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Original scientific paper

GEOCHEMISTRY AND MINERALOGY OF LEAD-ZINC MINE TAILINGS FROM THE ARTANA LANDFILL IN THE REPUBLIC OF KOSOVO

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A b s t r a c t: The aim of this work was to identify and characterize the chemical elements in the samples of flotation tailings from the Pb-Zn mine in the Artana landfill, Republic of Kosovo. A total of 38 tailings samples were analyzed for their geochemical composition using: inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and inductively coupled plasma – mass spectrometry (ICP-MS), as well as for their mineralogical composition using X-ray powder diffraction (XRPD) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). The geochemical data show that the content of most elements is in the following range: iron 5.8 – 31.9 %, calcium 0.69 – 13.4%, aluminium 0.08 – 1.98%, potassium 0.11 – 1.34%, lead 0.26 – 1.75%, and zinc 0.03 – 1.89%. The semi-quantitative X-ray diffraction (XRPD) analysis shows the information for the most common minerals with their average content: pyrite 37.38%, basanite 25.28%, anhydrite 18.62% and quartz 16.93%. The data obtained from the collected samples with different instrumental techniques (ICP-AES and SEM-EDX) show a good correlation for the content of the following metals: Fe, Ca, Al, K and Pb.

Key words: Pb-Zn tailings; ICP-AES; ICP-MS; XRPD; SEM-EDX; Artana landfill; Kosovo

INTRODUCTION

Since the beginning of civilization, humans have exploited metals, coal, industrial minerals and rocks to produce goods, energy and building materials. Therefore, these mining activities have created great wealth (Hudson-Edwards et al., 2011). Tailings ponds are mixtures of crushed rock and processing fluids from mills, washes or concentrators that remain after the extraction of economic metals, minerals, mineral fuels or coal from the mine resource (Kossoff et al., 2014). Tailing dams as deposits of tailings from active mines, mainly of polymetallic mineral raw materials, are usually located near the mines with open pit or underground exploitation and have long been treated as potential environmental contaminants, but more recently also as economically potential raw materials (Serafimovski et al., 2021a). The chemical composition of tailings depends on the mineralogy of the ore body, the nature of processing fluids used to extract the economic metals, the efficiency of the extraction process and the degree of weathering during storage (Kossoff et al., 2014; Serafimovski et al., 2021b).

Numerous studies have been devoted to the geology of the Artana/Novo Brdo ore deposit, the exploitation of which dates back some 3,000 years (Féraud and Deschamps, 2009). The silver mines of Novo Brdo were particularly important and the town itself became one of the riches places in the Balkans for many centuries (Vuković and Weinstein, 2002; Rizaj et al., 2008). The Artana mine, which was historically known as a gold and silver mine, and according to some statistical data, the total resources were estimated at 2,700,000 tons with 4.43 % lead, 5.42 % zinc, 141 ppm silver and 1.0 ppm gold (Sadiku et al., 2021; Ellis, 2005; ICMMK – Independent Commission for Mines and Minerals of Kosovo, 2011). In the valley of Kriva River, there are still two deposits of tailings from the Artana concentrator, which was closed in the 1960s. They are located 2 km north of the village of Artana, near the Novo Brdo mine and downstream of the old Marec concentrator, which is now closed (Féraud and Deschamps, 2009). The landfills are located on the banks of the Marec river and are considered typical environmental hotspots. The first landfill covers an area of two hectares and contains 350,000 tons of slag, while the second landfill is located 1.7 km from the first, covers an area of four hectares and contains 2,000,000 tons of slag (Sadiku et al., 2021).

The aim of this work was to study the geochemical and mineralogical composition of lead-zinc mine tailings of the Artana landfill in order to assess the level of valuable metals for their economic value and also the content of heavy metals as potentially toxic elements for the environment.

MATERIALS AND METHODS

Study area

Artana/Novo Brdo is a town and municipality located in the district of Prishtina in Kosovo. According to the 2011 census, it has a population of 6,729 inhabitants. The center of the municipality is the village of Bostane. The municipality of Artana includes 33 villages covering an area of 204 km². The area of the municipality of Artana is dominated by typical continental climate. However, due to the high altitude, some parts of the municipality are characterized by mountainous climate. Temperatures are the lowest in January and the highest in July and August. In the last 20 years, the average annual precipitation has ranged from 910 mm in 2002 to 540 mm in 2008 (Linder et al., 2016).

Sampling and sample digestion

The tailing samples were taken from the Artana 1 landfill, with an area of about 24,000 m^2, and the drillings were distributed as homogeneously as possible (Figure 1). A total of 38 tailing samples were taken at a depth of 40–60 cm. At each location 0.8–1 kg of tailing samples were collected and dried in an oven at a temperature of 105^{o}C for 24 hours. After grinding in the ball mill, the samples were ground with a mortar and stored for further geochemical and mineralogical analysis.

The collected samples of flotation tailings were digested for total analysis using by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and inductively coupled plasma – mass spectrometry (ICP-MS) techniques. The total digestion method was used due to the high content of silicates in the samples, which is why hydrofluoric acid was also used (ISO:14869-1:2001).

Procedure. Approximately 0.250 gram of the finely ground sample is accurately weighed and placed at the bottom of a cleaned 100 ml teflon beaker. A few drops of water are added to the sample to moisten it. The beaker is then clamped in a stand and placed on a hot plate. Then 6 ml of concentrated HCl and 2 ml of concentrated HNO_3 are slowly added. The digestion (temperature of about 80^{o}C) is continued for 30 to 45 minutes. During this time, the temperature is increased to 100^{o}C. The beaker should be gently shake occasionally during this period. When the sample is almost evaporated, a mixture of 4.5 ml of concentrated HCO_4 and 15 ml of concentrated Hf is slowly added to the sample. The sample is heated for a further 90 minutes, stirring the mixture occasionally by gentle shaking. At the end of this time, a mixture of 5 ml of concentrated H_2O_2 is added in three portions. The wet salts are then dissolved with 3 ml of concentrated HCl and 1 ml of concentrated HNO_3. After this step is completed, the solution is quickly filtered through filter paper into a 50 ml volumetric flask. After filtration, the volumetric flask is filled up to the mark with distilled water.

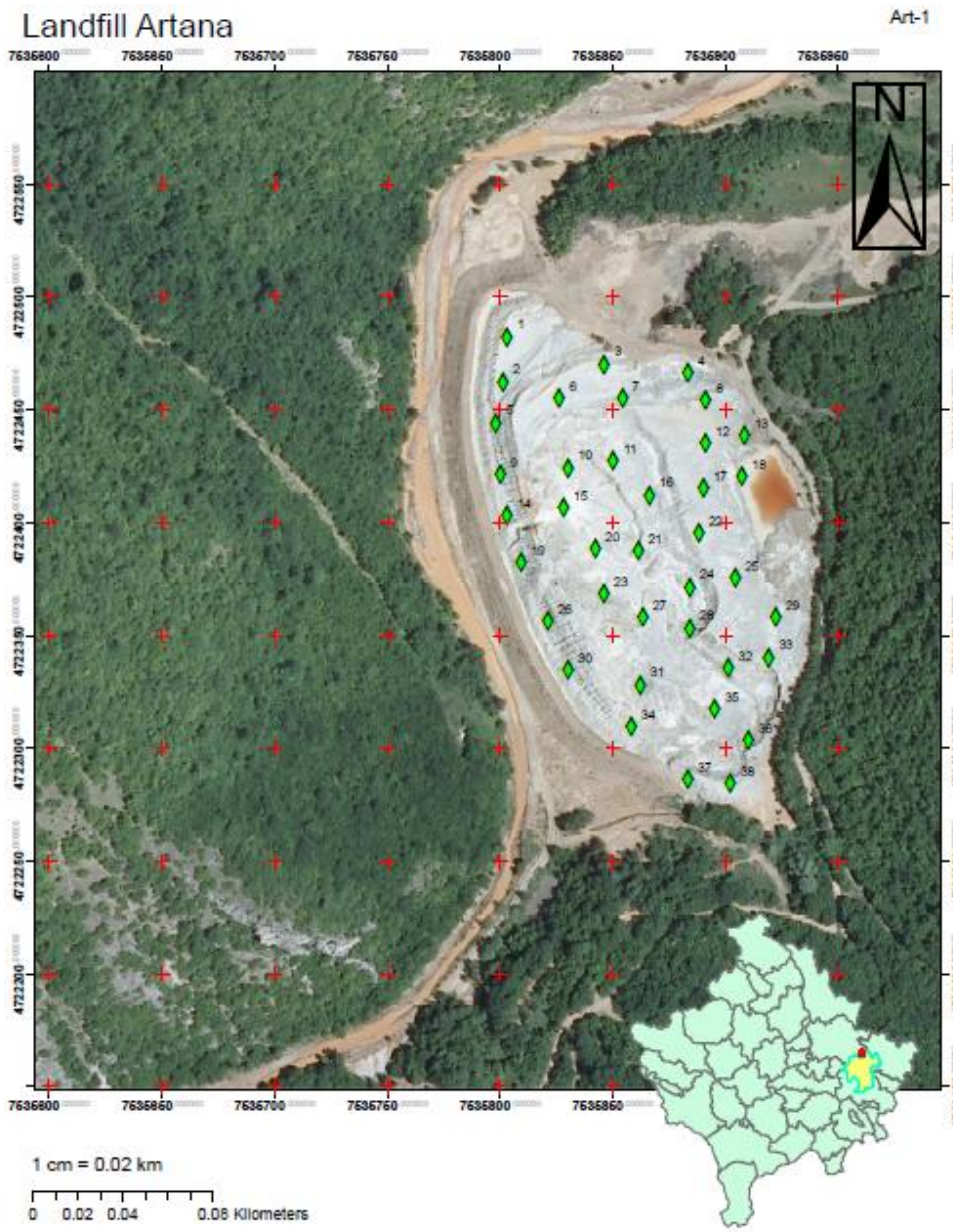

Fig. 1. The sampling points in the landfill Artana_1

Chemical analysis

By the application of inductively coupled plasma – atomic emission spectrometry (ICP-AES, Varian, model 715ES, Palo Alto, CA, USA), the concentrations of the following 20 elements were determined: Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V, and Zn. Balabanova et al. (2011) give the optimal instrumental conditions. Inductively coupled plasma – mass spectrometry (ICP-MS, Plasma Quant ICP-MS, Analytic, Jena, Germany) was used for the analysis of seven elements: Be, Co, Hg, In, Mo, Sb, and Tl. The standard solutions of the analyzed elements were prepared by dilution of 1000 mg/l solutions (11355-ICP Multi-Element Standard, Merck, Darmstadt, Germany).

Quality control was performed by analyzing certified reference soil and geological samples: soil sample JSAC 0401 (The Japan Society for Analytical Chemistry) and rock CRM samples undersaturated igneous rock SARM 3 NIM-L Lujaurite (SA Bureau of Standards, Pretoria, S. Africa), rock NCS DC71306 (GBW07114) (China National Analysis Center). The values obtained were found to be within the standard deviation of the certified reference materials.

Mineralogical analysis

The mineralogical composition of the samples was characterized by X-ray powder diffractometer (Empyrean, Panalytical). XRPD measurements were performed using Cu (anode) Kα: 1.540598 Å, the radiation source at a voltage 45 kV and current of 40 mA, Bragg-Brentano HD was used as detector (X-ray mirror). Spectral information was collected at the angle of 2 θ in the scan range 5–75 using Data Collector software. Identification of research phases was performed using HighScore software and the ICSD-COD database.

The scanning electron microscope (SEM-Vega 3 Tescan) was used for chemical characterization of the tailing samples. The high voltage was 30 kV, the working distance 10.4 mm, with an integrated EDX detector.

RESULTS AND DISCUSSION

Two tailings' landfills (Artana_1 and Artana_2) are located 2 km north of the village of Artana/Novo Brdo, near Novo Brdo mine and downstream of the old Marevc concentrator, which has now been abandoned. The Artana_1 landfill has 0.4 million tonnes and Artana_2 has 1.6 million tonnes of tailings. These tailings could have considerable economic value (Féraud and Deschamps, 2009; Šajn et al., 2022; Serafimovski et al., 2021a). Many recently published papers show that mining and tailings in Kosovo have led to increased levels of potentially toxic elements and contamination of the soil (Kastrati et al., 2024; Aliu et al., 2019), water (Kashtanjeva et al., 2023; Gashi et al., 2011), air (Paçarizi et al., 2023; Kastrati et al., 2022; Sopaj et al., 2022), and food (Kastrati et al., 2023; Mehmeti et al., 2021; Pacarizi et al., 2019).

In order to obtain more detailed information on the composition of the tailings in the Artana landfill, detailed studies were carried out on their composition in terms of the representation of 27 chemical elements, including potentially toxic elements (As, Cd, Hg, In, Pb, Sb, Tl, Zn), which, on the other hand, may represent an economic interest for their possible extraction and production. In addition, studies were carried out to determine the basic mineralogical composition using X-ray powder diffraction (XRPD). In order to compare the results of the analysis of the major chemical elements (Ca, Fe, Al, Pb, and K, as well as O, S, and Si) in the samples from the flotation tailings, an analysis by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) was also carried out.

Geochemical composition

A total of 38 tailings samples from the Artana_1 landfill were digested after processing and the solutions were analyzed using ICP-AES and ICP-MS. A total of 27 chemical elements were analyzed: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sr, Tl, V, and Zn. The basic statistics (average, median, minimum, maximum, and standard deviation) are given in Table 1. The most frequently occurring elements were Fe, Ca, K, Pb, Al, As, Zn, Na, and P, with contents of 17.63%, 3.21%, 0.60%, 0.51%, 0.45%, 0.38%, 0.24%, 0.18%, and 0.14%, respectively. These results were lower than those from the Pb-Zn slag damp from the Pb-Zn smelter in Veles, North Macedonia (Šajn et al., 2020). On the other hand, the average silver content (24.24 mg/kg) in tailing samples was higher than in the tailings samples (1.42 ppm) from Bor in Serbia (Serafimovski et al., 2021c). The results obtained for the Artana tailings compared to the average content of the analyzed elements in the tailings samples from the Badovc landfill near the town of Gračanica in Kosovo (Féraud and Deschamps, 2009), were lower for Fe, Zn, As, Al, and Cu, higher in average content for Ca, Cr, Sb, and V, but very similar in content for Ag, Ba, and Pb.

A matrix of correlation coefficients was created to determine for which elements their contents correlate with each other in the 38 samples analyzed. The Pearson correlation coefficients (r) for 27 elements in 38 tailings samples are shown in Table 2.

Table 1

Basic statistics of element concentrations in tailing samples (n=38)

Element	Unit	Average	Standard deviation	Median	Minimum	Maximum
Ag	mg/kg	24.2	11.5	21.3	12.2	66.7
Al	%	0.45	0.38	0.32	0.08	1.98
As	%	0.38	0.21	0.33	0.08	0.82
Ba	mg/kg	173	46.0	182	81.0	326
Be	mg/kg	0.09	0.05	0.08	0.02	0.27
Ca	%	3.21	2.65	2.75	0.69	13.4
Cd	mg/kg	41.4	48.0	23.7	0.79	207
Co	mg/kg	4.24	2.86	3.48	0.60	14.6
Cr	mg/kg	73.7	50.8	57.4	25.6	297
Cu	mg/kg	313	3870	116	41.9	1470
Fe	%	17.6	5.04	18.9	5.81	31.9
Hg	mg/kg	0.91	0.26	0.91	0.50	1.58
In	mg/kg	1.33	1.10	0.93	0.41	5.11
K	%	0.60	0.28	0.55	0.11	1.34
Li	mg/kg	6.13	2.78	5.27	2.25	18.9
Mg	mg/kg	877	357	803	281	1730
Mn	mg/kg	836	1876	162	33.2	10687
Mo	mg/kg	1.79	1.36	1.56	0.34	8.61
Na	%	0.18	0.13	0.15	0.07	0.84
Ni	mg/kg	35.2	19.2	34.6	10.2	98.0
P	%	0.14	0.01	0.13	0.11	0.16
Pb	%	0.51	0.33	0.37	0.26	1.75
Sb	mg/kg	141	45.3	131	69.0	298
Sr	mg/kg	23.5	9.50	21.7	9.70	55.3
Tl	mg/kg	2.73	1.90	2.40	0.56	9.85
V	mg/kg	21.7	16.6	15.7	3.78	67.4
Zn	%	0.24	0.42	0.06	0.03	1.89

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Pearson correlation (r) between 27 elements distributed in 38 tailing samples

	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg	In	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sb	Sr	Tl	V	Zn
Ag	1.00																										
Al	0.56	1.00																									
As	0.03	0.07	1.00																								
Ba	0.57	0.04	0.04	1.00																							
Be	0.11	0.27	0.07	–0.02	1.00																						
Ca	0.25	0.53	–0.12	–0.15	–0.08	1.00																					
Cd	–0.03	0.09	0.37	–0.08	0.33	–0.25	1.00																				
Co	–0.36	–0.24	0.16	–0.16	–0.12	–0.19	0.14	1.00																			
Cr	–0.25	0.06	–0.18	–0.07	0.06	–0.20	–0.14	0.06	1.00																		
Cu	0.17	0.33	0.55	–0.01	0.40	–0.14	0.63	–0.09	–0.15	1.00																	
Fe	–0.31	–0.31	0.43	–0.18	–0.21	–0.36	0.26	0.51	0.08	0.14	1.00																
Hg	0.43	0.12	–0.04	0.55	–0.15	0.05	–0.26	–0.06	–0.17	–0.14	–0.12	1.00															
In	0.13	0.26	0.52	0.01	0.45	0.05	0.55	–0.04	–0.19	0.75	0.04	–0.09	1.00														
K	0.68	0.57	–0.20	0.53	0.30	0.10	–0.13	–0.40	0.04	0.12	–0.71	0.29	0.08	1.00													
Li	0.00	0.35	–0.18	–0.08	0.47	–0.04	0.03	–0.22	0.34	0.01	–0.53	–0.06	–0.02	0.49	1.00												
Mg	0.50	0.53	0.39	0.26	0.39	0.29	0.33	–0.30	–0.26	0.64	–0.36	–0.03	0.62	0.52	0.16	1.00											
Mn	0.19	0.20	0.14	0.00	0.39	–0.19	0.77	–0.05	–0.15	0.68	0.13	–0.14	0.64	0.08	0.02	0.40	1.00										
Mo	0.29	0.42	0.11	–0.01	0.19	0.53	0.18	–0.28	–0.08	0.27	–0.21	–0.11	0.28	0.16	–0.02	0.39	0.23	1.00									
Na	0.01	0.15	–0.28	–0.10	0.20	0.27	–0.19	–0.24	0.16	–0.18	–0.30	–0.10	–0.13	0.17	0.57	–0.02	–0.11	0.10	1.00								
Ni	–0.30	0.05	0.09	–0.28	0.14	0.14	0.05	0.21	0.17	0.11	–0.13	–0.25	0.24	–0.11	0.20	0.08	0.01	0.09	0.05	1.00							
P	0.34	0.36	0.49	0.11	0.38	–0.04	0.40	–0.06	–0.16	0.65	–0.12	0.04	0.55	0.32	0.20	0.65	0.43	0.26	–0.07	0.27	1.00						
Pb	0.95	0.53	0.14	0.62	0.20	0.20	0.11	–0.33	–0.26	0.26	–0.25	0.37	0.29	0.64	–0.04	0.60	0.31	0.35	–0.02	–0.25	0.46	1.00					
Sb	0.61	0.43	–0.12	0.39	0.18	0.32	0.11	–0.36	–0.07	0.13	–0.22	–0.01	0.26	0.45	–0.12	0.52	0.33	0.40	–0.03	–0.18	0.13	0.66	1.00				
Sr	0.08	0.38	–0.15	–0.14	–0.16	0.93	–0.38	–0.15	–0.13	–0.24	–0.34	0.07	–0.04	0.04	–0.01	0.15	–0.32	0.40	0.40	0.15	–0.17	0.02	0.22	1.00			
Tl	0.37	0.13	–0.07	0.26	–0.07	–0.04	0.00	–0.23	–0.31	0.12	–0.30	0.35	0.01	0.47	0.01	0.36	0.18	–0.12	–0.11	–0.29	0.19	0.32	0.17	–0.07	1.00		
V	0.73	0.62	0.18	0.37	0.46	–0.07	0.25	–0.37	–0.03	0.50	–0.38	0.15	0.39	0.79	0.40	0.65	0.41	0.22	0.03	–0.04	0.63	0.76	0.42	–0.23	0.33	1.00	
Zn	0.04	0.14	0.08	–0.12	0.40	0.08	0.50	–0.09	–0.07	0.49	0.06	–0.23	0.58	–0.03	0.21	0.34	0.63	0.20	0.55	0.08	0.28	0.16	0.19	0.06	–0.04	0.20	1.00

An absolute value between 0.50 and 0.70 indicates a good correlation and a value between 0.70 to 1.00 indicates a strong correlation (Balabanova et al., 2010; Sopaj et al., 2022). The strongest positive correlations were between: Pb and Ag (0.95), Ca and Sr (0.93), V and K (0.79), V and Pb (0.76), V and Ag (0.73), Cd and Mn (0.77), Cu and In (0.75), as they have the same geogenic origin (Tiu et al., 2021). The highest number of strong and good correlations with other elements were for Mg, Pb, Cu, Ag, V, and In, but some other elements (Be, Cr, Tl, and Fe) did not have good correlation with other elements. In addition, a cluster analysis of the elements was performed to determine the significance of the matrix of correlation data and the relationships between the contents of the elements (Figure 2). The dendrogram of the distances of the correlation coefficients of the individual elements shows that the analyzed elements are divided into four groups that have similarities with the matrix of correlation coefficients. The hierarchical cluster analysis created using the Ward method is shown in Figure 2. In the cluster analysis, four groups of elements could be identified: the first cluster is formed by Fe, the second cluster by Ca, the third cluster by Pb, Zn, Al, K, and As, and the fourth cluster by other analyzed elements.

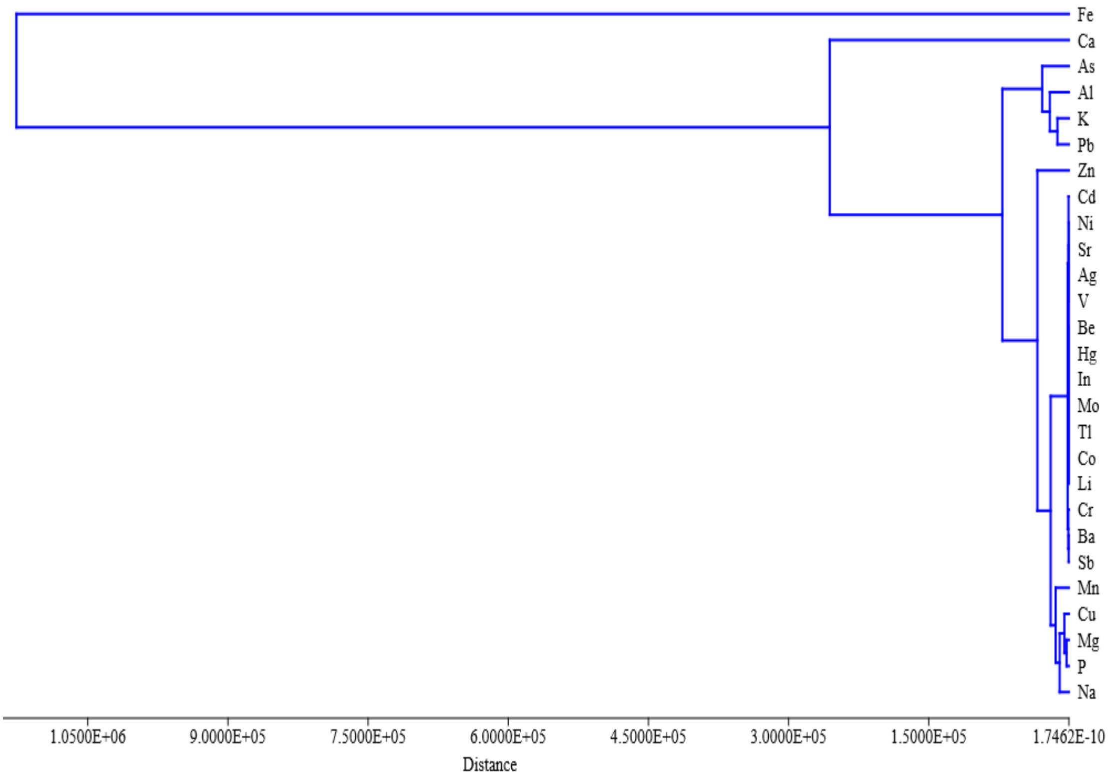


Fig. 2. The hierarchical clustering elements measured in tailing samples

Mineralogical composition

All tailings' samples were analyzed in the laboratory of the Geological Survey of Kosovo by X-ray powder diffraction (XRPD) after being ground with a ball mill and then with a mortar. The XRPD analysis of 38 analyzed samples identified seven different minerals: pyrite, basanite, anhydrite, quartz, jarosite, hydroniumjarosite, and kintoreite. A principal component analysis (PCA) was performed to determine the distribution of minerals in the tailings samples (Figure 3). PCA analysis revealed two principal components, with PC1 accounting for 57.22% and the PC2 accounting for 26.35%. Pyrite was the most abundant mineral, followed by basanite and anhydrite, and they did not correlate with each other. Three minerals (jarosite, hydroniumjarosite and kintoreite), which had a lower content in the samples, correlated well with each other as they formed in the oxidized parts of sulfide deposits or barren pyritiferous rocks (Cruells and Roca, 2022; Ceniceros-Gómez et al., 2018).

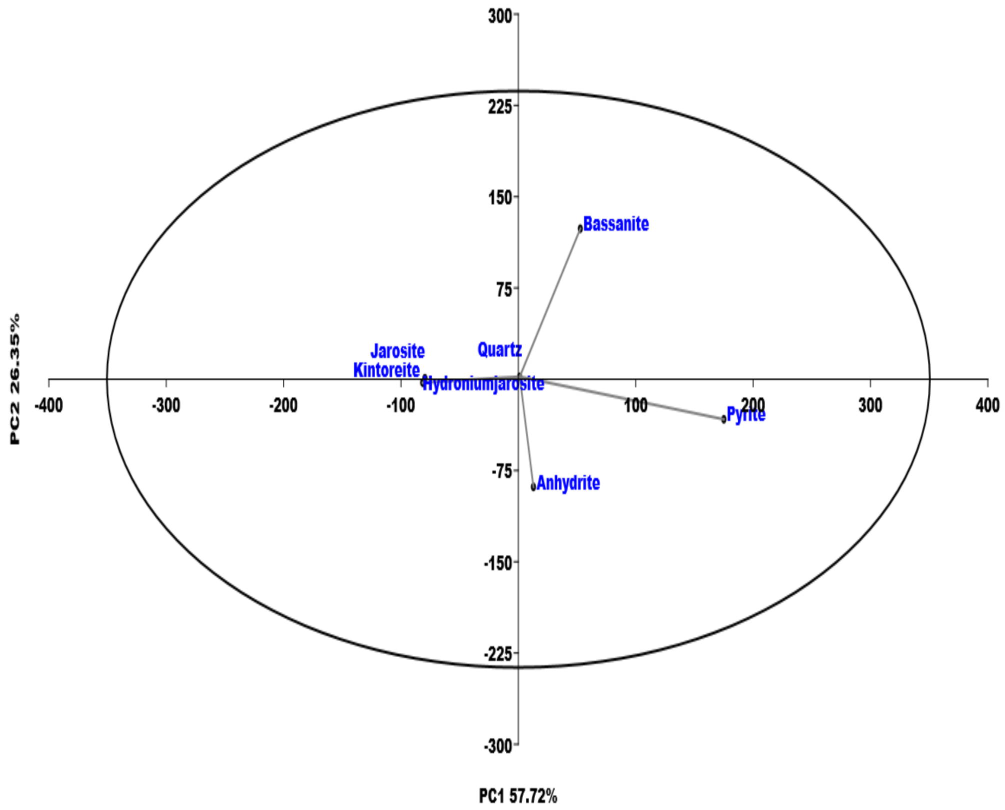


Fig. 3. Multivariate principal component analysis (PCA) of minerals for 38 tailings samples

The basic statistical data on the mineralogical composition of 38 tailing samples analyzed by X-ray powder diffraction (XRPD) are shown in Table 3. The average content of the main minerals determined was: pyrite (37.38%), basanite (25.82%), anhydrite (18.62%), and quartz (16.93%), and the sum of their average content was over 98%, while the other three minerals (jarosite, hydroniumjarosite, and kintoreite) were only involved with less than 2 percent. The minimum values for all minerals were 0.00%, and the maximum values vary depending on the mineralogy of the ore body and the process of extraction and storage (Kossoff et al., 2014; Serafimovski et al., 2021b).

Table 3

Basic statistics of mineralogical composition (%) in tailing samples (n = 38)

	Average	Median	Minimum	Maximum	Standard deviation
Pyrite	37.38	38.00	0.00	100	19.22
Basanite	25.82	27.00	0.00	100	19.67
Anhydrite	18.62	19.30	0.00	52.20	17.90
Quartz	16.93	16.50	0.00	48.40	8.50

The average iron content can be calculated from the average pyrite content (FeS_2) in the tailings from the landfill using the following equation:

$$\text{Fe (\%)} = \frac{Ar(\text{Fe})}{Mr(\text{FeS}_2)} \cdot \%(\text{FeS}_2) = \frac{55.85}{119.97} \cdot 37.38\% = 17.40\%$$

where *Ar*(Fe) is the relative atomic mass of Fe and *Mr* is the relative molecular mass of FeS_2.

The value calculated from the mineralogical data is very close to the value of 17.63% determined by ICP-AES, which is given in Table 1.

Based on the XRPD analysis of tailings sample No. T1, shown in Figure 4, three mineralogical phases could be identified: pyrite, anhydrite, and quartz. Pyrite is the most abundant in this sample, followed by the minerales anhydrite and quartz, with 46.7%, 44.8%, and 8.5%, respectively, while the content of other minerals was less than 0.5%. The most abundant elements analyzed by ICP-AES, for this tailings sample where: Fe, Ca, K, Pb, Al, As, and P, with contents of 21.06%, 2.88%, 0.41%, 0.26%, 0.24, 0.18%, and 0.14%, respectively.

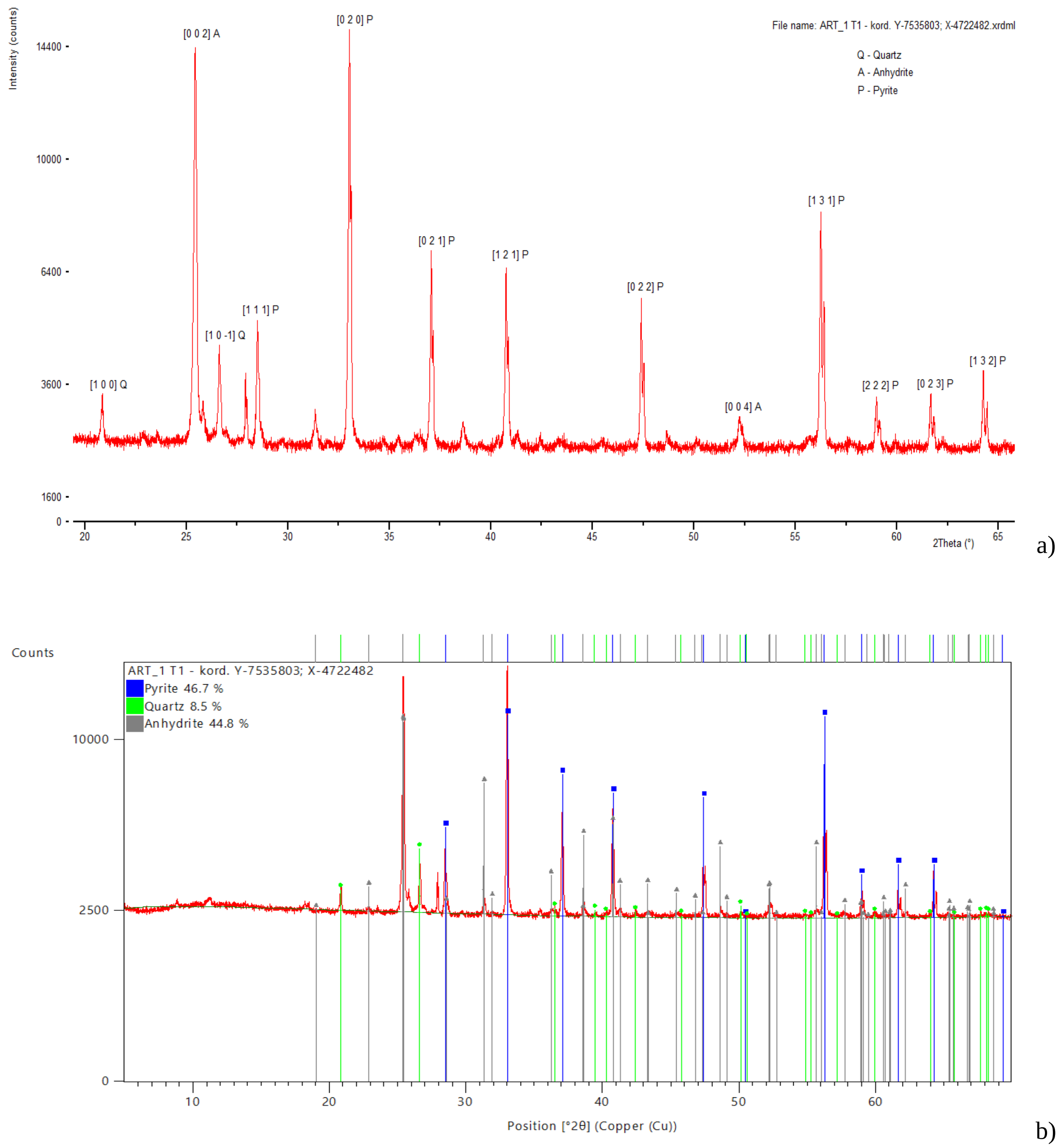
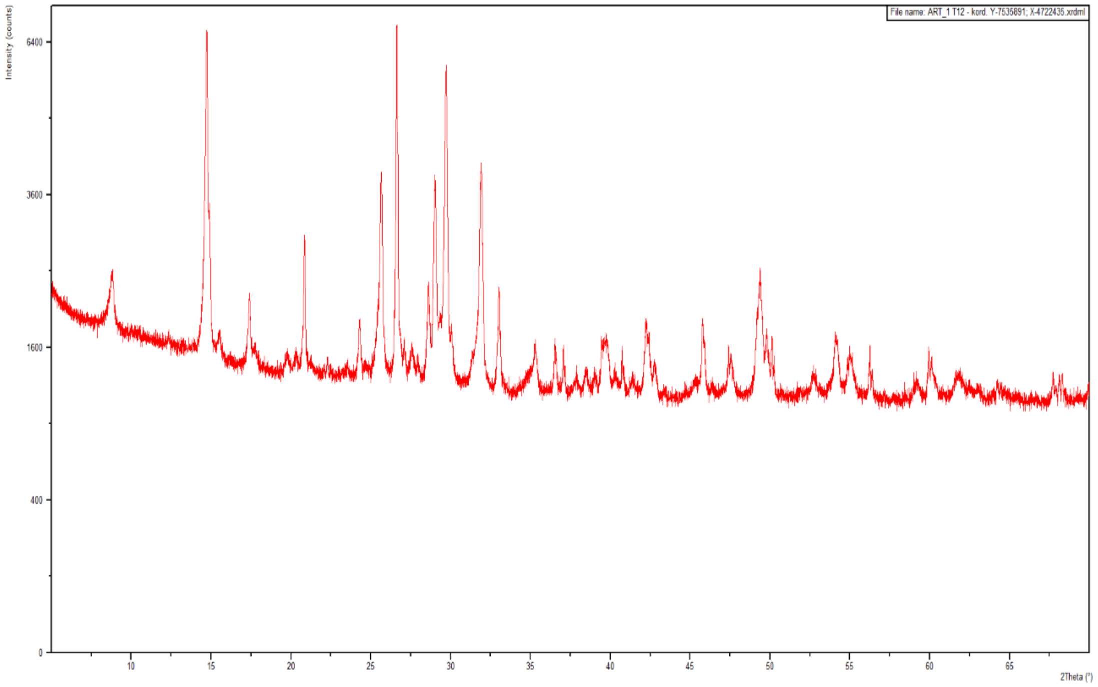
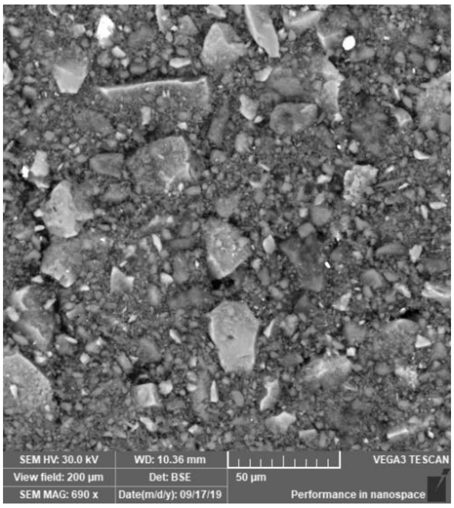


Fig. 4. XRPD spectrum of tailing sample T1 characterized by: a) Miller indices, b) percentage composition

In order to compare the mineralogical results with the geochemical results, the tailings sample from the location No. T12 was analyzed by XRPD and also by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), as shown in Figure 5. The results of the XRPD analysis for this tailings sample identified four main minerals: basanite (65.6%), quartz (19.7%), kintoreite (11%), and pyrite (9.2%). As the SEM has a built-in EDX detector, the contents of the elements are below 100 mg/kg (0.01%) could not be detected. A comparison of the results for Ca, Fe, Al, Pb, and K (Table 4) shows that the values of the two different analytical techniques, SEM and ICP-AES, are very close to each other.



a)



b)

Fig. 5. XRPD spectrum (a) and SEM-BSE photomicrographs (b) of the tailing sample T12

T a b l e 4

Chemical composition of sample No. T12 with SEM-EDX and ICP-AES

Chemical element	SEM-EDX (%)	ICP-AES (%)
O	52.73	
S	14.14	
Si	8.44	
Ca	12.25	12.58
Fe	7.12	7.09
Al	2.50	1.98
Pb	1.55	1.61
K	1.28	1.34
Total	100.00	

CONCLUSION

This study investigated the geochemical and mineralogical composition of the tailings in the Artana_1 landfill in the Republic of Kosovo. Several sophisticated instrumental techniques were used for this purpose: ICP-AES, ICP-MS, XRPD, and SEM-EDX. The data for the content of 27 chemical elements show that the most abundant elements are Fe, Ca, K, Pb, Al, As, Zn, Mn, and Cu, while Ag, Cd, Hg, In, Li, and Tl are also significantly present. These potentially toxic elements are therefore of great importance for the pollution of waters, river sediments, soils, air, and food, but may also be of economic interest for their possible extraction and production. The mineralogical results of the tailings indicate that the most frequently occurring minerals were pyrite, basanite, anhydrite and quartz.

REFERENCES

Aliu, M., Šajn, R., Stafilov, T. (2019): Enrichment of some potentially toxic elements in soils affected by Pb-Zn mining and metallurgical processing in the Mitrovica region, Kosovo. *Geologica Macedonica* **33** (1), 61–70.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2010): Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia. *Journal of Environmental Science and Health*, Part A, **45** (12), 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2011): Distribution of chemical elements in attic dust as reflection of their geogenic and anthropogenic sources in the vicinity of the copper mine and flotation plant. *Archives of Environmental Contamination and Toxicology* **61** (2), 173–84.

Ceniceros-Gómez, A. E., Macías-Macías, K. Y., De la Cruz-Moreno, J. E., Gutiérrez-Ruiz, M. E., Martínez-Jardines, L. G. (2018): Characterization of mining tailings in México for the possible recovery of strategic elements. *Journal of South American Earth Sciences* **88**, 72–79.

Cruells, M., Roca, A. (2022): Jarosites: formation, structure, reactivity and environmental. *Metals* **12** (5), 802.

Ellis, R. (2005): Kosovo, land of opportunity for European mining and energy. *Mining Journal, Special Publication*, Mining Communications, London.

Féraud, J., Deschamps, Y. (2009): French Scientific Cooperation 2007–2008 on the Trepça lead-zinc-silver mine and the gold pootential of Novo Brdo/Artana tailings (Kosovo). BRGM Report No RP-57204-FR, Scientific and Technical Centre, Mineral Resources Division, Orleans Cedex, France.

Gashi, F., Frančišković-Bilinski, S., Bilinski, H., Troni, N., Bacaj, M., Jusufi, F. (2011): Establishing of monitoring network on Kosovo rivers: preliminary measurements on the four main rivers (Drini and Bardhë, Morava e Binqës, Lepenc and Sitnica). *Environmental Monitoring and Assessment* **175**, 279–289.

Hudson-Edwards, K. A., Jamieson, H. E., Lottermoser, B. G. (2011): Mine waste: past, present, future. *Elements* **7** (6), 375–380.

ICMMK – Independent Commission for Mines and Minerals of Kosovo (2011): *Mining Resources, Mineral Site Artana (Novo Brdo)*, Prishtina.

Kashtanjeva, A., Vehapi, I., Kurteshi, K., Paçarizi, M., Berisha, A., Morina, R. (2023): Assessment of physico-chemical, microbiological parameters and diatom algae of Badovc Lake, Kosovo. *Polish Journal of Environmental Studies* **32** (3), 2155–2169.

Kastrati, G., Paçarizi, M., Sopaj, F., Tašev, K., Stafilov, T., Šajn, R., Millaku, F. (2022): Distribution and statistical analysis of major and trace elements in the bee pollen from the territory of Republic of Kosovo. *Journal of Environmental Science and Health*, Part A, **57** (10), 880–890.

Kastrati, G., Sopaj, F., Tašev, K., Stafilov, T., Šajn, R., Paçarizi, M. (2023): Analysis of chemical elements in honey samples in the territory of Kosovo. *Journal of Food Composition and Analysis* **124**, 105505.

Kastrati, G., Vataj, R., Sopaj, F., Tašev, K., Stafilov, T., Šajn, R., Paçarizi, M. (2024): Distribution and statistical analysis of chemical elements in soil from the territory of the Republic of Kosovo. *Soil and Sediment Contamination*: *An International Journal* **33** (2), 195–215.

Kossoff, D., Dubbin, W. E., Alfredsson, M., Edwards, S. J., Macklin, M. G., Hudson-Edwards, K. A. (2014): Mine tailings dams: characteristics, failure, environmental impacts, and remediation. *Applied Geochemistry* **51**, 229–245.

Linder, N., Mackenbach, M., Novák, J. (2016): Detailed technical design for acid mine water treatment in Novo Brdo mine, Artana/Kosovo. United Nations Development Programme (UNDP); In: Drebenstedl, C., Paul, M.(ecls), *Proceedings on IMWA 2016 – Mining Meets Water – Conflicst and Solutions*. Freiberg, Germany, pp. 608–615.

Mehmeti, A. R., Pacarizi, M., Hashani, I., DaciAjvazi, M., Govori, S., Maxhuni, A. (2021): Determination of heavy metals in honey by atomic absorption spectrometry. *Fresenius Environmental Bulletin* **30** (7), 8325–8328.

Pacarizi, M. A., Berisha, A., Halili, J. (2019): Electrochemical assessment of the presence of some heavy metals in honey samples in the industrial region of Mitrovica (Kosovo). *Journal of Environmental Protection and Ecology* **20** (1), 170–176.

Paçarizi, M., Stafilov, T., Šajn, R., Tašev, K., Sopaj, F. (2023): Mosses as bioindicators of atmospheric deposition of Tl, Hg and As in Kosovo. *Chemistry and Ecology* **39** (2), 123–136.

Rizaj, M., Beqiri, E., McBow, I., O'Brien, E. Z., Kongoli, F. (2008): The mineral base and productive capacities of metals and non-metals of Kosovo. *JOM* **60**, 18–22.

Sadiku, M., Kadriu, S., Kelmendi, M., Latifi, L. (2021): Impact of Artana mine on heavy metal pollution of the Marec river in Kosovo. *Mining of Mineral Deposits* **15** (2), 18–24.

Šajn, R., Stafilov, T., Boev, B., Serafimovski, T., Tasev, G., Ilijovski, Z., Boev, I. (2020): Geochemical properties of lead-zinc slag landfill from MHK Zletovo in Veles, North Macedonia. *Geologica Macedonica* **34** (2), 89–104.

Šajn, R., Ristović, I., Čeplak, B (2022): Mining and metallurgical waste as potential secondary sources of metals – A case study for the west Balkan region. *Minerals* **12** (5), 547.

Serafimovski, T., Ristović, I., Boev, B., Tasev, G., Boev, I., Serafimovski, D., Dolenec, M. (2021a): Mineralogical analysis of samples from the old Bor mine flotation tailing, Republic Serbia. *Natural Resources and Technologies* **15** (1), 37–50.

Serafimovski, T., Boev, B., Tasev, G., Boev, I., Serafimovski, D. (2021b): Mineralogical analysis of samples from the Bučim tailing dam drill holes. *Geologica Macedonica* **35** (2), 115–129.

Serafimovski, T., Ristović, I., Boev, B., Tasev, G., Boev, I., Serafimovski, D., Dolenec, M. (2021c): Some geochemical and mineralogical features of samples from old Bor's tailing dam. *Geologica Macedonica*, Special Issue No. **5** (5), 157–164.

Sopaj, F., Paçarizi, M., Stafilov, T., Tašev, K., Šajn, R. (2022): Statistical analysis of atmospheric deposition of heavy metals in Kosovo using the terrestrial mosses method. *Journal of Environmental Science and Health*, Part A, **57** (5), 335–346.

Tiu, G., Jansson, N., Wanhainen, C., Ghorbani, Y., Lilja, L. (2021): Ore mineralogy and trace element (re)distribution at the metamorphosed Lappberget Zn-Pb-Ag-(Cu-Au) deposit, Garpenberg, Sweden. *Ore Geology Reviews* **135**, 104223.

Vuković, M., Weinstein, A. (2002): Kosovo mining, metallurgy and politics: Eight centuries of perspective. *Journal of Minerals, Metals and Materials Society* **54**, 21–24.

Р е з и м е

ГЕОХЕМИЈА И МИНЕРАЛОГИЈА НА ОЛОВО-ЦИНКОВАТА РУДНИЧКА ЈАЛОВИНА ОД ДЕПОНИЈАТА ВО АРТАНА, РЕПУБЛИКА КОСОВО

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Клучни збопрови: јаловина Pb-Zn; ICP-AES; ICP-MS; XRPD; SEM-EDX; депонија Артана; Косово

Цел на оваа работа е идентификација и карактеризација на застапеноста на хемиските елементи во примероци од рудничката флотациона јаловина од Pb-Zn депонија Артана, Република Косово. Анализирани се вкупно 38 примероци од флотационата јаловина за утврдување на нејзиниот состав со примена на индуктивно спрегната плазма – атомска емисиона спекрометрија (ICP-AES) и индуктивно спрегната плазма – масена спектрометрија (ICP-MS), како и нејзиниот минералошки состав со примена на рендгенска прашковна дифракција (XRPD) и скенирачка електронска микроскопија со енергетско-дисперзивна рендгенска спектроскопија (SEM-EDX). Податоците од геохемиските испитувања покажуваат дека содржината на најзастапените елементи е со следниот редослед: железо 5,8–31,9%, калциум 0,69–13,4%, алуминиум 0,08–1,98%, калиум 0,11–1,34%, олово 0,26–1,75% и цинк 0,03–1,89%. Семиквантитативната анализа со рендгенска дифракција (XRPD) покажа дека најзастапени минерали и нивните содржини се следните: пирит 37,38%, басанит 25,28%, анхидрид 18,62% и кварц 16,93%. Резултатите за содржината на повеќето хемиски елементи (Fe, Ca, Al, K и Pb) во испитуваните примероци добиени со примена на различни инструментални техники (ICP-AES и SEM-EDX) покажуваат добро совпаѓање.