processes

MDPI

Article

Investigation of the Possibilities for the Recycling of Mixed Heterogeneous Lead Refinery Waste

Jasmina Dedić [1], Jelena Đokić [1,*], Gordana Milentijević [1], Irma Dervišević [1] and Maja Petrović [2]

[1] Faculty of Technical Sciences, University of Priština in Kosovska Mitrovica, 38220 Kosovska Mitrovica, Serbia; jasminavdedic@hotmail.com (J.D.); gordana.milentijevic@pr.ac.rs (G.M.); irma.dervisevic@pr.ac.rs (I.D.)
[2] Faculty of Technical Sciences, University of Novi Sad, 21000 Novi Sad, Serbia; majadjogo@uns.ac.rs
* Correspondence: jelena.djokic@pr.ac.rs

Abstract: The historical industrial waste deposit Gater was used to dispose of different metallurgy wastes from lead and zinc production. The metallurgical waste deposit was situated in the open space, between the tailing waste deposit Žitkovac and river Ibar flow. Large amounts of lead-containing wastes are produced in the non-ferrous metallurgical industry, such as lead ash and lead slag generated in Pb smelting, lead anode slime, and lead sludge produced in the raw lead refining process. In addition to the lead concentration, numerous valuable components are found in the lead refinery waste from the group of Critical Raw Materials, such as antimony, arsenic, bismuth, copper, nickel, magnesium, scandium, as well as Rare-Earth Elements. Samples with eight characteristic points were taken to obtain relevant data indicating a possible recycling method. The chemical composition analysis was conducted using ICP; the scanning was completed using SEM-EDS. The mineralogical composition was determined by using XRD. The chemical analysis showed a wide range of valuable metal concentrations, from Ag (in the range from 14.2 to 214.6, with an average 86.25 mg/kg) to heavy metals such as Cu (in the range from 282.7 to 28,298, with an average 10,683.7 mg/kg or 1.0683% that corresponds to some active mines), Ni and Zn (in the range from 1.259 to 69,853.4, with an average 14,304.81 mg/kg), Sc (in the range from 2.4 to 75.3, with an average 33.61 mg/kg), Pb (in the range from 862.6 to 154,027.5, with an average 45,046 mg/kg), Sb (in the range from 51.7 to 18,514.7, with an average 2267.8 mg/kg), Ca (in the range from 167.5 to 63,963, with an average 19,880 mg/kg), Mg (in the range from 668.3 to 76,824.5, with an average 31,670 mg/kg), and As (in the range from 62.9 to 24,328.1, with an average 5829.53 mg/kg). The mineralogy analysis shows that all metals are in the form of oxides, but in the case of As and Fe, SEM-EDS shows some portion of elemental lead, pyrite, and silica-magnesium-calcium oxides as slag and tailing waste residues. The proposed recovery process should start with leaching, and further investigation should decide on the type of leaching procedure and agents, considering the waste's heterogeneous nature and acidity and toxicity.

Keywords: lead refinery waste; lead tailing waste; metals recovery; Critical Raw Materials extraction; leaching

check for updates

Academic Editors: Md. Salatul Islam Mozumder, Rajan Kumar Thapa, Surajbhan Sevda and Nabin Aryal

Received: 28 February 2025
Revised: 25 April 2025
Accepted: 29 April 2025
Published: 30 April 2025

Citation: Dedić, J.; Đokić, J.; Milentijević, G.; Dervišević, I.; Petrović, M. Investigation of the Possibilities for the Recycling of Mixed Heterogeneous Lead Refinery Waste. *Processes* **2025**, *13*, 1380. https://doi.org/10.3390/pr13051380

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Today, large amounts of lead-containing wastes are produced in the non-ferrous metallurgical industry [1–3], especially in Pb and Zn metallurgy fields, such as lead ash and lead slag generated in Pb/Zn smelting, lead anode slime, and lead sludge produced in electrolytic refining. Other engineering fields [4–6] are also sources of Pb-bearing substances, including lead scrap and lead paste separated from spent lead–acid batteries [7].

In many countries, these lead-bearing wastes are classified as hazardous waste due to the high toxicity of lead [8].

They are greatly detrimental to the environment and human health if left untreated and abandoned directly to the environment [9]. Soil represents a direct sink for pollution that smelters emit into the atmosphere and for solid waste and slag that are deposited in the environment [10]. However, soil is not only a passive acceptor; polluted soil becomes a source of contamination for other components of the environment [11]. Heavy metals cannot be degraded and tend to accumulate and persist in soil [12]. Due to their high porosity and permeability, metals and metalloids in tailings become more soluble and easily transferred to other parts of the environment [13,14].

The impact of heavy metals on the environment, especially on the soil quality, was investigated by the [15,16] using the BCR procedure. Lead-bearing industrial wastes of Trepča were investigated and evaluated for their risks to the environment [17], and the issue of heavy metal penetration to the surface waters was observed, as the waste locations were in close vicinity to the river Ibar. The release of wind-borne particles and pollutants in the form of gases from metallurgical plants into the atmosphere during ore processing and from landfills is the main source of soil pollution with heavy metals in this area [18].

However, these wastes generally contain considerable amounts of other valuable metals, such as gold (Au) and silver (Ag). Not recycling these metals enormously challenges the circular economy.

Pyrometallurgy is the predominant methodology around the world for primary lead production.

Impurities found in lead have a detrimental effect on its quality; they increase its strength, reduce its malleability, make it difficult to obtain lead bleach and glaze, and reduce its resistance to the action of acids and other chemical materials. For these reasons, the standardization of pure lead is carried out, which must not contain more than 0.008–0.01% impurities. Additionally, 99.97% pure lead was obtained in Trepča. Achieving this quality requires careful refining, the task of separating all impurities from lead and obtaining other valuable elements. This process utilizes chemicals such as caustic soda, soda ash, or lime, as well as fluxing agents. The removal of impurities and other metals from crude lead, including sulfur, copper, nickel, arsenic, antimony, bismuth, zinc, calcium, and magnesium, as well as extraction of silver and gold, involves several stages. Sulfur is used to remove copper, and tin (Sn) is removed after that through oxidation with either chlorine (Cl_2) or ammonium chloride (NH_4Cl), generating tin chloride ($SnCl_2$) skims. Arsenic and antimony are removed using a mixture of sodium nitrate ($NaNO_3$) and sodium hydroxide (NaOH). The obtained skims comprise a mixture of oxides, containing approximately 25% antimony, 10% arsenic, and 65% lead. After softening, silver is extracted using the Parkes process, and the remaining zinc is removed by vacuum distillation and treatment with sodium hydroxide (NaOH). These products of lead refinery contain the raw materials, listed as Critical Raw Materials (CRMs), needed for achieving green energy transition in the EU [19,20], such as arsenic, antimony, bismuth, copper, nickel, magnesium, feldspar, and Rare-Earth Elements.

The lead refinery waste was deposed on the ground and left to weathering for decades. The complex variety of processes in the environment affects the distribution and efficient sequestration of heavy metals, which causes their release or transformation into different species [21].

The mineralogical and geochemical evolution of sulfide-rich waste can be expressed by slight changes in the primary paragenesis or deep transformations, which end in new mineralogical structures [22,23]. Newly formed minerals can include intermediate terms,

such as clay minerals, hydrated salts, metal oxides, arsenates, carbonates, phosphates, and natural elements [24,25].

The composition of the main and trace elements of primary minerals, as well as the Eh-pH conditions, determine the composition and nature of these secondary phases [26]. Metal–sulfate minerals, which, although metastable, deserve special attention [27,28].

The possibility of using the metallurgical waste of Trepča for extracting CRM was investigated by [29,30]. However, the authors focused on the slag generated in the process of lead oxide reduction in the shaft furnace. Even though the lead shift furnace slag is abundant, the metal waste from the other technological processes can also be significant for the high price of the components present in the waste.

The study aimed to investigate lead refinery waste for two reasons: its adverse environmental impact on the region and the possible valorization of valuable Critical Raw Materials. The process of the extraction of the valuable elements from the lead refinery waste is determined by waste composition, and mineralogical forms. The complex characterization of the heterogenous waste is performed to determine the method and conditions under which recycling is possible in the waste site.

In previous studies, some of the authors were focused on the recovery of valuable components in mineral processing as the first phase of ore treatment [31], as well as a part of the waste management strategy for scrap containing REEs. The elements in the waste were either in the formation of the rocks in the mining process or impurities in the metal waste, with special attention paid to nuclear raw material, as scandium is found in different ore bodies, such as lateritic ores [32,33], vanadium-titanium magnetite ores [34], and Rare-Earth ores [35,36], and usually ends up in the resulting wastewater and slag [37]. Therefore, secondary resources become the primary source for scandium extraction, such as titanium dioxide waste acid [38,39], red mud [40–42], tungsten slag [43], bauxite slag [44–46], Rare-Earth slag [47], and fly ash [48]. The authors evaluated the most efficient procedures, such as a sulfuric acid bake and leach route for extracting REEs from ores and concentrates [49]. The Rare-Earth Elements (REEs) from the iron ore mine tailings are considered a resource, and after beneficiation, they are concentrated in apatite and monazite minerals [50].

2. Materials and Methods

2.1. Study Area

Landfill “Gater” has an irregular and very elongated shape, with a length in the longest part of about 480 m and a width from 80 m in the narrowest part to approximately 160 m in the widest part. The landfill is clearly defined (Figure 1): from the south by the Zvečan-Raška road, from the west by Nasip and the Zvečan-Zubin Potok road, from the north side is the road and the field of flotation tailings (partially rehabilitated and recultivated, also from the process at RMHK “Trepča”, and on the east side along the Kosovo Polje-Belgrade line, it is oriented almost correctly in the north–south direction, with a slight deviation in the direction of the altitude height between 490 and 500 m, and in relation to the surrounding terrain, it is almost flat, with some deviations ranging from 0.5 to 2.5 m lofty, while, in the extreme part, on the northern side, there is a large excavation about 2–2.5 m deep, which was created during the last cleaning of the landfill.

The landfill’s surface is mainly made of hardened tailings, partially fine and very fine granulation, almost sandy in appearance, and ranging in color from reddish-brown to dark brown. In places where lead chlorides are present, it is also white. Concrete structures that exist are mostly present either in the whole or in part of the site.



Figure 1. Landfill "Gater".

2.2. Sampling Procedure

Characterization of the landfill "Gater" as a deposit of inhomogeneous structure that has changed over time could not previously be determined. The sampling was aimed at covering different metallurgical wastes from different stages of the processes. Unfortunately, the company documents do not record a strict line separating the different refining methods and the agents used in the refining process. In the field intended for processing, characteristic points were determined based on several factors that indicated the existence of certain and sought-after pollutants that significantly affect the composition of the waste. The primary goal was to visually find those points in order to proceed to the sample and a more detailed analysis based on other primary indicators, such as weight, color, granulometric composition, and the company's internal records on the dumping sites.

Samples were taken from eight characteristic points (Figure 2), and in order to obtain relevant data that indicate a possible remediation method, sampling was performed from the surface and a depth of 300 mm. The initial investigation performed prior to the formal research showed that the composition of the waste was not significantly changed in the deeper layers of the waste piles, as previously presented in [15].



Figure 2. Characteristic points of the samples.

The analyzed soil samples were taken from the surface (8 samples) and at a depth of 300 mm (8 samples) using a shorter probe of 1 m in length, "meia–cana". The collected soil samples were air-dried indoors at room temperature for a week. After drying to constant

weight, for the purpose of the chemical analysis, the soil samples were homogenized and then ground to a grain size of <2 mm to determine heavy metal concentrations.

2.3. Instrumental Testing

For the future consideration of the lead refinery waste for the recovery of valuable metals and arsenic, the chemical composition is the first stage of characterization. Chemical analysis will show the exact concentration of all constituents of the waste. Chemical tests were performed on an ICP-AES device, Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, UK). The calibration standard used is ILM 05.2 ICS Stck 1, produced by VGH Labs, Inc-Part of LGS Standards, Manchester, NH, USA. Sulfur quantification was done on the emission line: S I 182,034 nm, and the calibration curve had a coefficient correlation of 0.99963. Microwave digestion, ETHOS 1, Advanced Microwave Digestion System, Milestone, Milan, Italy, with an HPR-1000/10S high-pressure segmented rotor was used for sample preparation. The mass of the solid sample was 0.1 g.

The reagents, 5 mL of ultrapure water, 5 mL of HNO_3 (65%, Sigma-Aldrich, St. Louis, MO, USA), and 3 mL of H_2O_2 (30%, Sigma-Aldrich), were used to dissolve the samples. The preparation of ultra-pure water was done as follows: demineralization of water on ion exchange columns (conductivity 1.5 μS/cm). Classical distillation of demineralized water over $KMnO_4$ and passing the water through the apparatus was used to obtain ultra-pure water (conductivity 0.055 μS/cm) on the apparatus Barnstead™ GenPure™ Pro (Thermo Scientific, Dreieich, Germany).

To investigate the microstructure of the waste, particles, aggregates, and composition on the surface, the qualitative and semi-quantitative analyses were made. Microstructural tests were performed using a scanning electron microscope (SEM), model JSM 6460, JEOL, with an energy-dispersive spectrometer (EDS), Oxford Instruments (Abingdon, UK). The samples were annealed at 1000 °C to dry, homogenize, and then glue to a double-sided adhesive tape to place them in the electron microscope.

X-ray diffractometry is performed to define the mineralogical composition and determine the bonds between elements, compounds, and ions. Diffractometric tests, X-ray diffractometry (XRD), were performed on a powder diffractometer D2 PHASER, Bruker. The device is equipped with a dynamic scintillator detector and a ceramic X-ray tube made of copper (KFL-Cu-2 K) with a 2θ range from 50 to 750 with a phase shift of 0.020. TOPAS 4.2 software was used to interpret the obtained diffractograms with the ICDD PDF2 (2013) database.

3. Results

3.1. Chemical Analysis

The results of the waste composition analysis are presented in Table 1.

Table 1. Results of the waste composition analysis.

Samples	H, mm	Elements mg/kg																		
		Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Na	Ni	Pb	S	Sb	Sc	Si	Zn
Sample 1	0	114.2	2428.1	59.2	7366.5	13.8	41.7	39.1	13,921	22,348.9	4.2	4682.5	1044.8	149.1	82,811.6		259.4	2.4	170,325.4	7953.4
	300	14.2	1428.1	-	14,376.5	-	24.6	19.8	923.2	42,168.5	-	668.3	1763.2	54.8	64,527.8		232.4	37.7	21,242.4	4963.6

Table 1. *Cont.*

Samples	H, mm	Elements mg/kg																		
		Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Na	Ni	Pb	S	Sb	Sc	Si	Zn
Sample 2	0	134.6		53.6	3362.5	11.6	31.4	59.1	23,624.2	52,646.9	21.2	76,824.5	12,144.8	172.1		21,861.6	162.4	13	14,1365.4	9983.4
	300	94.2		52.2	6386.5	-	51.2	42.6	13,641.2	41,368.9	-	56,682.5	11,494.8	143.5		12,381.6	263.7	23	16,1326.4	69,853.4
Sample 3	0	214.6	24,328.1	-	36,356.5	23.8	61.9	-	6921.7	202,358.9	-	64,682.5	-	184.1	2811.4	92,742.8	62.4	61	71,325.4	3963.4
	300	-	6478.1	-	31,876.5	-	43.2	-	942.6	195,635.9	-	16,482.5	-	52.4	862.6	68,578.4	-	30.6	62,325.4	253.4
Sample 4	0	134.2	14,368.1	42.2	376.5	-	61.7	142.1	10,021.6	232,578.9	-	-	7494.8	132.1	72,821.6	-	169.4	56.1	71,325.6	7853.4
	300	91.2	4438.1	23.2	176.5	-	62.7	163.1	13,964.2	164,358.7	-	-	1104.6	119.4	22,411.6	-	82.4	34.1	81,325.4	5943.7
Sample 5	0	87.9	4745.4	84.6	63,963.9	13.7	14.2	136.1	3170.9	101,677.3	4.7	7463.3	5433.7	135.8	32,944.6	-	6485.9	6.3	-	9339
	300	54.9	1755.4	74.6	396,23.9	11.4	24.6	132.7	6370.2	112,657.3	-	2463.1	2483.7	-	12,644.6	-	-	6.3	-	4379
Sample 6	0	66.3	7062.9	68	25,982.3	11.5	26.2	178.9	9278	39,837.9	5.3	20,225.9	32,529.5	305.2	154,027.5	21,326.4	514.7	5.1	-	1.259
	300	-	8462.9	48	24,852.3	-	-	124.9	6988.2	86,847.8	-	68,235.9	224,39.5	-	36,837.5	10,234.5	51.7	3.7	-	18,592.6
Sample 7	0	76.3	-	94.2	28,592.3	21.5	22.6	128.6	12898	52,847.4	15.3	14,235.9	31,359.5	35.2	54,537.5	-	18,514.7	59.5	-	25,934.6
	300	14.3	62.9	41.2	5852.3	-	-	-	282.7	112,847.9	-	20,265.7	-	-	4037.5	-	-	75.3	-	12,574.8
Sample 8	0	24.3	62.9	36	15,962.3	31.8	54.2	198.6	19,688.2	38,947.9	14.3	61,235.7	31,539.4	314.7	74,537.5	-	414.7	60.9	-	42,695.4
	300	-	162.9	-	12,982.3	-	-	198.6	28,298	62,847.9	-	29,235.9	32,529.5	20,315.2	14,837.5	-	-	62.7	-	4592.6

3.2. SEM-EDS Analysis

Microstructure investigations were conducted in all eight samples at two depths: 0 and −300 mm. The microstructure of the samples on the surface is shown in Figure 3.

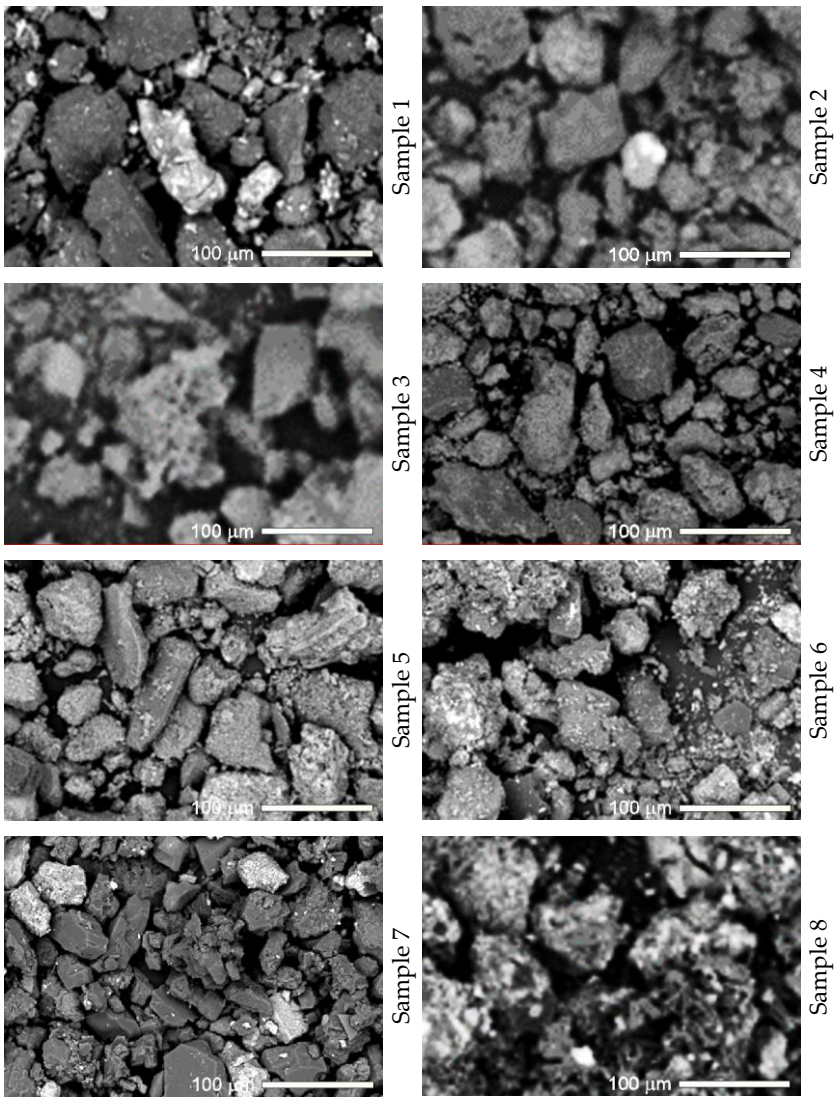


Figure 3. Microstructure of the lead refinery waste, all samples on the surface.

Table 2 shows the detected elements on the sample surface using the semi-qualitative sample analysis method.

Table 2. Semi-qualitative analysis of the samples.

Samples	H, mm	Detected Elements on the Sample Surface (mass. %)																
		O	Na	Mg	Al	Si	S	K	As	Cl	Fe	Cu	Zn	Pb	Ca	Ti	Mn	Sb
Sample 1	0	52.76	1.19	0.85	6.3	17.55	-	1.47	-	-	5.77	2.42	1.84	8.55	0.86	-	-	-
	300	57.15	1.79	0.57	7.27	18.65	-	1.61	-	0.53	4.66	0.53	-	6.39	1.1	0.27	-	-

Table 2. *Cont.*

Samples	H, mm	Detected Elements on the Sample Surface (mass. %)																
		O	Na	Mg	Al	Si	S	K	As	Cl	Fe	Cu	Zn	Pb	Ca	Ti	Mn	Sb
Sample 2	0	73.51	0.83	0.79	4.83	12.17	1.56	0.86	-	-	4.93	-	-	-	-	0.2	-	-
	300	74.24	0.63	0.89	4.61	13.15	-	0.81	-	-	4.86	0.21	-	-	0.35	0.25	-	-
Sample 3	0	49.24	-	8.46	1.64	5.64	8.21	0.36	1.91	-	21.21	-	0.14	-	2.63	-	0.65	-
	300	52.26	-	-	0.98	4.28	12.08	0.29	0.65	-	25.44	-	-	-	3.18	-	0.36	-
Sample 4	0	48.61	0.47		1.23	5.38	7.76	0.24	1.08	0.15	26.17	0.64	0.77	7.5	-	-	-	-
	300	49.55	-	-	1.7	3.59	11.15	0.27	0.86	-	17.05	0.84	-	7.39	6.18	-	-	-
Sample 5	0	50.78	1.19	0.91	2.06	6.99	8.15		1.16	2.45	16.3	0.81	1.55	4.09	3.42	-	-	2.14
	300	74.98	-	-	1.44	3.33	7.45	-	0.31	-	7.98	0.26	0.55	1.05	2.65	-	-	-
Sample 6	0	49.28	5.09	1.97	3.41	10.27	3.32	1.01	1.5	0.32	6.16	1.31	2.98	11.72	1.69	-	-	-
	300	48.28	2.19	8.86	5.75	13.73	1.85	0.86	0.96	0.13	9.54	0.89	1.55	2.45	2.96	-	-	-
Sample 7	0	50.46	2.74	0.65	6.42	19.27	-	1.99	-	-	6.59	1.34	2.68	4.24	1.42	-	-	2.2
	300	59.35	2.51	2.69	5.02	15.98	-	1.61	-	-	10.36	0.98	0.86	0.63	0.98	-	-	-
Sample 8	0	48.37	3.7	8.95	3.59	9.81	6.8	1.17	-	0.3	2.88	0.94	3.79	8.23	0.94	-	-	-
	300	59.76	2.91	3.56	5.02	15.98	-	1.61	-	-	7.36	-	0.86	2.43	0.9	-	-	-

After the observation of all the samples surfaces on H = 0 and H = 300 mm, there are specific morphology at the spectra with a high concentration of heavy metals (bright particles) and a specific microstructure.

3.3. Mineralogical Analysis

The results of the diffractometry analysis are presented in Figure 4.

To analyze the samples' acidity and ability to dissolve into different solvents, including water and pH values, conductivity measurements are performed and presented in Table 3.

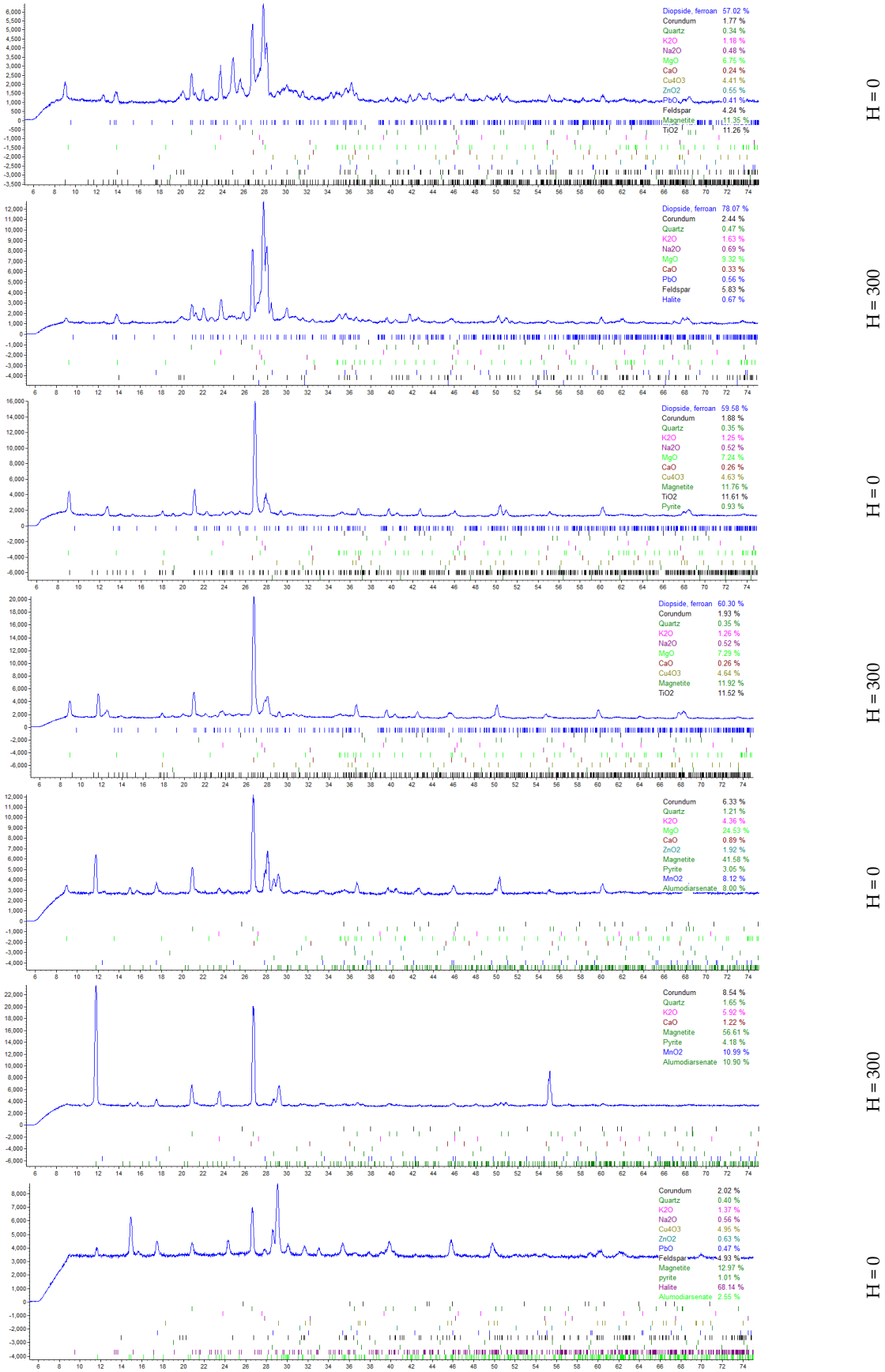


Figure 4. *Cont.*

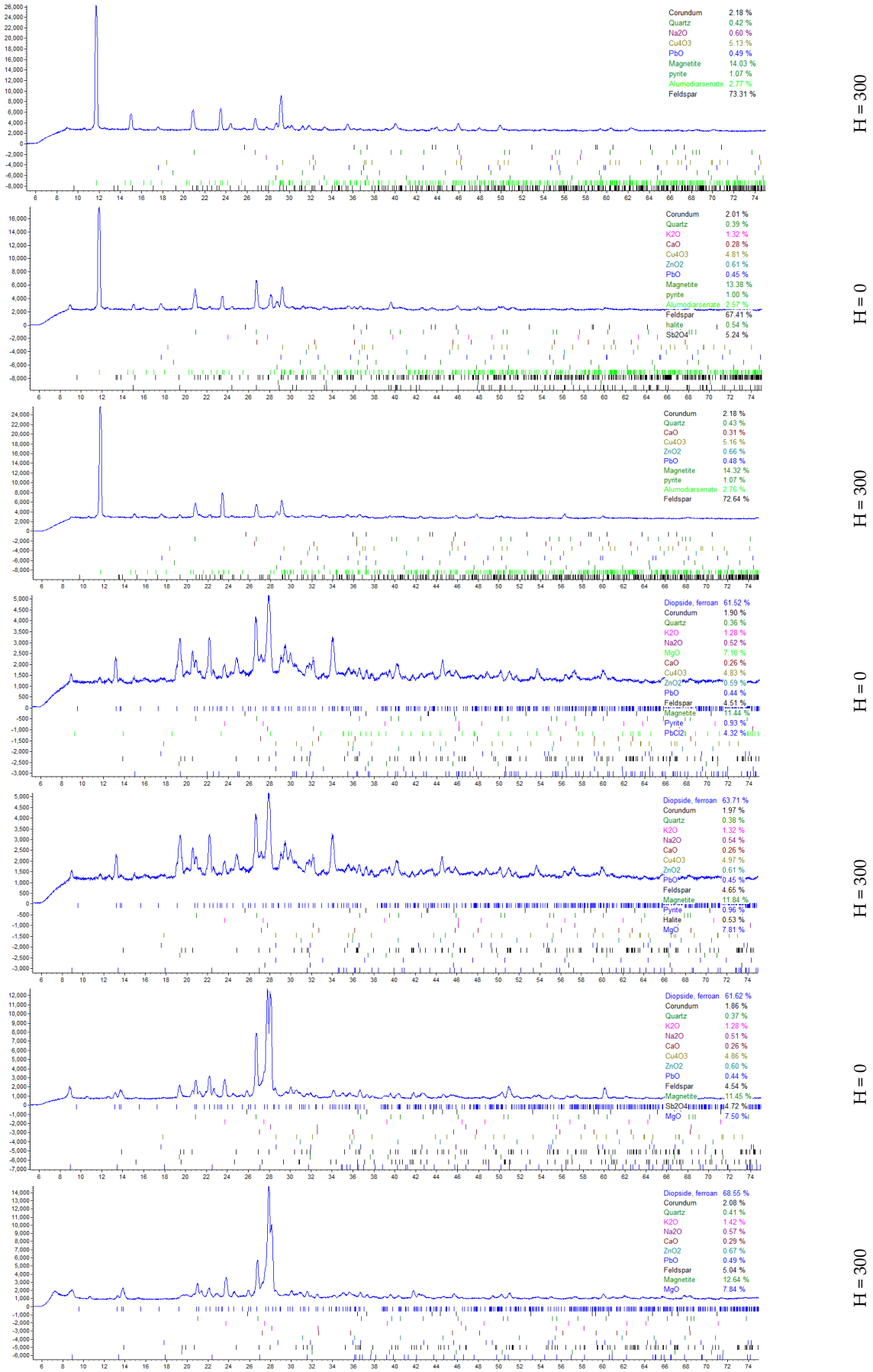


Figure 4. *Cont.*

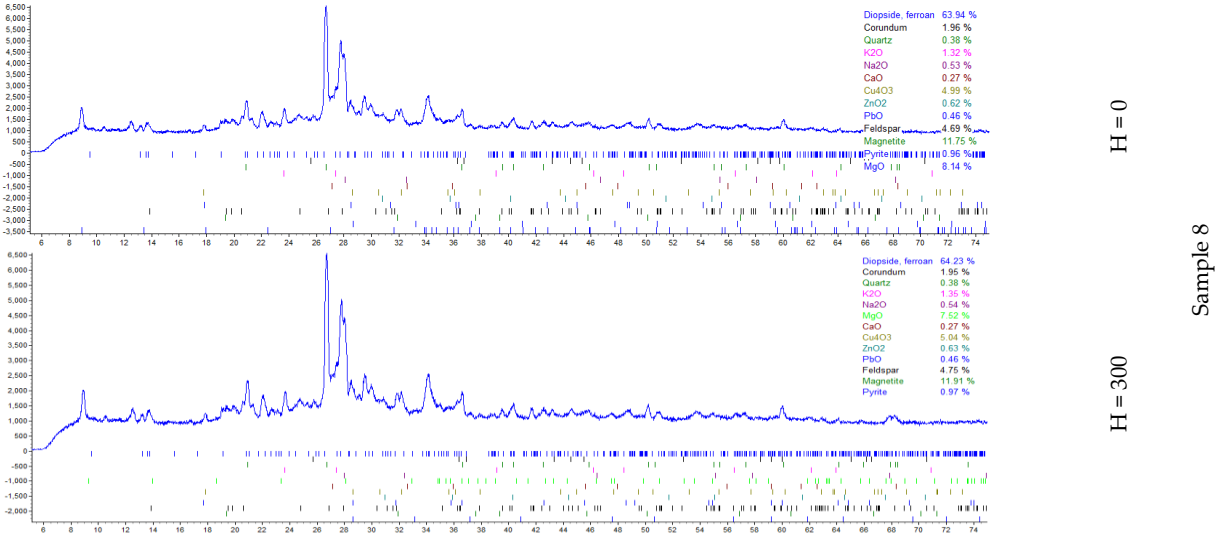


Figure 4. Diffractograms of the samples 18 on the waste surface (left) and at the 300 mm depth (right).

Table 3. pH values and conductivity of the samples.

Sample	pH Value	Conductivity (µS/cm)
1	5.23	318
2	7.15	236
3	6.67	1075
4	4.27	1273
5	2.86	2630
6	2.80	2110

4. Discussion of the Results

The chemical and mineralogical composition of the lead refinery waste points to a heterogenous, acidic, small-grained waste structure. As presented in Table 1, lead and zinc are highly concentrated, and the treatment process depends on the mineralogical composition. From the Critical Raw Materials list, silver, as the accompanying metal to the lead–zinc ore in the ore body, is found in all the samples (ranging from 14.2 to 214.6 mg/kg, with an average value of 86.25), with a concentration that corresponds to the lead ore composition (89 mg/kg average value in Trepča mines). That points out that the lead refinery process was not well done, and the amount of silver in the waste requires recycling or revalorizing the lead refinery waste. Copper is the product of the first phase of the lead refinery process. Its concentration is very high (ranging from 297 to 28,298 mg/kg, with an average value of 10,683 mg/kg or 1.0683%, which corresponds to some active mines). However, there are also significant amounts of antimony in samples 5 and 7 (6485.9 mg/kg and 18,514.7 mg/kg, respectively). Extremely high arsenic concentrations in Sample 3 and Sample 4 (24,231 and 14,368 mg/kg, respectively) prove the origin of that waste pile to be tailing waste from the minerals processing phase of the lead and zinc production process. The compounds found in the mineralogical analysis correspond to the chemical and semi-qualitative analysis presented above. Sample 1 contains heavy metals and arsenic only in the form of oxides. Sample 2 shows the presence of pyrite, a material used in lead concentrate agglomerative roasting but also as the constituent of tailing waste from ore processing. Sample 3, besides pyrite, also contains alumodiarsenate in a very high concentration, showing the form of arsenic in the waste. The diffractogram of Sample 4 included halite, a NaCl mineral, from the mixture of agents used in the second phase of the refinery, and the removal of As, Sb, and Sn, which were crystallized during the

aging process. The essence of alkaline refining is as follows: Liquid dirty lead is heated to (420–450) °C and passed through a molten mixture of sodium hydroxide and sodium chloride. Impurities contained in the lead are oxidized by oxygen from the air, and the oxidation process is greatly accelerated by the use of NaCl. $NaNO_3$ melts at 308 °C and decomposes upon further heating, releasing oxygen and forming $NaNO_2$. NaCl is an active oxidizer of arsenic, antimony, and tin and serves to form sodium arsenates, stannates, and antimonates from higher oxides of arsenic, tin, and antimony. Sodium hydroxide, in the presence of sodium chloride, oxidizes impurities better—that is, binds impurities and compounds better. Alumodiarsenate is not the only compound that is a byproduct in the second phase of lead refinery, as presented in the diffractogram of Sample 5. As presented in Figure 4, there is also a high concentration of Sb_2O_4, pointing out that the byproduct of raw lead softening, alkaline refining by the Harris process in Trepča produced minerals that can be utilized for arsenic and antimony extraction as Critical Raw Materials. Sample 6 includes $PbCl_2$ as the product of the lead dezincification process that was used in Trepča in the period of 1960–1970. The chlorination process is used very rarely today and is based on the reaction of gaseous chlorine and a liquid bath. Since lead contains a small amount of zinc, according to the law of mass action, lead is essentially chlorinated. Samples 7 and 8 are similar and contain dust from copper extraction. In the final refinement, the lead contains 0.03 to 0.07% Ca, 0.12 to 0.18% Mg, and up to 0.05% Zn. The task of this final refining is to remove these impurities.

All of the above impurities have a significantly greater affinity for oxygen than lead, which leads to the removal of these impurities.

This operation is usually carried out in boilers using sodium hydroxide and sodium nitrate as oxidants. The resulting intermediate product is in powder form and is called Ca–Mg dust. All the samples, excluding no. 2, no. 7, and no. 8, contain Ca–Mg dust in the form of oxides. The rest of the Ca and Mg content is in the form of constituents in Ferroan–Diopside.

The feldspar content in Samples 1, 4, and 7 are normal for the surrounding soil in the mining region, but the content in Sample 6 is much higher than usual. However, feldspar is a group of minerals commonly found in rocks, such as granite and gneiss, and is not directly related to the lead refining process. Therefore, it is not a typical component of lead refinery waste. By checking the old company's records, it was found that the dumping site was used to store some construction materials and road maintenance, and that could be a possible origin of feldspar's presence but also partially of the halite presence. When it comes to the differences between the waste pile surface and the waste mineralogical composition at the 300 mm depth, the occurrences of the heavy metals are consistent with the findings of the BCR analysis done by the authors before [15]. Most of the copper and zinc have not penetrated deep throughout the depth column, but the forms of their occurrences remained the same. Scandium is present in Samples 3, 4, 7, and 8 in the waste generated in As, Sn, and Sb removal, and it can be expected to be in the form of arsenate, antimonate or stannate.

Lead refinery waste represents a valuable source of Critical Raw Materials, precious, such as Ag (in the range from 14.2 to 214.6, with an average of 86.25 mg/kg); heavy metals, such as Cu (in the range from 282.7 to 28,298, with an average 10,683.7 mg/kg or 1.0683% that correspond to some active mines), Ni and Zn (in the range from 1.259 to 69,853.4, with an average 14,304.81 mg/kg), Sc (in the range from 2.4 to 75.3, with an average 33.61 mg/kg), Pb (in the range from 862.6 to 154,027.5, with an average 45,046 mg/kg), Sb (in the range from 51.7 to 18,514.7, with an average 2267.8 mg/kg), Ca (in the range from 167.5 to 63,963, with an average 19,880 mg/kg), Mg (in the range from 668.3 to 76,824.5, with an average 31,670 mg/kg), and Sn; metalloid, such as arsenic (in the range from

62.9 to 24,328.1, with an average 5829.53 mg/kg); and minerals, such as feldspar. The feldspar content was from 4.24% in most of the samples up to 73.31% in Samples 4 and 5. The large content of the feldspar was not found in the ore as a gauge mineral. It was proved that most heavy metals are in oxide form, except for As. The chemical, mineralogical, and structural composition of lead refinery waste presents an environmental threat due to its small-grained structure. Small-grained lead-bearing material is scattered by air dispersion, penetration along the depth column, and the possibility of entering the water flow less than 50 m from the waste deposit. Lead is present in the form of oxide, chloride, and carbonate. There is a need for lead extraction to decrease the waste's toxicity, as $PbCl_2$ and $PbCO_3$ are soluble in the soil [51,52], enhanced by the acidity of the waste (see Table 3), and thus could be transported into the nearby river with the soil particles by erosion.

For the valuable metals recovery processes, there are several solutions: returning to the sintering roasting process, oxidation roasting with subsequent hydrometallurgical processing, velcroing together with other recycled materials (slag), aqueous leaching with subsequent solution processing, sulfation with subsequent hydrometallurgical processing, direct leaching with sulfuric acid, the ammonia dust processing method, alkaline electrochemical leaching of dust, dust processing in a flame furnace, and dust processing in an electric furnace. Pyrometallurgy methods are not applicable to the amount and values of the waste, as the primary lead pyrometallurgy in Trepča is not operational, so the waste cannot be returned to the shaft, rotary, or electric furnace. Bioleaching is well established for the minerals in the reduced form, such as sulfates. However, bioleaching of the oxides is still in the experimental phase. The oxidative dissolution mechanism by acidophilic sulfur-oxidizing bacteria and iron-oxidizing bacteria requires reduced mineral phases [53]. Bioleaching is one of the most investigated techniques for the extraction of metals from oxidized ores and secondary wastes. Bioleaching is based on redox reactions, producing organic or inorganic acids and, finally, the excretion of agents. The redox reactions are based on transferring electrons from minerals to microorganisms or on the bacterial oxidation of ferric ions, as presented in the investigation of the mechanism and kinetics of AMD in the lead and zinc mine in the mining region of Trepča [53] in the case of acid mine drainage formation due to the pyrite concentration, oxygen presence, and ore disturbances. Lead refinery waste is highly oxidized due to the weathering, and bioleaching is not the first choice for treatment. Hydrometallurgical processes include metal dissolution, concentration and purification, and metal recovery. The chemical composition of the metallurgy waste, mineralogical composition, and grain size of the waste particles directly impacts the best treatment process. The most used treatments for metal recovery are electrowinning and precipitation. The most challenging part is selecting the methods for metal extraction, either solvent extraction or ion exchange from metallurgical waste containing many metals, metalloids, or other valuable minerals [54]. In order to investigate As recovery from the metallurgy waste, the authors carried out leaching on copper smelting ash by adopting the acid leaching process, and the results indicate that As_2O_3, $PbAs_2O_6$, $Pb_2As_2O_7$, and $Zn_3(AsO_4)_2$ were effectively dissolved in acidic solution in the leaching process [55]. In summary, arsenic and its compounds are more easily dissolved in acid, and sulfuric acid can strengthen the leaching efficiency. However, the complexity of the material requires further investigation into achieving optimal procedures and chemical agents. Sulfuric acid is recommended for arsenic removal from lead and zinc dust, and HCL and HNO_3 are investigated for the extraction of REEs from iron ore mine tailings. Most of the REEs are constituents of the minerals bastnasite, monazite, and xenotime. The usual way to dissolve them is the sulfuric acid bake process [56]. The results of the acidic leaching are the sulfates, which are used for the further process of electrowinning. The problem with lead refinery waste is that, even if most of the oxides will be transferred into the sulfates, the separation

of sulfates prior to further extraction could be difficult. Even though the amount of waste is insufficient for the construction of the recycling facilities and investments in sophisticated equipment, leaching, bioleaching, and acidic leaching on piles can be the best purpose technology for treatment. As a result, only aqueous leaching with subsequent solution processing, hydrometallurgy processing, direct leaching with sulfuric acid, and bioleaching are recommended methods for further research.

5. Conclusions and Recommendations for the Future

Heterogenous lead refinery waste was investigated for two reasons: the adverse environmental impact on the region and the possible valorization of valuable Critical Raw Materials. By analyzing the chemical composition, microstructure, and mineralogical composition, the following valuable components are found to have potential for recycling: PbZn Cu Ag Sb, As Ca, and Mg Sc are found to be in the mixture originating from As, Sn, and Sb removal, so it is expected to be in the same form. As, Ag, and Sc, from the latest CRM list, exceed the concentrations in the raw minerals, thus showing the future research potential of the lead refinery waste. Even though the amount of waste in this location is insufficient for the construction of recycling facilities and investments in sophisticated equipment, leaching, bioleaching, and acidic leaching on piles can be the best treatment technology. Leaching and bioleaching are recommended based on the composition of metal and arsenic bearing compounds. Considering the acidic nature of the waste, small-grained structure, complex oxides and salts created in the lead refinery process, further investigations and comparisons will define and optimize the treatment of heterogeneous mixed lead refinery waste.

Author Contributions: Conceptualization, J.Đ. and G.M.; methodology, J.D., I.D.; validation, J.D., J.Đ. and G.M.; formal analysis, J.D. and I.D.; investigation, J.D. and J.Đ.; data curation, and M.P.; writing—original draft preparation, J.D. and J.Đ.; writing—review and editing, J.Đ., I.D. and G.M.; supervision, J.Đ. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Lassin, A.; Piantone, P.; Burnol, A.; Bodénan, F.; Chateau, L.; Lerouge, C.; Crouzet, C.; Guyonnet, D.; Bailly, L. Reactivity of waste generated during lead recycling: An integrated study. *J. Hazard. Mater.* **2007**, *139*, 430–437. [PubMed]
2. Ellis, T.W.; Mirza, A.H. The refining of secondary lead for use in advanced lead-acid batteries. *J. Power Sources* **2010**, *195*, 4525–4529.
3. Sahu, K.K.; Agrawal, A.; Pandey, B.D. Recent trends and current practices for secondary processing of zinc and lead. Part II: Zinc recovery from secondary sources. *Waste Manag. Res. J. Int. Solid Wastes Public Cleansing Assoc. Iswa.* **2004**, *22*, 248–254.
4. Milentijević, G.; Nedeljković, B.; Đokić, J. Implementation the environmental protection system in the territory of the Kosovska Mitrovica and Zvečan municipalities. *Min. Metall. Eng. Bor.* **2014**, *4*, 193–216.
5. Kelmendi, M.; Sadiku, M.; Kadriu, S.; Dobroshi, F.; Igrishta, L.; Baruti, B. Research of heavy metals on the agricultural land in bajgora region, kosovo. *Acta Chem. Iasi.* **2018**, *26*, 105–122.
6. Kelmendi, M.; Baruti, B.; Hyseni, S.; Durmishaj, B.; Nikshiqi Kadriu, S. The influence of industrial deposition in earth pollution with heavy metals in Mitrovica. In Proceedings of the 11th International Multidisciplinary Scientific Geo Conference SGEM, Albena, Bulgaria, 18–24 June 2011; Volume 3, pp. 701–708.
7. Prathumratana, L.; Kim, R.; Kim, K.W. Lead contamination of the mining and smelting district in Mitrovica, Kosovo. *Environ. Geochem. Health.* **2020**, *42*, 1033–1044.
8. Nannoni, F.; Protano, G.; Riccobono, F. Fractionation and geochemical mobility of heavy elements in soils of a mining area in northern Kosovo. *Geoderma* **2011**, *161*, 63–73.

9. Nikolić, B.; Jakšić, L. Historical review and actual situation of metallurgy at Kosovo and Metohija. *J. Min. Metall.* **2005**, *41B*, 135–140.
10. Castillo, S.; Jesús, D.; De La Campa, A.M.S.; González-Castanedo, Y.; Fernández-Caliani, J.C.; Gonzalez, I.; Romero, A. Contribution of mine wastes to atmospheric metal deposition in the surrounding area of an abandoned heavily polluted mining district (Rio Tinto mines, Spain). *Sci. Total Environ.* **2013**, *449*, 363–372.
11. Gholizadeh, A.; Borůvka, L.; Seberioon, M.M.; Kozák, J.; Vašát, R.; Němeček, K. Comparing different data pre-processing methods for monitoring soil heavy metals based on soil spectral features. *Soil Water Res.* **2015**, *10*, 218–227.
12. Amponsah-Dacosta, F. A field-scale performance evaluation of erosion control measures for slopes of mine tailings dams. In Proceedings of the 10th International Conference on Acid Rock Drainage and IMWA Annual Conference, Santiago, Chile, 21–24 April 2015.
13. Souissi, R.; Souissi, F.; Chakroun, H.K.; Bouchardon, J.L. Mineralogical and Geochemical Characterization of Mine Tailings and Pb, Zn, and Cd Mobility in a Carbonate Setting (Northern Tunisia). *Mine Water Environ.* **2012**, *32*, 16–27.
14. Gray, N.F. Acid mine drainage composition and the implications for its impact on lotic systems. *Water Res.* **1998**, *32*, 2122–2134.
15. Dedic, J.; Djokic, J.; Galjak, J.; Milentijevic, G.; Lazarevic, D.; Šarkočević, Ž.; Lekic, M. An Experimental Investigation of the Environmental Risk of a Metallurgical Waste Deposit. *Minerals* **2022**, *12*, 661. [CrossRef]
16. Galjak, J.; Đokić, J.; Dervišević, I.; Milentijević, G.; Mojsić, M.; Živković, B. Assessment of Pollution and Distribution of Heavy Metals in the Soil Near the Flotation Tailings Gornje Polje. *Pol. J. Environ. Stud.* **2022**, *31*, 4097–4106. [CrossRef]
17. Milentijević, G.; Nedeljković, B.; Lekić, M.; Nikić, Z.; Ristović, I.; Djokić, J. Application of a Method for Intelligent Multi-Criteria Analysis of the Environmental Impact of Tailing Ponds in Northern Kosovo and Metohija. *Energies* **2016**, *9*, 935. [CrossRef]
18. Đokić, J.; Arsić, N.; Milentijević, G. Natural Disasters in Industrial Areas. In *Natural Risk Management and Engineering*; Springer Tracts in Civil Engineering; Gocić, M., Aronica, G., Stavroulakis, G., Trajković, S., Eds.; Springer: Cham, Switzerland, 2020. [CrossRef]
19. European Commission. Report on Critical Raw Materials in the Circular Economy. 2018. Available online: http://publications.europa.eu/en/publication-detail/-/publication/2d43b7e2-66ac-11e7-b2f2-01aa75ed71a1/language-en/format-PDF/source-32064602 (accessed on 7 January 2025).
20. European Commission. Critical Raw Materials for the EU: 2023 Final Report. 2023. Available online: https://ec.europa.eu (accessed on 8 January 2025).
21. Brown, G.E., Jr.; Foster, A.L.; Ostergren, J.D. Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 3388–3395. [CrossRef]
22. Pérez-López, R.; Nieto, J.M.; Alvarez-Valero, A.M.; Almodôvar, G.R. Mineralogy of the hardpan formation processes in the interface between sulfide-rich sludge and fly ash: Applications for acid mine drainage mitigation. *Am. Mineral.* **2007**, *92*, 1966–1977.
23. Lottermoser, B.; Ashley, P. Mobility and retention of trace elements in hardpan-cemented cassiterite tailings, north Queensland, Australia. *Environ. Geol.* **2006**, *50*, 835–846.
24. Valente, T.; Lealgomes, C. Occurrence, properties and pollution potential of environmental minerals in acid mine drainage. *Sci. Total Environ.* **2009**, *407*, 3.
25. Brill, H.; Floc'h, J.P. Le devenir des metaux provenant des anciennes mines; l'Exemple du Massif Central français. *Geologues* **2001**, *130*, 233–241.
26. Heikkinen, P.M.; Räisänen, M.L.; Johnson, R.H. Geochemical characterization of seepage and drainage water quality from two sulphide mine tailings impoundments: Acid mine drainage versus neutral mine drainage. *Mine Water Environ.* **2009**, *28*, 38–49.
27. Hammarstrom, J.M.; Seal, R.R., II; Meier, A.L.; Jackson, J.C. Weathering of sulfidic shale and copper mine waste: Secondary minerals and metal cycling in Great Smoky Mountains National Park, Tennessee, and North Carolina, USA. *Environ. Geol.* **2003**, *45*, 35–57.
28. Harris, D.L.; Lottermoser, B.G.; Duchesne, J. Ephemeral acid mine drainage at the Montalbion silver mine, North Queensland. *Aust. J. Earth Sci.* **2003**, *50*, 797–809.
29. Šajn, R.; Alijagić, J. Secondary deposits as a potential REEs source in South-Eastern Europe. *Minerals* **2024**, *14*, 120. [CrossRef]
30. Šajn, R.; Ristović, I. Mining and metallurgical waste as potential secondary sources of metals—A case study for the West Balkan region. *Minerals* **2022**, *12*, 547. [CrossRef]
31. Yıldız, T.D.; Tombal-Kara, T.D.; Kurşun-Ünver, İ. Challenges and recovery opportunities in waste management during the mining and enrichment processes of rare earth elements containing ores. Chapter 11. In *Trash or Treasure: Entrepreneurial Opportunities in Waste Management*; Singh, P., Borthakur, A., Eds.; Springer: Cham, Switzerland, 2024; pp. 277–306. ISBN 978-3-031-55130-7. [CrossRef]
32. Souza, A.G.O.; Aliprandini, P.; Espinosa, D.C.R.; Tenório, J.A.S. Scandium Extraction from Nickel Processing Waste Using Cyanex 923 in Sulfuric Medium. *JOM* **2019**, *71*, 2003–2009.

33. Hu, J.; Zou, D.; Chen, J.; Li, D. A novel synergistic extraction system for the recovery of scandium (III) by Cyanex272 and Cyanex923 in sulfuric acid medium. *Sep. Purif. Technol.* **2020**, *233*, 115977.
34. Cao, X.; Zhang, T.-A.; Zhang, W.; Lv, G. Solvent Extraction of Sc(III) by D2EHPA/TBP from the Leaching Solution of Vanadium Slag. *Metals* **2020**, *10*, 790. [CrossRef]
35. Zhang, W.; Zhu, H.; Liu, S.-F.; Ning, S.-Y.; Wei, Y.-Z. Scandium recovery from ion-adsorption rare earth concentrate with HEHEHP as extractant. *J. Cent. South Univ.* **2021**, *28*, 679–689.
36. Batchu, N.K.; Vander Hoogerstraete, T.; Banerjee, D.; Binnemans, K. Separation of rare-earth ions from ethylene glycol (+LiCl) solutions by non-aqueous solvent extraction with Cyanex 923. *RSC Adv.* **2017**, *7*, 45351–45362.
37. Wang, W.; Pranolo, Y.; Cheng, C.Y. Metallurgical processes for scandium recovery from various resources: A review. *Hydrometallurgy* **2011**, *108*, 100–108.
38. Chen, Y.; Ma, S.; Ning, S.; Zhong, Y.; Wang, X.; Fujita, T.; Wei, Y. Highly efficient recovery and purification of scandium from the waste sulfuric acid solution from titanium dioxide production by solvent extraction. *J. Environ. Chem. Eng.* **2021**, *9*, 106226.
39. Hedwig, S.; Yagmurlu, B.; Huang, D.; von Arx, O.; Dittrich, C.; Constable, E.C.; Friedrich, B.; Lenz, M. Nanofiltration-Enhanced Solvent Extraction of Scandium from TiO_2 Acid Waste. ACS Sustain. *Chem. Eng.* **2022**, *10*, 6063–6071.
40. Agrawal, S.; Dhawan, N. Process flowsheet for extraction of Fe, Al, Ti, Sc, and Ga values from red mud. *Miner. Eng.* **2022**, *184*, 107601.
41. Borra, C.R.; Pontikes, Y.; Binnemans, K.; Van Gerven, T. Leaching of rare earths from bauxite residue (red mud). *Miner. Eng.* **2015**, *76*, 20–27.
42. Habibi, H.; Mokmeli, M.; Shakibania, S.; Pirouzan, D.; Pourkarimi, Z. Separation and recovery of titanium and scandium from the red mud. *Sep. Purif. Technol.* **2023**, *317*, 123882.
43. Liu, H.; Liu, H.; Nie, C.; Zhang, J.; Steenari, B.-M.; Ekberg, C. Comprehensive treatments of tungsten slags in China: A critical review. *J. Environ. Manag.* **2020**, *270*, 110927.
44. Anawati, J.; Azimi, G. Integrated carbothermic smelting—Acid baking—Water leaching process for extraction of scandium, aluminum, and iron from bauxite residue. *J. Clean. Prod.* **2022**, *330*, 129905.
45. Borra, C.R.; Blanpain, B.; Pontikes, Y.; Binnemans, K.; Van Gerven, T. Comparative Analysis of Processes for Recovery of Rare Earths from Bauxite Residue. *JOM* **2016**, *68*, 2958–2962.
46. Meng, F.; Li, X.; Shi, L.; Li, Y.; Gao, F.; Wei, Y. Selective extraction of scandium from bauxite residue using ammonium sulfate roasting and leaching process. *Miner. Eng.* **2020**, *157*, 106561.
47. Ray, A.R.; Mishra, S. Hydro metallurgical technique as better option for the recovery of rare earths from mine tailings and industrial wastes. *Sustain. Chem. Pharm.* **2023**, *36*, 101311.
48. Mostajeran, M.; Bondy, J.-M.; Reynier, N.; Cameron, R. Mining value from waste: Scandium and rare earth elements selective recovery from coal fly ash leach solutions. *Miner. Eng.* **2021**, *173*, 107091.
49. Li, X.; Azimzadeh, B.; Martinez, C.E.; McBride, M.B. Pb Mineral Precipitation in Solutions of Sulfate, Carbonate and Phosphate: Measured and Modeled Pb Solubility and Pb^{2+} Activity. *Minerals* **2021**, *11*, 620. [CrossRef]
50. Peelman, S.; Sun, Z.H.I.; Sietsma, J.; Yang, Y. Hydrometallurgical Extraction of Rare Earth Elements from Low Grade Mine Tailings. In *Rare Metal Technology 2016*; Alam, S., Kim, H., Neelameggham, N.R., Ouchi, T., Oosterhof, H., Eds.; Springer: Cham, Switzerland, 2016. [CrossRef]
51. Wilson, D.J. *Hazardous Waste Site Soil Remediation: Theory and Application of Innovative Technologies*, 1st ed.; CRC Press: Boca Raton, FL, USA, 1994. [CrossRef]
52. Sethurajan, M.; van Hullebusch, E.D.; Nancharaiah, Y.V. Biotechnology in the management and resource recovery from metal bearing solid wastes: Recent advances. *J. Environ. Manag.* **2018**, *211*, 138–153.
53. Galjak, J.; Đokić, J.; Gurešić, D.; Jovic, S.; Milentijević, G. Evaluation of acid mine drainage kinetics in the lead-zinc mine. *Arab. J. Geosci.* **2020**, *13*, 354. [CrossRef]
54. Gunarathne, V.; Rajapaksha, A.U.; Vithanage, M.; Alessi, D.S.; Selvasembian, R.; Naushad, M.; You, S.; Oleszczuk, P.; Ok, Y.S. Hydrometallurgical processes for heavy metals recovery from industrial sludges. *Crit. Rev. Environ. Sci. Technol.* **2022**, *52*, 1022–1062.
55. Alka, S.; Shahir, S.; Ibrahim, N.; Ndejiko, M.J.; Vo, D.-V.N.; Manan, F.A. Arsenic removal technologies and future trends: A mini review. *J. Clean. Prod.* **2021**, *278*, 123805. [CrossRef]
56. Demol, J.; Ho, E.; Soldenhoff, K.; Senanayake, G. The sulfuric acid bake and leach route for processing of rare earth ores and concentrates: A review. *Hydrometallurgy* **2019**, *188*, 123–139. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.