by sieving on Tyler's series of sieves, and chemical analysis was performed on the same sample. Mineralogical analysis by size classes was performed on the initial sample. The mineral composition of the initial sample was determined by X-ray XRD analysis on a PHILIPS diffractometer, model PW - 1710. The ore preparation was first examined on an optical polarizing microscope of the brand "JENAPOL-U", from the Carl Zeiss-Jena company, and then tests were performed on the preparation with a scanning by electron microscopy (SEM) on the SEM model JEOL JSM-6610LV - with magnification X 5-300,000.

Investigation of physical properties of starting sample

On the starting sample of Pb-Zn slag max. over size 5mm, the gross moisture was determined. After that, the primary sample was homogenized and divided into two samples using the quartering method, one half of which was set aside as a reserve, and the other half of the sample was used to prepare the sample for physico-chemical and mineralogical characterization. The method of sample preparation for physico-chemical and mineralogical characterization is shown in Figure 1.

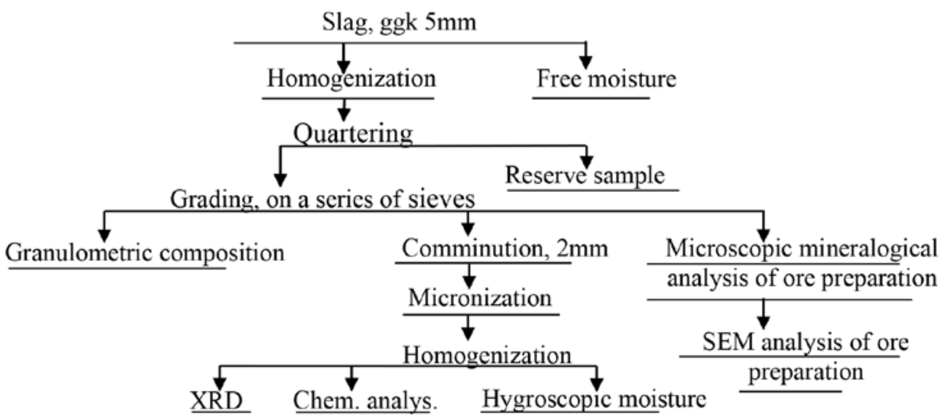

Figure 1. Written scheme of preparation of waste Pb-Zn slag "Topionica"-Veles for physico-chemical and mineralogical analysis

Physical-chemical and mineralogical characterization of the sample
Physico-chemical and mineralogical properties were determined on samples of Pb-Zn slag from "Topionica"-Veles. These tests were the basis that helped us to validate the raw material and design a program of its technological tests.

Physical characterization of the sample
As part of the physical characterization of Pb-Zn slag from the starting raw material, a sample was taken on which the free moisture content and granulometric composition were determined. The hygroscopic moisture was determined on the starting sample crushed to -0.2 mm.

Determination of moisture content of Pb-Zn slag samples
Free and hygroscopic moisture was determined on the sample of Pb-Zn slag, on three initial samples of Pb-Zn slag "Topionica"-Veles. Free moisture was determined on a sample with a max. over size of -5.0+0.00 mm, at room temperature for 24 hours. Hygroscopic moisture was determined on samples, Pb-Zn slag, crushed to a coarseness of -0.2 mm, which were dried at 105 °C, for a duration of t=4h. The obtained results for both types of moisture represent the arithmetic mean of the measured values for each of the three samples. Free moisture in the slag sample is 0.0957%, and hygroscopic 0.11%.

Determination of the granulometric composition of the Pb-Zn slag sample
The granulometric composition of the initial samples of Pb-Zn slag "Topionica"-Veles, ggk 5mm was determined by sieving on Tyler's series of sieves, where the last sieve is in the set with an opening of 0.1mm. The granulometric composition data, obtained by sieving, are shown in Figure 2, for the Pb-Zn slag sample of "Topionica"-Veles. The average diameter (d50) of the sample of Pb-Zn slag is 0.695 mm, and the upper size limit of the sample was 1.772 mm.

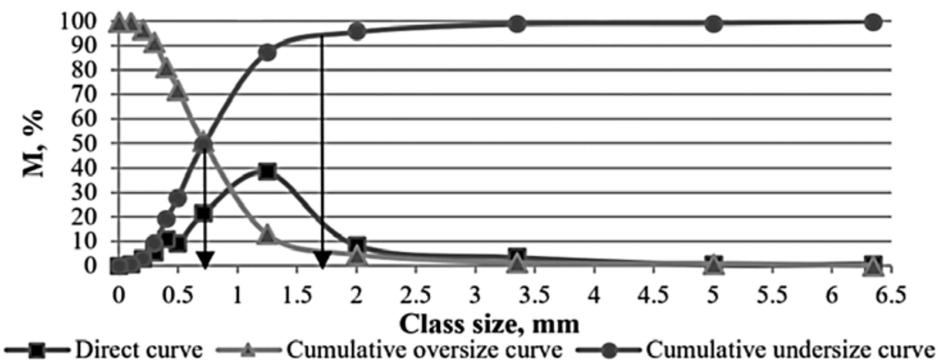

Figure 2. Diagram of the granulometric composition of Pb-Zn slag "Topionica"-Veles

Chemical characterization of the sample

The chemical composition of the starting sample of Pb-Zn slag on which the laboratory tests were performed is shown in table 2.

Table 2. Content of the basic components of the Pb-Zn slag starting sample of "Topionica"-Veles

Component	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	loss on ignit.	Pb	Zn	S	Ag, ppm
Content, %	17.43	7.43	12.39	2.135	0.391	0.565	47.68	0.503	incr. in mass 5.98	2.24	7.10	2.10	27.53

Chemical analysis of the initial Pb-Zn slag sample from "Topionica"-Veles showed that this sample differs from those analyzed by other chemical laboratories. Namely, in this sample the Pb and Zn content is about 1.3% lower than in the previous analyses. A significantly lower Ag content of 27.53g/t was also obtained (Table 2), while in the 2018 analysis, the Ag content in the sample was over 64g/t. During annealing there was an increase in mass (Table 2) of 5.98%, it is obvious that the components present in the Pb-Zn slag reacted and that the resulting compound has a greater mass than the initial one that was annealed.

Qualitative-quantitative mineralogical tests of Pb-Zn slag samples

Mineralogical analysis was carried out on several samples: on the initial sample of Pb-Zn slag, in order to determine the inclusion-freeness of minerals in the sample. X-ray diffraction (XRD) analysis was performed on the micronized starting sample of Pb-Zn slag. Microscopic examinations were performed on the ore preparation.

1. Sample: "Pb-Zn slag" - X-ray diffraction method

The presence of the following phases was determined in the analyzed sample: amorphous phase, vistite, sphalerite, galena, cerusite, galenite/akermanite. The most abundant phase in the analyzed sample is the amorphous phase, while vistite and then all other phases are significantly less represented. Practically, all the other phases, except for vistita, are on the threshold of detection by this method. The diffractogram of the tested sample is shown in Figure 3.

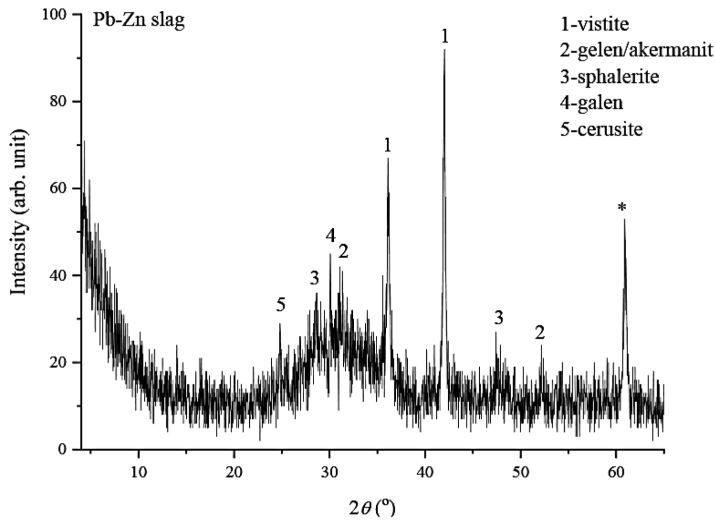

Figure 3. Diffractogram of the "Pb-Zn slag"

2. Sample: "Pb-Zn slag" - microscopic method

Based on the obtained qualitative mineralogical analysis, the following phase composition was determined: amorphous phase, lead alloys, zinc alloys, vistite, sphalerite, galena, cerusite, elemental silver, elemental copper, elemental iron, magnetite, spinel, rutile, hematite, troilite. The most abundant phase is the amorphous phase (glassy matrix) of spinel, silicate and mixed (spinel-silicate) composition, while vistite, which appears as skeletal separations in the glassy matrix, is significantly less abundant. Based on SEM analysis, it is about Fe-Mn-Zn spinels. Lead and zinc alloys are next in order of abundance. Based on SEM analysis, these alloys are dominantly with copper. The grains of these phases are up to 100 µm, and appear almost exclusively as inclusions or inclusions, and in the best case, simple to complex inclusions with a glassy matrix of elemental iron and wistite, while those larger than 100 µm are mostly free or in the form of simple inclusions. The largest dimensions of these phases go up to 300 µm. The presence of visible and "invisible" (structural) silver was not determined in zinc alloys. Lead alloys almost always occur in the form of regular spheres. Unlike zinc alloys, the presence of visible, but also "invisible" (structural) silver was found in lead alloys, which was confirmed by SEM analysis. Silver is oval-shaped, and in the form of smaller wires whose dimensions go up to 5 µm. Apart from these alloys, elemental silver and copper also occur in the glassy matrix and vistite in the form of small inclusions that rarely exceed 2-3 µm (silver) and 7-8 µm (copper). Elemental silver often occurs in grain cracks. Galena and sphalerite are in a subordinate position in relation to Pb and Zn alloys, and they are almost exclusively in the form of simple to complex inclusions with these alloys. Cerusite is on the trail. In addition to vistite, magnetite, hematite, troilite and spinel, iron also occurs in elemental form, but also as pyrite and arsenopyrite in a significantly smaller amount. Mikrofotografije su date na slikama 4-12.

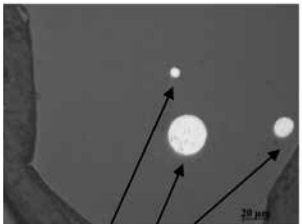

Figure 4. Inclusions of a spherical lead alloy in a glassy matrix. Rejected light, air, II Nicols.

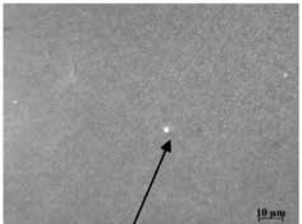

Figure 5. Inclusion of elemental silver (shiny white spot) in the glassy matrix. Reflected light, oil, II Nicols.

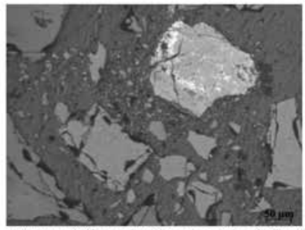

Figure 6. Complex intergrowth of Pb-Zn alloys with sphalerite, galena, and cerusite (dark gray). Reflected light, air, II

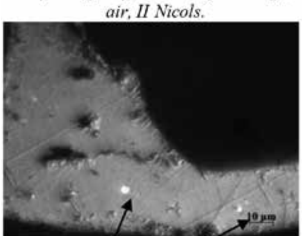

Figure 7. Oval inclusions of elemental silver (bright white spots) in lead alloy. Reflected light, oil, II Nicols.

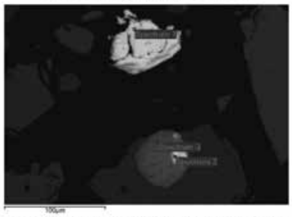

Figure 8. SEM micrograph of oxidized lead alloy grain.

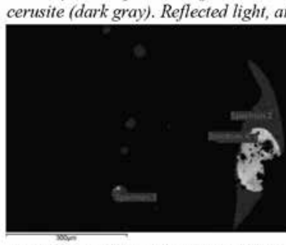

Figure 9. SEM micrograph of oxidized lead alloy grain.

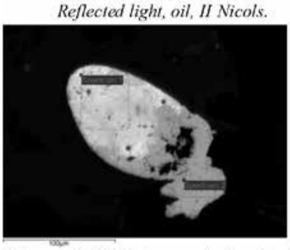

Figure 10. SEM micrograph of oxidized lead alloy grain.

Figure 11. SEM microphotograph of oxidized copper and zinc grain.

Figure 12. SEM micrograph of oxidized lead alloy grain.

Table 3. Chemical analyzes of selected Pb-Zn slag sample grains.

Figure	Pb	Cu	Fe	As	Sb	O	Fe	Ca	Si	Al	Zn	Ag
8./1	75.23	0.79	0.70	-	-	22.40	-	-	-	-	-	-
8./2	55.73	16.77	3.76	1.1	13.30	8.62	-	-	-	-	-	-
9./1	82.69	2.36	-	-	-	14.95	-	-	-	-	-	-
9./4	79.05	3.50	0.95	-	-	16.50	-	-	-		-	-
10./1	84.62	2.36	-	-	-	13.01	-		-		-	-
10./2	76.23	-	0.54		-	21.81	-	1.41	-	-	-	-
11./1	-	36.97	8.94	-	-	8.81	-	2.53	3.56	1.28	33.10	-
12./1	90.70	0.46	-	-	-	7.76	-	-	-	-	-	0.97

CONCLUSION, OPINION AND SUGGESTIONS

Physico-chemical and mineralogical tests were performed to determine the physico-chemical properties and mineral composition of the Pb-Zn slag sample "Topionica"-Veles. These investigations represent the basis and foundation for further technological tests that should define the procedure for processing and separating Pb-Zn slag from "Topionica"-Veles, and obtaining commercial products before all separations, non-ferrous metals, and silver. Based on the physico-chemical and mineralogical properties of the Pb-Zn slag samples from "Topionica"-Veles, the following can be concluded:

The sample is not homogeneous and its chemical and mineral composition varies greatly. The composition of slag is very complex and non-heterogeneous, and there is a presence of mineral and amorphous phases in it. Amorphous (slag phase) consists of spinel and ferrite (complex mineral and amorphous compounds are formed at higher and higher temperatures and are a mixture of alumino-silicate and iron compounds). In the waste Pb-Zn slag sample, in addition to the amorphous phase, there are alloys of non-ferrous metals with iron, galena and sphalerite minerals, and alumino-silicates.

Examinations using an electron microscope (SEM) have established that lead-copper alloys and zinc-copper alloys occur in the slag (the content of other metals in these alloys is lower). Lead and zinc do not form common alloys, but alloys of these metals form mutual amalgams, especially in classes above 100 μm to 300 μm, however, lead and zinc alloys occur to a lesser extent and in finer classes up to 40 μm.

Silver as a precious metal is very scattered, that is, it appears in the amorphous phase (figure 5, size up to 2-3 μm), then in lead alloys (figure 6, size up to 5-6 μm), and in addition, there is invisible silver in lead alloys. In the SEM microphotograph of Figure 12 (Table 3), it can be seen that there is structural silver (chemically determined by SEM) in the grain of the lead alloy which was recorded at a concentration of 0.97%. In addition, it should be said that silver in zinc alloys has not been determined as either free or structural.

Further tests should examine the possibility of concentrating non-ferrous metals into their collective concentrate, in which the maximum possible amount of silver would be separated. These tests should be performed by gravity concentration and magnetic separation procedures. Magnetic separation should separate most of the elemental iron, magnetite and vistite, as well as the amorphous phase composed of spinel and ferrite that contains iron in its structure. Gravitational concentration should separate non-ferrous metal concentrates from the non-magnetic glassy matrix.

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