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Article

Preliminary Study of Geochemical, Mineralogical and Magnetic Susceptibility Properties of Flotation Tailings from the Pb-Zn-Cu-Ag Rudnik Mine, Serbia

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Abstract

Samples of flotation tailings generated during the exploitation and processing of Zn–Pb–Cu–Ag ore from the Rudnik mine (Serbia) were investigated for their mineralogical, geochemical, and magnetic susceptibility properties. The flotation tailings consist of a complex mineral assemblage, including silicates, carbonates, sulfides, phosphates, sulfates, oxides, hydroxides, and native elements. Quartz and calcite dominate the coarse fraction (>500 µm), accompanied by epidote, andradite, and diopside. Sulfide minerals are concentrated in finer fractions (<400 µm), with pyrite and arsenopyrite being the most abundant, followed by pyrrhotite, sphalerite, galena, and chalcopyrite. These sulfides form intricate intergrowths or occur as dispersed grains within a silicate–carbonate matrix. Post-depositional oxidative alteration is moderately developed, with pyrite being replaced by hematite, galena by cerussite, and chalcopyrite by malachite. Geochemical analyses reveal that SiO₂ (avg. 38.98 wt%), Fe₂O₃ (avg. 23.68 wt%), and Al₂O₃ (avg. 8.95 wt%) dominate the composition. Economically significant metals include Zn (avg. 0.47 wt%), Pb (avg. 0.20 wt%), Cu (avg. 0.11 wt%), Ag (max. 19 µg/g), and Bi (max. 130 µg/g). Mass magnetic susceptibility shows a significant correlation with S ($r = 0.92$), Co ($r = 0.90$), and Bi ($r = 0.87$); moderate correlation with Fe₂O₃, Al₂O₃, and As; and negative correlation with Mn, TiO₂, Zn, and Pb. The ferromagnetic phase (*sensu lato*) most likely originates from hematite formed during pyrite alteration, as well as from pyrrhotite and goethite.

Keywords: flotation tailings; Rudnik mine; mineralogy; geochemistry; magnetic susceptibility

1. Introduction

Mine tailings are increasingly recognised as a potential source of mineral raw materials in response to growing metal demand and the need for sustainable resource management. Their characterisation and the recovery of valuable components have become an important part of contemporary resource and environmental policies [1]. Mine tailings often contain significant amounts of metals that could not be recovered with the technologies available at the time of mining, were not economically viable, or were not analysed (or could not be analysed) at that time. In Serbia, tailings generated from polymetallic Pb–Zn mines are the second largest source of waste in the metal mining sector, due to an annual ore production of approximately 500 thousand tonnes [2]. Despite their potential as secondary sources of metals, tailings from polymetallic deposits in Serbia have received limited scientific attention [3,4]. Until recently, only flotation tailings from the Grot mine had been subject to preliminary investigation [5]. More recent studies have examined flotation

tailings from the Rudnik mine, including mineralogical and environmental assessments [6], and the flotation behaviour of minerals [7–9].

The Rudnik mine, situated in central Serbia, is one of the most prominent and long-standing polymetallic mining sites. It hosts economically significant concentrations of Pb, Zn, Cu, and Ag and has been continuously exploited since 1953, with a total of over 14 million tonnes of ore extracted to date [10]. The mine exploits a distal skarn deposit formed during Oligocene to Early Miocene magmatic-hydrothermal events, consistent with other deposits associated with volcano-intrusive complexes in the Balkan Peninsula [11–13]. Sulfide ore is predominantly hosted within epidote-bearing skarn and occurs as massive bodies, stockwork veinlets, and disseminated mineralisation. The main sulfide minerals include sphalerite, galena, and chalcopryrite, with pyrrhotite, arsenopyrite, and pyrite as common gangue phases. Metal concentrations in ore vary considerably, ranging from 0.94 to 5.66 wt% Pb, 0.49 to 4.49 wt% Zn, 0.08 to 2.18 wt% Cu, and 50 to 297 µg/g Ag [14].

Decades of mining and flotation processing of polymetallic ore have resulted in a tailings storage facility covering ~30 ha, with over 11 million tonnes (7 million m³) of material deposited to date (Figure 1a, b). This flotation tailings, representing the residual fraction after beneficiation of PbS, ZnS, and CuFeS₂ concentrates, has evolved from initially supporting only Pb and Zn recovery to including Cu concentrates since 1988. Their mineralogical composition and heterogeneity position them simultaneously as a potential secondary resource and as a factor influencing long-term environmental impact. Consequently, the tailings storage facility represents both a challenge and an opportunity—requiring proper management to mitigate ecological risks while offering scope for revalorization through modern processing technologies. In this context, characterisation becomes essential for advancing sustainable resource management and circular economy strategies.

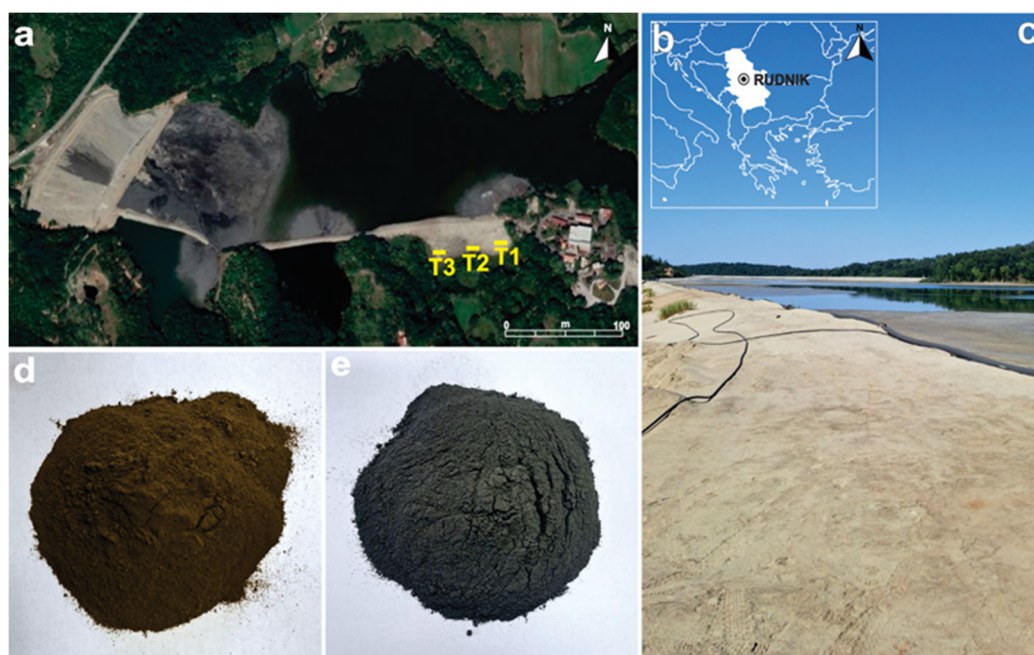


Figure 1. (a) Satellite image of the Rudnik mine flotation tailings showing the positions of sampled trenches (T1, T2, T3), source: Google Maps [15]. (b) Location of the Rudnik flotation tailings in the Republic of Serbia, SE Europe. (c) Field photograph of the mine flotation tailings site. (d) Sample brown-colored flotation tailings. (e) Sample grey-colored flotation tailings.

The present study provides the first comprehensive dataset on the mineralogical, geochemical, and magnetic susceptibility properties of flotation tailings samples from the Rudnik mine, thereby strengthening the knowledge base required for sustainable management and potential valorisation of tailings as secondary raw material sources in future.

2. Materials and Methods

2.1. Sampling

Samples were obtained from three vertical trenches excavated within the tailings body, which occupies the bed of a former dry creek (Figure 1a). In total, 16 samples (designated RW1–RW16) were collected (Table 1). Trench T1 was sampled at 0.5 m intervals, whereas trenches T2 and T3 were sampled at 1 m intervals to evaluate vertical heterogeneity within the flotation tailings material. All samples were quartered: one quarter was stored in bags as a reference, while the opposite quarter was used for mineralogical analyses. The remaining two quarters from each trench were homogenised to produce composite samples that represent the vertical profiles. These composites were subsequently subdivided and prepared for further geochemical analyses and mass magnetic susceptibility measurements.

Table 1. Details of flotation tailings samples, including trench, sample designation, depth, and material description.

Trench	Samples	Depth (m)	Material description
T1	RW1	0.0-0.5	Grey material
	RW2	0.5-1.0	
	RW3	1.0-1.5	
	RW4	1.5-2.0	Brown material
	RW5	2.0-2.5	
	RW6	2.5-3.0	
	RW7	3.0-3.5	Grey material, interbedded with Brown
	RW8	3.5-4.0	
	RW9	0.0-1.0	
T2	RW10	1.0-2.0	Grey material
	RW11	2.0-3.0	Brown material
	RW12	3.0-4.0	Grey material
	RW13	0.0-1.0	Grey material
T3	RW14	1.0-2.0	Brown material
	RW15	2.0-3.0	Brown material
	RW16	3.0-4.0	Grey material

2.2. X-Ray Diffraction (XRD)

X-ray diffraction analyses were done on a "PHILIPS" X-ray diffractometer, model PW-1710, with a curved graphite monochromator and a scintillation counter. The intensities of diffracted CuK α X-rays ($\lambda=1.54178\text{\AA}$) were measured at room temperature in intervals of $0.02^{\circ}2\theta$ and time of 1s in the range from 4 to $65^{\circ}2\theta$. The X-ray tube was operated at a voltage of 40 kV and a current of 30 mA, while the slits for directing the primary and diffracted beams were set to 1 mm and 0.1 mm, respectively.

2.3. Optical and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)

Optical analyses were performed at the University of Belgrade, Faculty of Mining and Geology, using a Zeiss Axio Imager 2 reflected light microscope, and at the Institute for Technology of Nuclear and Other Mineral Raw Materials (ITNMS), using a Carl Zeiss-Jena JENAPOL-U polarising microscope for both reflected and transmitted light. Samples were subsequently examined with a scanning electron microscope (SEM, JSM-6610LV, JEOL Inc., Tokyo, Japan) operated at 20 kV. Mineral identification was supported by energy-dispersive X-ray spectrometry (EDS, Xplore 30, Oxford Instruments, UK), with a detection limit of approximately 0.1 wt% based on internal

standards. Backscattered electron (BSE) micrographs were used to evaluate mineral homogeneity and identify potential zoning features.

2.4. X-Ray Fluorescence (XRF)

The chemical composition of the selected samples were performed using the SPECTRO Xepos C energy dispersive X-ray fluorescence (ED-XRF) spectrometer, with an air-cooled X-ray tube with a thick Pd/Co binary alloy anode operating at 50kV voltage and at tube power of 50W. The analyses were performed on fine-grained powder samples of 5g.

2.5. Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the fine-grained powder materials were recorded using a Perkin Elmer Spectrum Two equipped with the Universal ATR accessory. The spectrum of each powder sample was recorded in the mid-infrared range 1600–400 cm^{-1} with 20 scans and a spectral resolution of 4 cm^{-1} .

2.4. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Selected trace elements (Cu, Pb, Zn, Co, Ni, Mn, Cr, Ba, As, Bi, and Ag) were analysed with a PERKIN-ELMER AVIO 200 ICP-OES. Plasma was generated by argon combustion in an oxygen stream, and a full-wavelength field detector simultaneously measured spectral ranges around the lines of interest. Sample digestion and preparation were carried out using an acid mixture ($\text{HNO}_3:\text{HCl} = 3:1$). The detection limit of the AVIO 200 ICP-OES is in the $\mu\text{g/L}$ (ppb) range, typically 0.1–100 $\mu\text{g/L}$ depending on the element. Standard reference material OREAS 135 was used for calibration and quality control (<https://www.oreas.com/crm/oreas-135/>).

2.5. Laboratory Measurement of Magnetic Susceptibility (MS)

Magnetic susceptibility was measured at room temperature ($\sim 20^\circ\text{C}$) under a low magnetic field of 400 A/m using an MFK-1A Kappabridge (AGICO Instruments, Brno, Czech Republic) with a sensitivity of 2×10^{-8} SI. Volume magnetic susceptibility was determined on dry samples of fixed volume (20 cm^3). Sample mass was measured with a Radwag AS 220 R2 Plus analytical balance, accurate to four decimal places, to calculate mass magnetic susceptibility. Each sample was measured five times, and the mean value was used for further analysis. Before measurements, the magnetic susceptibility of the plastic bag and instrument holder was determined and used to correct the final values.

3. Results

3.1. Mineralogy

3.1.1. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) analysis of flotation tailings samples (RW1–RW16) reveals a consistent and complex mineral assemblage predominantly composed of silicate, carbonate, sulfate, and sulfide minerals (Figure 2, Table 2). Quartz and calcite are the most abundant phases across all samples. Sulfide minerals, including pyrite, sphalerite, chalcopyrite, galena, pyrrhotite, and arsenopyrite, accompany them. Accessory minerals such as chlorite, dolomite, and gypsum were also identified, while minor diffraction peaks suggest the presence of additional gangue minerals, including kaolinite or related clays, plagioclase, orthoclase, muscovite, anatase, and goethite.

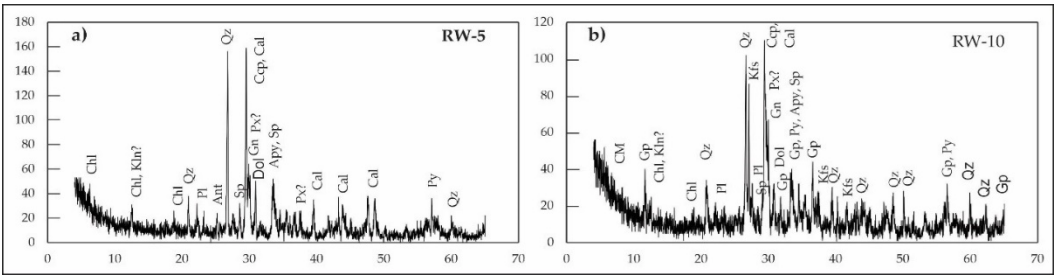


Figure 2. Representative XRD diffractograms of flotation tailings samples from the Rudnik mine: (a) sample RW-5, (b) sample RW-10. Abbreviations [16]: Apy – arsenopyrite, Ccp – chalcopyrite, Gn – galena, Po – pyrrhotite, Py – pyrite, Qz – quartz, Sp – sphalerite, Kfs – K-feldspar, Ant – anatase, Gp – gypsum, Chl – chlorite, Kln – kaolinite, Pl – plagioclase, Cal – calcite, CM – clay mineral, Px – pyroxene.

Table 2. Minerals and their relative abundance in flotation tailings samples from the Rudnik mine. Mineral identification was based on optical microscopy, SEM-EDS, and XRD analyses. Abundance categories: Major – minerals consistently present as dominant or abundant phases across most samples. Moderate – minerals regularly observed in moderate quantities; detectable but not dominant. Minor – minerals present in trace to low quantities; observed only sporadically or in specific samples.

Group of minerals	Mineral	Rel. abundance	Confirmation method
Silicates, phosphates, carbonates, sulphates	Quartz	Major	XRD, Optical, SEM-EDS, FTIR
	Calcite	Major	XRD, Optical, SEM-EDS, FTIR
	Epidote	Moderate	SEM-EDS
	Ca-garnet (grossular–andradite)	Moderate	SEM-EDS
	Orthoclase (K-feldspar)	Moderate	XRD, SEM-EDS, FTIR
	Ca-clinopyroxene (diopside–hedenbergite)	Moderate	SEM-EDS
	Apatite	Minor	SEM-EDS
	Zircon	Minor	SEM-EDS
	Gypsum	Minor	XRD
	Chlorite	Minor	XRD
	Plagioclase	Minor	XRD
Sulfides and native elements	Pyrite	Major	XRD, Optical, SEM-EDS
	Arsenopyrite	Moderate	XRD, Optical, SEM-EDS
	Pyrrhotite	Moderate	XRD, Optical, SEM-EDS
	Sphalerite	Moderate	XRD, Optical, SEM-EDS
	Chalcopyrite	Moderate	XRD, Optical, SEM-EDS
	Galena	Moderate	XRD, Optical, SEM-EDS
	Native bismuth	Minor	Optical, SEM-EDS
	Native silver	Minor	Optical, SEM-EDS
	Native copper	Minor	Optical, SEM-EDS
Oxides and hydroxides (weathering minerals)	Pentlandite	Minor	Optical, SEM-EDS
	Hematite	Moderate	Optical, SEM-EDS
	Bismite	Minor	Optical, SEM-EDS
	Cerussite	Minor	Optical, SEM-EDS
	Malachite	Minor	Optical, SEM-EDS
	Anatase	Minor	XRD
	Goethite	Minor	XRD, SEM-EDS

3.1.2. FTIR Analysis

The Fourier transform infrared spectroscopy (FTIR) was used for profiling the mine tailing samples components. The component identification based on characteristic band vibrations in the fingerprint region of $1600\text{--}400\text{ cm}^{-1}$ is shown in Figure 3. In the fingerprint region, the most intensive broad complex band in the $1100\text{--}950\text{ cm}^{-1}$ range is assigned to the in-plane Si–O–Si stretching vibration in silicates. The bands at ca 1163, 1086 (shoulder), doublet 799 and 778, are assigned to stretching and banding vibrations in quartz. The strong and wide band at $1440\text{--}1420\text{ cm}^{-1}$ is assigned to carbonates. Specifically, bands 876 and 712 cm^{-1} are assigned to calcite. The intensities of quartz and carbonate bands suggest that those minerals are the most abundant, which is consistent with optical and XRD investigations. In addition, the bands belonging to feldspar and sulfates are also observed, the latter consistent with the gypsum identified by XRD.

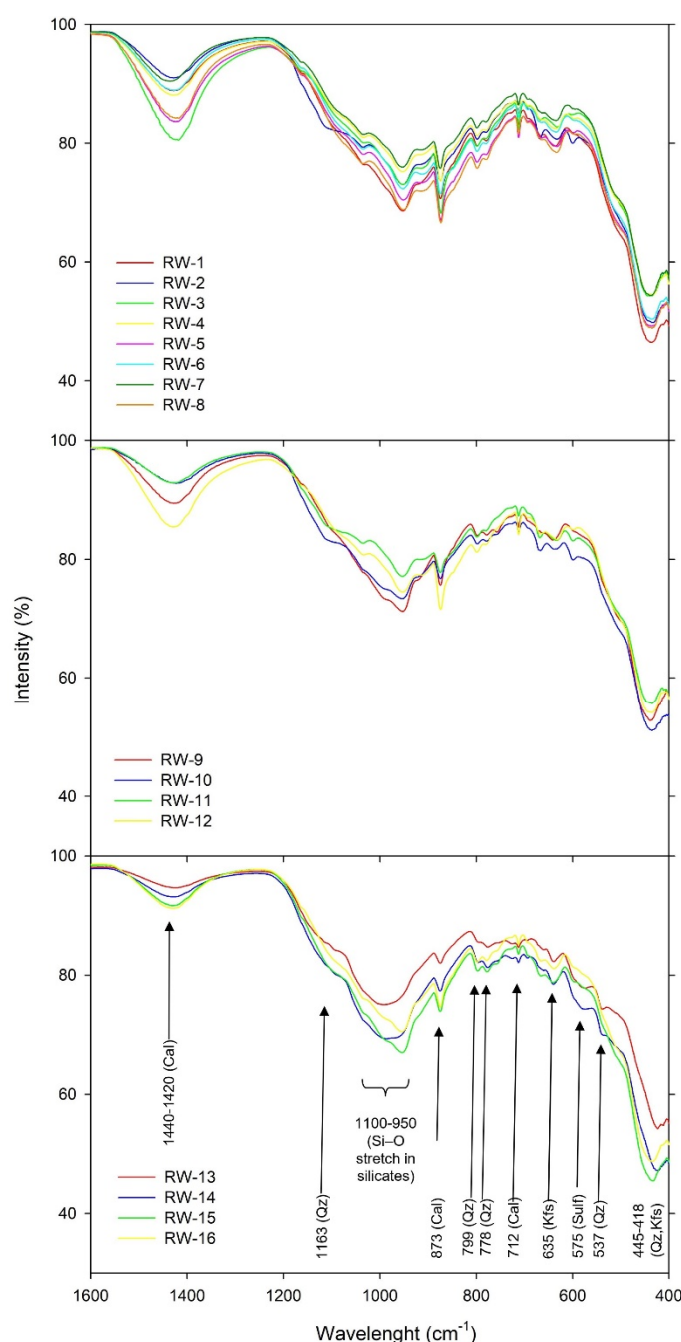


Figure 3. FTIR spectra in the fingerprint region ($1600\text{--}400\text{ cm}^{-1}$) of flotation tailing from the Rudnik mine. Abbreviations [16]: Cal — calcite, Kfs — K-feldspar, Qz — quartz, Sulf — sulfates.

3.1.3. Optical and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)

Optical and SEM-EDS analyses support the XRD results and provide additional insight into the textural and spatial relationships among the identified minerals (Table 2). The tailings comprise a heterogeneous mixture of sulfides, native elements, and secondary oxidation products, embedded within a matrix dominated by silicates and carbonates (Figure 4a). Most grains range in size from 200 to 400 μm . Sulfides and alteration products often appear as finer particles ($<100\ \mu\text{m}$), whereas silicates and carbonates tend to form coarser grains ($>500\ \mu\text{m}$).

Quartz is the most abundant, occurring as large, homogeneous, often euhedral grains that frequently exhibit well-developed intergrowths with sulfide minerals, particularly pyrite and sphalerite (Figure 4a, b).

Calcite, epidote, garnet, and orthoclase are also common, most frequently occurring as dispersed grains of various sizes, and less commonly as intergrowths on sulfide grains (Figure 4a, b). Ca-pyroxenes, diopside-hedenbergite, occur as subhedral to euhedral grains, though they are present only in minor quantities. Apatite and zircon appear as small, very rare, and dispersed grains.

Pyrite and arsenopyrite represent the most abundant sulfide minerals within the tailings, predominantly occurring as isolated grains and, to a lesser extent, as intergrowths with silicate phases (Figure 4c). Pyrite grains display considerable size variability, often reaching coarse dimensions up to 400 μm . These grains are homogeneous, with rare inclusions of chalcopyrite and galena, which appear as droplet-shaped inclusions up to 40 μm in length. Partial to complete oxidation of pyrite is frequent, with hematite commonly present as a secondary alteration mineral (Figure 4a, b). Arsenopyrite occurs as isolated, homogeneous, and unaltered grains of sizes comparable to pyrite (Figure 4c).

Pyrrhotite is less abundant relative to pyrite and arsenopyrite and occurs intergrown with galena, sphalerite, and chalcopyrite (Figure 4d). It occasionally contains flame- or vein-like pentlandite exsolutions less than 5 μm in length.

Among economically significant sulfides, sphalerite is the most prevalent. It occurs as individual grains that host chalcopyrite inclusions ranging from 10 to 40 μm and, less frequently, as simple intergrowths with other minerals, especially sulfides such as galena and chalcopyrite (Figure 4e). Sphalerite grains range from below 50 μm to 500 μm in size.

Galena is commonly observed in complex intergrowths with sphalerite, chalcopyrite, and various silicate, oxide, and carbonate minerals, while isolated grains are subordinate. Its grain size ranges from 50 to 250 μm . Sometimes, galena is associated with native bismuth, native silver, and bismite (Figure 4f, g). Secondary alteration along some grain boundaries is evidenced by the occurrence of cerussite (Figure 4h).

Chalcopyrite forms fine impregnations within sphalerite or as small inclusions and simple intergrowths with Fe-sulfides (Figure 4d, e). Grain sizes range from submicron to 100 μm . The chalcopyrite is rarely altered, although minor malachite coatings have been present on some grain surfaces.

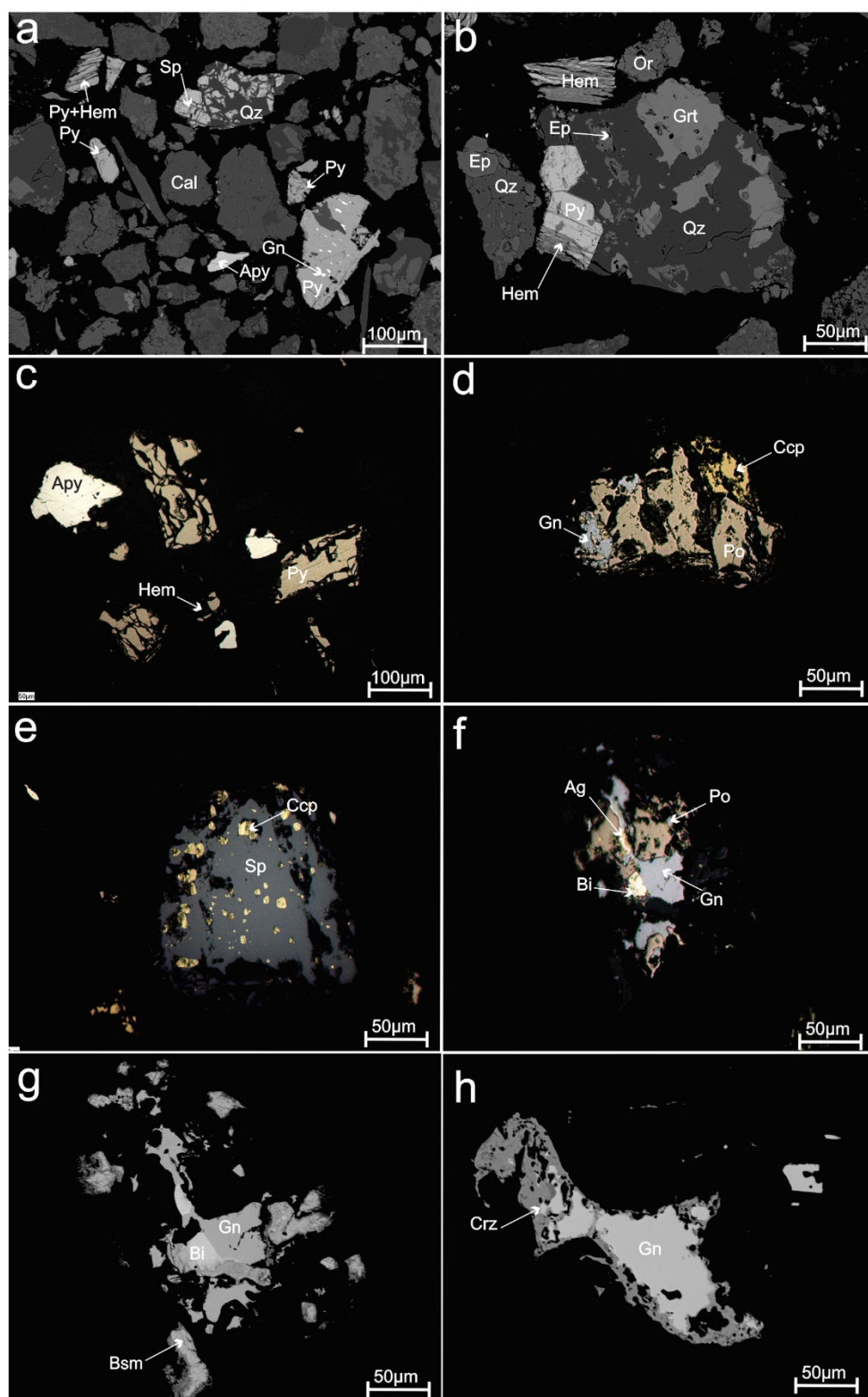


Figure 4. Photomicrographs (a–d: reflected light; e–h: backscattered electron images) of tailings from the Rudnik mine. a) Quartz and calcite grains associated with sulfides in the flotation tailings; b) quartz grain associated with garnet, pyrite, epidote, and hematite; c) pyrite and arsenopyrite grains; d) intergrowth of pyrrhotite, chalcopyrite, and galena; e) sphalerite grain with chalcopyrite inclusions; f) pyrrhotite with galena hosting inclusions of native silver and native bismuth; g) galena grain associated with native bismuth and bismite; h) galena grain partly altered to cerussite along the rim. Abbreviations [16]: Ag – native silver; Apy – arsenopyrite; Bi – native bismuth; Bsm – bismite; Ccp – chalcopyrite; Crz – cerussite; Ep – epidote; Gn – galena; Grt – garnet; Hem – hematite; Or – orthoclase; Po – pyrrhotite; Py – pyrite; Qz – quartz; Sp – sphalerite.

3.1. Geochemistry

3.1.1. X-Ray Fluorescence (XRF) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The most abundant oxide in all samples is SiO₂ (33.81–44.30 wt%; Table 3), followed by Fe₂O₃ (19.02–28.74 wt%) and Al₂O₃ (7.69–10.57 wt%). Sulfur (S) contents vary widely (2.20–12.30 wt%). Among metals, Zn shows the greatest enrichment (0.21–0.79 wt%), followed by Pb (0.14–0.32 wt%) and Cu (0.05–0.17 wt%). Manganese (Mn) is present in moderate amounts (0.104–0.189 wt%), whereas Cr is consistently low (≤ 0.036 wt%). Arsenic (As) displays a broad range (0.012–0.732 wt%). Nickel (Ni) (0.011–0.023 wt%) and Co (0.003–0.007 wt%) contents remain consistently low. Bismuth (Bi) is present in trace yet potentially significant amounts (0.002–0.013 wt%), while Ag content is lower (6 to 19 $\mu\text{g/g}$).

Table 3. Major oxide, sulfur, and metal contents, and mass magnetic susceptibility (MS) in flotation tailings samples from the Rudnik mine (oxide and sulfur contents determined by XRF; metals contents by ICP-OES).

Sample	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	S (%)	Cu (%)	Pb (%)	Zn (%)	Co (%)	Ni (%)	Mn (%)	Cr (%)	Ba (%)	As (%)	Bi (%)	Ag ($\mu\text{g/g}$)	MS [e-6 m ³ kg ⁻¹]
RW1	44.30	0.55	9.98	21.31	2.20	0.06	0.15	0.24	0.003	0.016	0.164	0.018	0.003	0.132	0.004	8	1.465
RW2	35.74	0.50	8.30	23.02	2.24	0.10	0.21	0.70	0.003	0.011	0.161	0.016	0.002	0.034	0.004	11	1.997
RW3	35.10	0.45	7.69	22.59	3.28	0.15	0.23	0.79	0.003	0.013	0.189	0.021	0.002	0.039	0.004	16	1.528
RW4	35.10	0.48	7.96	25.17	5.05	0.14	0.26	0.76	0.004	0.014	0.180	0.036	0.001	0.040	0.006	19	2.230
RW5	34.45	0.52	7.82	25.88	4.54	0.16	0.25	0.72	0.004	0.014	0.177	0.036	0.002	0.035	0.007	16	2.766
RW6	40.23	0.53	8.71	21.31	2.94	0.09	0.14	0.40	0.003	0.012	0.150	0.021	0.001	0.012	0.003	11	2.034
RW7	43.01	0.48	9.05	23.31	3.99	0.07	0.15	0.32	0.003	0.012	0.164	0.022	0.001	0.014	0.004	12	2.428
RW8	37.24	0.52	8.13	23.31	4.25	0.14	0.28	0.68	0.004	0.013	0.164	0.025	0.001	0.016	0.005	15	1.673
RW9	43.87	0.47	9.43	19.02	4.22	0.05	0.14	0.25	0.003	0.023	0.123	0.019	0.001	0.732	0.002	11	2.363
RW10	38.31	0.52	8.66	22.88	3.11	0.07	0.16	0.27	0.003	0.015	0.145	0.017	0.001	0.266	0.003	8	0.687
RW11	33.81	0.53	7.84	25.45	2.66	0.13	0.32	0.70	0.003	0.012	0.156	0.015	0.001	0.065	0.003	12	1.217
RW12	37.66	0.47	8.22	23.45	2.93	0.10	0.25	0.70	0.003	0.011	0.188	0.016	0.001	0.032	0.004	13	1.502
RW13	41.73	0.37	10.17	28.74	12.30	0.17	0.20	0.27	0.007	0.018	0.105	0.027	0.002	0.541	0.013	14	4.643
RW14	41.30	0.45	10.24	27.31	10.90	0.14	0.15	0.22	0.007	0.019	0.104	0.025	0.002	0.550	0.012	13	4.724
RW15	43.23	0.63	10.57	21.02	4.16	0.08	0.21	0.24	0.003	0.018	0.119	0.017	0.001	0.195	0.002	8	1.965
RW16	38.73	0.52	9.26	20.59	3.49	0.05	0.17	0.21	0.003	0.017	0.132	0.016	0.001	0.163	0.002	6	1.991
Avg.	38.98	0.51	8.95	23.68	4.53	0.11	0.20	0.47	0.004	0.014	0.151	0.022	0.001	0.179	0.004	12	2.201
SD	3.48	0.05	0.93	2.50	2.80	0.04	0.05	0.23	0.001	0.003	0.027	0.006	0.000	0.221	0.003	3.38	1.140

Pearson correlation analysis is performed to assess the relationships among oxides, elements, and magnetic susceptibility (MS) (Figure 5).

Strong positive correlations ($r \geq 0.7$) are between SiO₂ and Al₂O₃ ($r = 0.87$). Al₂O₃ is also positively correlated with Ni ($r = 0.71$), while Fe₂O₃ shows strong positive correlations with Cu ($r = 0.82$), Bi ($r = 0.87$), and Co ($r = 0.79$). Sulfur (S) is strongly correlated with Co ($r = 0.97$) and Bi ($r = 0.91$), while with Cu and Ag ($r = 0.81$), as well as Zn and Mn ($r = 0.79$), also show strong positive correlations. Ni is strongly correlated with As ($r = 0.89$), and Bi with Co ($r = 0.97$). Ag is positively correlated with Cr ($r = 0.77$) and Zn ($r = 0.71$).

Moderate positive correlations ($0.4 \leq r < 0.7$) are between SiO₂ and Ni ($r = 0.61$) and As ($r = 0.55$), Al₂O₃ and S ($r = 0.50$) and As ($r = 0.63$), Fe₂O₃ and S ($r = 0.71$) and Cr ($r = 0.55$), S and Cu ($r = 0.53$) and Cr ($r = 0.45$), Cu and Pb ($r = 0.61$) and Co ($r = 0.62$), Ni and SiO₂ ($r = 0.61$) and Al₂O₃ ($r = 0.71$), Co and Cr ($r = 0.49$), Cr and Cu ($r = 0.64$) and Fe₂O₃ ($r = 0.55$), Ag and Pb ($r = 0.54$) and Mn ($r = 0.43$).

Strong negative correlations ($r \leq -0.7$) are between SiO₂ and Zn ($r = -0.86$) and Pb ($r = -0.76$), Al₂O₃ and Zn ($r = -0.88$), Mn and Al₂O₃ ($r = -0.82$) and Ni ($r = -0.76$), and Zn and Ni ($r = -0.69$).

Moderate negative correlations ($-0.7 < r \leq -0.4$) are between TiO₂ and Fe₂O₃ ($r = -0.55$), S ($r = -0.63$), Co ($r = -0.61$), and Cu ($r = -0.46$), S and Mn ($r = -0.64$), Cu and Al₂O₃ ($r = -0.33$), as well as Ag and SiO₂ ($r = -0.51$), TiO₂ ($r = -0.50$), and Al₂O₃ ($r = -0.530$).

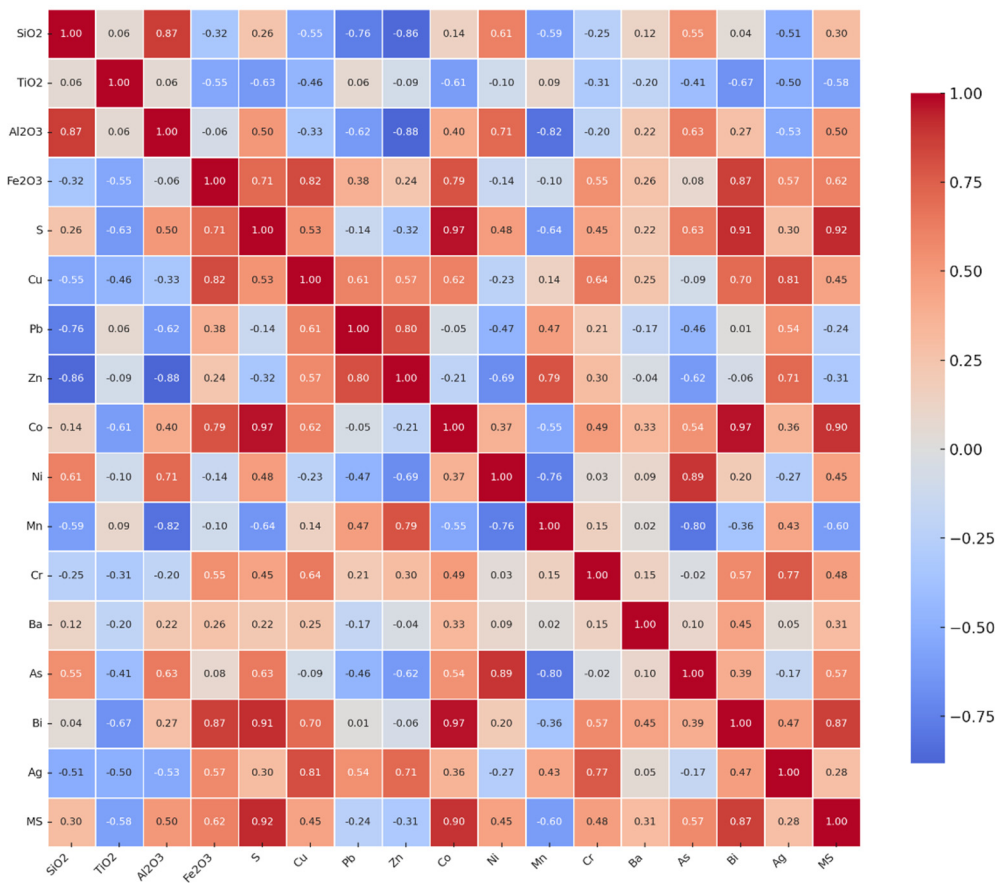


Figure 5. Correlation matrix of oxides, elements and magnetic susceptibility (MS) of flotation tailings samples from the Rudnik mine. The colorbar on the right represents the values of the correlation coefficient (r) between pairs of variables (in this case, chemical elements, oxides and magnetic susceptibility).

2.5. Magnetic Susceptibility

Mass magnetic susceptibility (MS) values of the flotation tailings samples exhibit considerable variability, ranging from $0.687 \times 10^{-6} \text{ m}^3\cdot\text{kg}^{-1}$ to $4.724 \times 10^{-6} \text{ m}^3\cdot\text{kg}^{-1}$, with an average value of $2.201 \times 10^{-6} \text{ m}^3\cdot\text{kg}^{-1}$ (Table 3). The highest values were recorded in samples RW13 and RW14, while the lowest were observed in RW10 and RW11. This variation reflects differences in the geochemical and mineralogical composition of the tailings, particularly the presence of iron-rich ferromagnetic minerals (*sensu lato*) that demonstrate affinity toward specific metals (Figure 5).

Strong positive correlations ($r \geq 0.7$) with MS have S ($r = 0.92$), Co ($r = 0.90$), Bi ($r = 0.87$), and Ag ($r = 0.87$). Moderate positive correlations have Fe₂O₃ ($r = 0.62$), As ($r = 0.57$), Cr ($r = 0.48$), Al₂O₃ ($r = 0.50$), Cu ($r = 0.45$), and Ni ($r = 0.45$). Moderate negative correlations are observed for Mn ($r = -0.60$) and TiO₂ ($r = -0.58$). Zn shows a weak negative correlation with MS ($r = -0.31$). Strong negative correlations ($r \leq -0.7$) with MS are not observed.

4. Discussion

The polymetallic ore from the Rudnik mine is characterised by complex microtextural intergrowths of gangue and ore minerals, which can adversely influence ore processing efficiency [17,18]. In the flotation tailings, the dominant gangue minerals are quartz and calcite, accompanied by epidote, andradite, and diopside, reflecting the skarn-type mineralogy of the primary ore [13,19]. These gangue minerals are commonly intergrown with sulfides, forming fine-grained sulfide phases that are either embedded within or dispersed throughout a predominantly silicate–carbonate matrix. Among sulfides, pyrite, arsenopyrite, and pyrrhotite are dominant, followed by economically valuable sphalerite, galena, and chalcopyrite.

Post-depositional oxidative alteration is mostly pronounced near the surface, where atmospheric exposure promotes the oxidation of sulfides. Comparable alteration features are also observed at several depths within the tailings, mainly in material previously exposed at the surface and later buried by younger tailing material. Pyrite is particularly susceptible, frequently replaced by hematite along grain boundaries or via pseudomorphosis, illustrating natural weathering processes [20]. Galena and chalcopyrite are likewise transformed, forming cerussite and malachite, respectively, whereas other sulfides remain relatively unaltered, resulting in heterogeneous oxidation patterns throughout the tailings. In comparison with nearby sites, oxidation in the Rudnik flotation tailings appears relatively limited [21].

Geochemical data corroborates these mineralogical and petrographic observations. Elevated SiO_2 and Al_2O_3 contents confirm the prevalence of silicate and aluminosilicate gangue minerals, while increased Fe_2O_3 and S concentrations indicate a significant abundance of iron sulfides such as pyrite and pyrrhotite. Sulfur concentrations vary considerably (2.20–12.30 wt%), reflecting vertical heterogeneity in sulfide distribution (Figure 6). Base metal contents—Zn (up to 0.79 wt%), Pb (up to 0.32 wt%), and Cu (up to 0.17 wt%)—provide further evidence of inefficiencies in historical ore processing. Although present in low concentrations, trace elements such as Ag and Bi may still hold economic significance for potential future recovery.

The sulfur content along the vertical profile of the T2 and T3 trenches indicates its decrease with depth, which further indicates the progressive decomposition of sulfide minerals with time (i.e. depth) and the migration of liberated sulfur in the form of sulfate via pore waters within the tailings body.

Correlation analysis provides additional insights into the geochemical controls of the tailings. The strong positive correlation between SiO_2 and Al_2O_3 ($r = 0.87$) is typical of aluminosilicate minerals (feldspars, clay minerals), which, together with quartz, dominate the gangue matrix. Conversely, significant positive correlations between Fe_2O_3 and Cu, Bi, Co, as well as between S and Co, Bi, highlight the controlling role of sulfide phases—chiefly pyrite, pyrrhotite, and arsenopyrite—in the geochemical behaviour of these elements [22]. Correlations such as Cu–Ag, Zn–Mn, and Ni–As further reflect well-documented mineralogical linkages, including chalcopyrite with Ag, sphalerite with Mn, and arsenopyrite with Ni and As [23,24]. The exceptionally strong correlation between Bi and Co ($r = 0.97$) suggests a close association within Fe-sulfide phases, with possible implications for the recovery of critical metals [25]. Negative correlations between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and Zn/Pb highlight the contrast between the silicate–carbonate matrix, which is poor in metals, and the sulfide phases, which serve as the primary hosts of base metals. Similarly, negative associations between Mn and $\text{Al}_2\text{O}_3/\text{Ni}$ indicate that manganese is linked to carbonate and oxide minerals, whereas Ni is predominantly controlled by the presence of sulfides.

Magnetic susceptibility (MS) data further reinforce these geochemical patterns. Strong positive correlations between MS and S, Co, Bi, and Ag demonstrate that sulfides and their alteration products (hematite, goethite) are the principal carriers of the magnetic signal [26]. The highest MS values were measured in Fe-sulfide-rich samples (RW13, RW14), whereas samples dominated by the silicate–carbonate matrix yielded much lower values (Figure 6). Negative correlations with Mn and TiO_2 suggest that oxide and carbonate phases reduce the overall magnetic response.

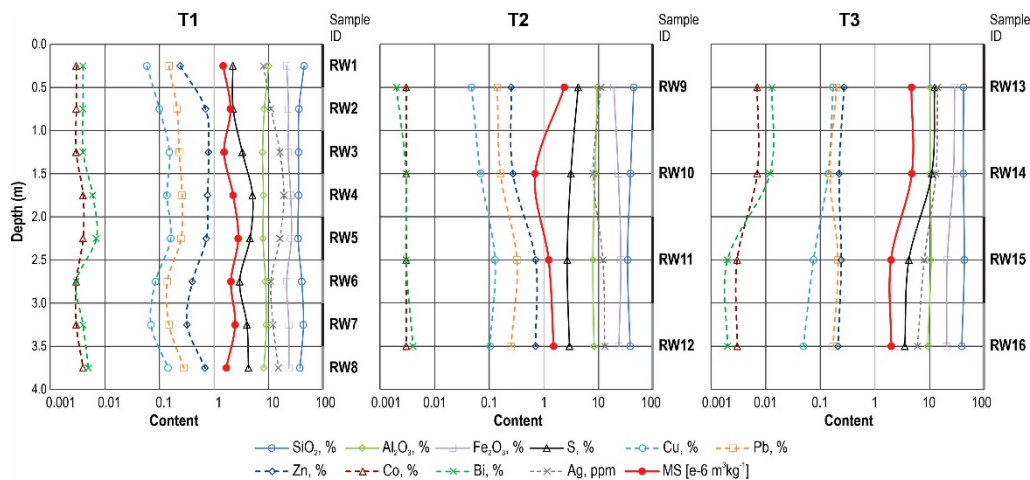


Figure 6. Distribution of major oxides and trace elements, and magnetic susceptibility (MS) in flotation tailings samples from the Rudnik mine.

5. Conclusions

The flotation tailings of the Rudnik mine exhibit mineralogical and geochemical characteristics that reflect the complexity of the primary ore, the efficiency of mineral liberation and phase selectivity during flotation, as well as post-depositional alterations, including sulfide oxidation and secondary mineral formation. Key findings include:

- Complex mineral associations and microtextural intergrowths of rock-forming minerals with sulfides hinder efficient flotation, resulting in fine-grained sulfides within the flotation tailings.
- Flotation tailings are dominated by quartz and calcite, accompanied by epidote, andradite, and diopside. Economically valuable sulfides, including sphalerite, galena, and chalcopyrite, are mostly finer than 400 μm and occur as intergrowths or as free grains within the flotation tailings.
- Post-depositional oxidation is moderately developed; pyrite is often replaced by hematite, galena by cerussite, and chalcopyrite by malachite, while other sulfides remain relatively unaltered.
- High SiO_2 and Al_2O_3 confirm the dominance of silicate and aluminosilicate gangue, whereas elevated Fe_2O_3 and S reflect the presence of iron sulfides. Zn, Pb, and Cu concentrations are below 1%, while minor elements such as Ag and Bi, although present at low levels, may hold future economic potential.
- Mass magnetic susceptibility supports the mineralogical observations: samples with higher Fe_2O_3 and S show elevated susceptibility, whereas samples with lower Fe_2O_3 exhibit reduced susceptibility, consistent with XRD and SEM-EDS analyses.

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