

The valorization of flotation tailings in terms of the concept of the circular economy: characterization, environmental risk assessment, and waste utilization routes

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Abstract: Flotation tailings originating from copper ore processing were evaluated in terms of chemical and mineralogical features, leaching, and resource potential. The results demonstrated that flotation tailings show varying degrees of the leachability of elements when exposed to different pH conditions (2–13); the Zn, Cu and Co leachabilities decrease as pH increases, whereas Mo, Ag and Sb revealed U-shaped leaching trend as a function of pH. Flotation tailings were found to be fairly reactive when exposed to water leaching and rainfall conditions. The environmental risk analysis demonstrated Zn to be the most susceptible element to liberation from the flotation tailings studied. Recovery tests demonstrated sulfuric acid to be slightly more efficient extracting agent as compared to citric acid. Hybrid approach to metal recovery was rather unsuitable for studied tailings due to lower extraction yield (not exceeding 20%) as compared to chemical treatment (not exceeding 40%).

Keywords: flotation tailings, recovery, extraction, waste management

INTRODUCTION

Production of goods beneficial for the development of society is strongly dependent on the supply of raw materials (Achzet & Helbig 2013). Among them, metals are inevitably a part of technological progress and demand (Tilton 2015). All electric and electronic products indispensable for life contain metals and therefore their production is not expected to drop, but current forecasts rather highlight an increase in the sector of metal production. Unfortunately, everyday users of all metal containing goods tend not to think

about the environmental consequences associated with its production. It is extremely important to keep in mind that metal production is linked to the generation of waste and emissions, therefore the use of metal made products and their replacement with new goods in households should be done with common sense and reason (Mitlin 1992). Pyrometallurgical metal production generates waste including slag, ashes, mattes and flotation tailings (Kamradt et al. 2018, Bakalarz 2019, Piatak & Ettler 2021). Researchers dealing with the environmental impact assessment of flotation tailings disposal have already raised the issue of

the potentially hazardous character of such wastes and recommended their appropriate landfilling (Yilmaz 2011, Baran et al. 2013, Edraki et al. 2014).

In Poland, flotation tailings are a result of the treatment of sediment-hosted strata-bound copper deposits, associated with Kupferschiefer formations that also host deposits of other metals, such as Ag (Kucha 2007, Borg et al. 2012). Every year, ca. 30 million tons of copper ore are exploited and processed into copper concentrate (containing also metals such as Ag, Au, Ni, Se, Pb) using froth flotation (Bakalarz 2021). This process leaves huge amounts of waste behind – an average of 28 million tons of tailings every year (Kotarska 2012, Bakalarz 2021). Since the flotation process is neither 100% selective nor fully efficient, some metals are left in the tailings, which allows them to be classified as anthropogenic deposits of metals (Chmielewski et al. 2010). Some of the metals present in the orebody, such as Co, Mo, REE, V (among others) are not recovered during processing, and end up in the flotation tailings and slag (Kamradt et al. 2018, Bakalarz 2019, Mikoda et al. 2019).

The increasingly large volumes of flotation tailings being produced, combined with the rapid growth of industrialization worldwide, raises a number of concerns about the decreasing availability of sites suitable for landfills and, as a result, waste disposal costs and environmental concerns are increasing (Hellweg et al. 2005, Baran et al. 2013). The limited space available for disposal and mounting evidence on the adverse environmental impacts of tailings have resulted in increased urgency in environmental risk assessment. Although any waste landfilling is at present the least suitable management option, a vast amount of material is present at numerous disposal sites worldwide (Lottermoser 2011, Lekovski et al. 2013, Shengo 2021). What is important is that such disposal leads to the tailings being exposed to a wide variety of chemical and biological factors including e.g., pH and Eh variations, the presence of inorganic and organic acids, and the activity of microbial communities collectively defined as “bioweathering” (Gadd 2010). Metal-bearing tailings with long-term exposure to bioweathering may undergo dissolution and subsequently may lead to elevated concentrations of potentially toxic metals being released into the immediate surroundings. The environmentally persistent metal contaminants may find their way

into living organisms, causing various toxicological effects (Norwood et al. 2003, Baran et al. 2013). Furthermore, it is important to note that the composition of tailings may be unique between the producers, therefore studies dedicated to environmental risk assessment should consider specific residues individually.

An additional concern related to the metallurgical industry is the problem of the depletion of natural resources. However, a deeper consideration of this problem shows that real estimates would be more optimistic provided that secondary resources are taken into account in the calculation of resources (Arndt et al. 2017). Industrial wastes end their life cycle while they could be effectively used as processing products. In this regard, current research focuses on the investigation of treatment methods that could be applied for the recovery of residual metals contained in wastes. Launching a large-scale recovery reactors dedicated for industrial wastes is currently still under development, but steps in research made towards optimization of conditions as well as the comparison of specific treatments for solids exhibiting various characteristics are important to address knowledge gaps in this newly and intensively developing research area (Gümüşsoy et al. 2023). Romero-García et al. (2019) employed a combined approach to recover metals from flotation tailings; the recovery yield of 80–90% (Cu and Zn) was achieved, whereas Pb and Ag extraction reached over 96%. As the result of this process, the quartz-bearing residue with notable gold concentration was generated rendering it more suitable for further Au recovery process (Romero-García et al. 2019). Likewise, Lorenzo-Tallafigo et al. (2022) implemented (bio)hydrometallurgical approach consisting of several leaching steps leading to a recovery yield of up to 96%. The leaching approach using sulfuric acid as lixiviant enabled the recovery of up to 70% of Cu while simultaneously maintaining Fe recovery at the level of 3% (Antonijević et al. 2008).

This study was undertaken to explore the reactivity of flotation tailings in the environmental context as well as to assess their recovery potential. A combined geochemical approach including chemical and mineralogical characterization, solid reactivity and its susceptibility to releasing metals as well as metal recovery potential was undertaken.

MATERIALS AND METHODS

Preparation of reagents and waste samples

Four different tailing samples were taken from three copper ore processing plants, where concentrates of three different types of ores (carbonate, sandstone and shale) are prepared by froth flotation. Samples were named as follows: OL (the tailings from the flotation of the feed with the biggest share of shale fraction), OP (tailing from the concentrate with the biggest share of dolomite ore), OR1 and OR2 (tailings from sandstone ore concentrate). The samples of tailings were received in the form of water-suspended dust from the pipeline systems used to transport the pulp to the tailing pond. The suspension was dried at 75°C for 48 hours in order to receive laboratory samples for further analyses. The temperature of 75°C was set to avoid the decomposition of the gypsum present in tailings to other calcium sulfate components, such as bassanite, which is a gypsum decomposition product at 98°C (Allen & Kramer 1953). The small grain size of the samples (<500 µm) meant that comminution operations (e.g. milling) were not needed for the experiments.

Tailings characterization

A set of standard methods used to determine mineralogical and chemical composition of solid samples was implemented. The bulk chemical composition of tailings was determined using the ICP-OES method after lithium borate/tetraborate fusion and the digestion of the melt with HNO₃ in the Bureau Veritas laboratory (Vancouver, Canada). The total C and S content was determined by LECO combustion. The LOI (loss on ignition) was determined by sample sintering at 1000°C (both procedures conducted by Bureau Veritas).

The phase composition of the powder samples was performed using X-Ray diffractometry (XRD) using a Rigaku MiniFlex 600 apparatus (with a scintillation counter equipped with a lithium iodide detector, Rigaku, Japan) with the following operation parameters: Cu-K α radiation, 3–75° 2 θ range, 0.05° counting step. The data obtained with the XRD were processed using XRAYAN software coupled with a PDF-4 database.

The mineralogical analysis of samples was carried out using reflected light microscopy with

a Nikon Eclipse LV100 microscope (Nikon, Japan). The samples were embedded in resin in 1-inch diameter rings, and subsequently polished using diamond paste (oil was used as a lubricant). The areas selected by reflected light observations were examined with a scanning electron microscope with energy-dispersive spectroscopy (SEM-EDS). The device used in this study was a FEI Quanta 200 FEG coupled with an EDAX spectrometer (FEI, USA). The following fixed parameters were used in the analysis: low vacuum mode, 20 kV accelerating voltage, 10 nA beam current, 50 s counting time, 34° take-off angle.

The pH of tailing samples (hereafter called paste pH) was determined using the EPA 9045D method, in which a liquid to solid ratio of 1:1 is applied to obtain a paste. The paste was stirred for 5 minutes and then the pH measurements were made.

Environmental assessment of tailing materials

The reagents used in the study were purchased from Chempur, Poland, and were of analytical grade. The water used in this study was ultrapure water (Millipore Milli-Q). Stock solutions of reagents were prepared by dissolving a given reagent in ultrapure water to obtain a solution of the desired molar concentration.

The metal release from flotation tailings was assessed via three different standardized static leaching protocols including USGS field leaching test, the distilled water extraction and the EPA 1312 synthetic precipitation leaching procedure. The results of leaching tests were compared to the Polish law regulation on substances particularly harmful to the aquatic environment and conditions to be met when discharging sewage into waters or into the ground, as well as when discharging rainwater or snowmelt into water or into water facilities (*Rozporządzenie...* 2019) to determine the impact of land-filled material on the surrounding environment.

The USGS field test is a quick procedure designed to perform material evaluation in the field, at low cost, and without the disturbance of the sample caused by mechanical or chemical processing (Hageman & Briggs 2000). This test has been proven to supply well correlated results with lab tests, e.g. EPA 1312. In this test, samples of 5 g

of each waste were mixed with 100 mL of distilled water (liquid-solid ratio of 20:1) in PET bottles. After closing each bottle, the mixture was shaken manually for 5 minutes.

The distilled water extraction was based on the EN 12457-2:2002 standard (CEN 2002). In this procedure, the liquid-solid ratio was 10:1 (100 mL of distilled water and 10 g of each sample). The experiment was also performed in closed PET bottles placed on an orbital shaker, set at 100 rpm, for 24 hours.

The EPA 1312 procedure was designed to simulate the impact of rainfall on the landfilled waste material (Lackovic et al. 1997, Hageman et al. 2015). The experiment was performed in closed PET bottles, where the portion of 5 g of each sample and 100 mL of extraction liquid (distilled water acidified to pH 4.2 ± 0.05 with the mixture of sulfuric and nitric acid at 3:2 mass ratio) was shaken in an orbital shaker set at 100 rpm for 18 hours.

The leaching tests were performed according to the standard protocol (U.S. EPA 2012) in the pH range of 2–13. For selected flotation tailing, a different quantity of water-diluted acid (2M HNO₃) and base (1M KOH) were prepared depending on the amount required to reach the desired pH values. The experiments were carried out with a liquid to solid ratio of 10 using 5 g of flotation tailing and 50 mL of solution at a rotation speed of 150 rpm during 24 h.

The eluents after all procedures were treated in the same manner. After shaking (either manual or automatic) the mixtures were left for 15 minutes to allow particles to settle. Subsequently, the samples of supernatants (15 mL) were taken by syringes, filtered using syringe filters (0.45 µm, Pureland®)

and acidified with 0.1 mL of Suprapur 65 wt.% HNO₃ (Merck). Samples were stored at 4°C until the ICP-MS analysis.

Recovery experiments

Flotation tailing (OL) was subjected to extraction with mineral (H₂SO₄ and biologically produced H₂SO₄), and organic acids (citric acid). The first set of leaching experiments was carried out with H₂SO₄ at different acid concentrations (0.1 mol·L⁻¹, 0.5 mol·L⁻¹, and 1 mol·L⁻¹), pulp density 1% (PD 1%) and extraction time 24 h. In addition, various pulp densities (1%, 5% and 10%) were applied to study its effect on extraction efficiency with normality equivalent (2N) citric and sulfuric acids. The leaching solutions were prepared by dissolving the appropriate amount of stock solution (95 wt.% H₂SO₄ analytical grade, citric acid analytical grade, Merck) in 1 L of ultrapure water. The waste fraction used for the screening experiments was <200 µm. The experiments were performed in a polypropylene flask placed in a horizontal shaker (150 rpm). All leaching experiments were carried out in duplicate. The leachates were filtered using 0.45 µm polytetrafluoroethylene syringe filters, acidified using 2% volume Suprapur 65 wt.% HNO₃ (Merck) and stored at 4°C until the ICP-MS analysis.

Forms of metal occurrence in tailing samples

The fractionation of metals in examined samples of tailings was determined via a three-step sequential extraction procedure (BCR), followed by a fourth step – acid-soluble residual fraction (Pueyo et al. 2008). The subsequent steps of the extraction are described and presented in Table 1.

Table 1

Parameters of sequential extraction with targeted fractions according to BCR procedure followed by the fourth step (Pueyo et al. 2008)

Step	Chemical agent	pH	SSR	Conditions	Time [h]	Fraction
I	40 cm ³ 1M C ₂ H ₄ O ₂	3	1:40	shaking (RT)	16	exchangeable (F1)
II	40 cm ³ 0.1M [NH ₃ OH]Cl	2	1:40	shaking (RT)	16	reducible (F2)
IIIa	2 × 10 cm ³ 30% H ₂ O ₂	ns	1:10	heating (85°C)	2 × 1	oxidizable (F3)
IIIb	50 cm ³ 1M C ₂ H ₇ NO ₂	2	1:50	shaking (to complete the reaction)	16	oxidizable (F3)
IV	10 cm ³ aqua regia	ns	1:10	digestion (130°C)	2	residual (F4)

RT – room temperature, SSR – sample-to-solvent ratio, ns – not specified.

In general, 1 g samples of tailings were mixed with the following amounts of reagents: (I) 40 mL of glacial acetic acid (0.11M, pH 3) for the determination of the exchangeable fraction; (II) 40 mL of 0.11M hydroxylamine hydrochloride (with pH adjusted to 2) for the determination of the reducible fraction; (III) boiling 2 times in 10 cm³ of 30% H₂O₂ followed by 50 mL of ammonium acetate (1M, pH adjusted to 2) for the determination of the oxidizable fraction; (IV) 10 cm³ of aqua regia for the determination of the fraction bound to crystal lattice of the material. After each step, solid samples were rinsed with deionized water. The leachates were filtered through paper filters, acidified with 0.1 mL of 65% HNO₃ and stored at 4°C prior to analysis.

Environmental risk assessment

The selected results of sequential extraction experiments (for metals such as Al, Cu, Fe, Pb and Zn) served as the basis for calculations of indices that depict the environmental risk posed by the examined tailings. In this work, two risk indices were calculated: reduced partition index (I_R) and risk assessment code (RAC).

The reduced partition index (I_R) is often used to give an overview of the relative binding form of metals to the solid material (Miretzky et al. 2011). It is calculated from the formula:

$$I_R = \sum_{i=1}^k i^2 \frac{F_i}{k^2} \quad (1)$$

where i is the index number of the sequential extraction step, $k = 4$ (total steps in sequential extraction), and F_i is the percentage of a particular metal in fraction i . The values of I_R are between 0.06 and 1.00. The lower I_R value, the weaker the binding of a metal, which corresponds to higher mobility.

The RAC index is indirectly related to I_R (the higher the RAC, the lower the I_R) and reflects the mobility of metals (Gusiatin & Kulikowska 2014). It is defined by Equation (2):

$$\text{RAC} = \frac{C_m}{C_{\text{total}}} \times 100\% \quad (2)$$

where C_m is a metal concentration in exchangeable fraction and C_{total} is the total concentration of the given metal. Based on the F_i fraction, the RAC

can have values from 1% to 100%: <1% (no risk), 1% to 10% (low risk), 11% to 30% (medium risk), 31% to 50% (high risk), and >50% (very high risk) for a given metal.

Environmental analysis

The net acid generation (NAG) test that was developed for assessment of ARD generation potential of landfilled materials and closed mine operations (Stewart et al. 2006, Räisänen et al. 2010). The test involved a single addition of 250 mL of 15% H₂O₂ to 2.5 g portions of pulverized (<75 µm) samples (solid to liquid ratio = 1:100). The mixture was left to react overnight. After the reaction, the whole sample was heated to a gentle simmer (to remove excess H₂O₂) and subsequently the pH was measured (NAGpH). The next step was the titration of samples with 0.1 N NaOH to achieve pH values of 4.5 and 7.0. The amount of NaOH used is then used for calculations of acid generation potential (in kilograms H₂SO₄ per ton of tailing). The second parameter related to the presence of sulfur in the sample is the maximum potential acidity (MPA). This is used for samples with a total sulfur concentration greater than 0.3 mass%. This parameter is calculated with the simple formula:

$$\text{MPA} = \%S \times 30.6 \quad (3)$$

where MPA – max. potential acidity [kg H₂SO₄/t], %S – total sulfur concentration in the sample [mass%].

The other illustration of environmental risk is the Ficklin diagram that is often used in the geochemical assessment of different mine wastes (Gomes & Valente 2024). The basis for plotting this diagram is the water-soluble amount of metals such as Cd, Co, Cu, Ni, Pb and Zn. Therefore, the measured concentrations of these elements in water leachates (procedure described in section *Environmental assessment of tailing materials*) were plotted against the pH values of tailing samples.

Analysis of liquid samples

The liquid samples after the experiments were analyzed for metal ions using inductively coupled plasma mass spectrometry (ICP-MS; Thermo

Scientific iCAP RQ(C2) device) according to the ISO 17294-2:2016 protocol (ISO 2016). The apparatus was calibrated using multielement ICP standards provided by Merck (Germany). The QA/QC was performed by analyzing blank and duplicate samples and duplicate analysis of randomly chosen samples. The limits of quantification for the specific elements were as follows [$\text{mg}\cdot\text{L}^{-1}$]: Al – 0.005, Cd – 0.0003, Co – 0.0002, Cu – 0.001, Fe – 0.02, Ni – 0.001, Pb – 0.0001, Zn – 0.001.

The results from the liquid samples were processed using MS Excel 2016 software. The geoenvironmental data were also obtained from calculations in MS Excel 2016. The graphs were prepared from the Excel files using Grapher 17 software.

Concentrations of elements (Ag, Al, As, Bi, Ca, Cd, Ce, Co, Cu, Fe, Pb, Sb, V, Mo, Zn, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in the leachates resulting from pH-dep and recovery experiments were determined by inductively coupled plasma mass spectrometry (ICP-QQQ-MS 8800 Triple Quad, Agilent Technologies, Japan). This instrument is equipped with a MicroMist nebulizer and a Peltier-cooled (2°C) Scott-type spray chamber for sample introduction. This instrument contains an octopole-based collision/reaction cell, located in-between two quadrupole analyzers. It was operated in a gas mode, with O_2 flowing at 0.3 mL/min (30%) and He flow set at 5 mL/min. All parameters were manually optimized to provide the best signal intensity and stability. The Mass Hunter software for ICP-QQQ-MS (Agilent Technologies, Japan) was used to control the instrument and to process the data.

The determinations by ICP-QQQ-MS were performed using calibration curves obtained from the diluted stock of multi-element standard at 100 $\mu\text{g}/\text{mL}$ (VHG Labs, Manchester, USA). The reagents used were ultrapure, and the water was de-ionized to a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ in a Direct-Q[®] UV3 Ultrapure Water System apparatus (Millipore, France). The analytical quality control was verified by the analysis of certified reference materials, i.e. SRM no. 1643f, no. 2709a (National Institute of Standards and Technology, Gaithersburg, USA) and SPS-SW1 (Spectra pure Standards As, Oslo, Norway). High compliance with reference values was found.

RESULTS AND DISCUSSION

Mineralogy and geochemistry of tailings

The results of the phase characterization of flotation tailings are shown in Figure 1. The phases present in the tailings are quartz, carbonates (represented by calcite and dolomite), clay minerals (represented by mica and kaolinite) as well as some feldspars. The comparison of 4 XRD patterns of tailing samples are shown in Figure A1 (Appendix). The patterns show that the feed rock for the flotation process affects the volumetric proportion of the individual phases in the samples. The detected phases are visible on SEM images (Fig. 2). Beyond the main phases, which are somewhat indistinguishable on the SEM images, some phases such as framboidal pyrite (Fig. 2B) and other sulfides (galena, Cu-Fe sulfides; Fig. 2C, D) can be pointed out in the samples. These results are congruent with earlier studies (Duczmal-Czernikiewicz et al. 2012, Duczmal-Czernikiewicz & Suchan 2015, Pawlikowski & Bożęcki 2016). In general, the mineralogy of the tailings is similar to the orebody, but depleted in metal-bearing phases, which is due to flotation being applied before. The other components that could occur in the Kupferschiefer flotation tailings are gypsum, barite, strontianite, halite, as well as trace amounts of ore minerals, such as pyrite, marcasite, galena, chalcopyrite, among others such as bornite, covellite, enargite and sphalerite (Antonijević et al. 2008, Pawlikowski & Bożęcki 2016, Kamradt et al. 2018, Bakalarz 2019). Apart from the mineral composition of the tailings, the major difference is the grain size which is affected by comminution processes such as milling. The particle size of a material is a crucial factor that affects its specific surface area, consequently higher reactivity can be expected if grain size is reduced (Beckingham et al. 2016).

The phase composition is reflected by the chemical composition, shown in Table 2. The dominating components of the tailing samples are SiO_2 and CaO , which is directly related to the lithological properties of the feed ore which mostly contains sandstone, carbonates and shale in different proportions.

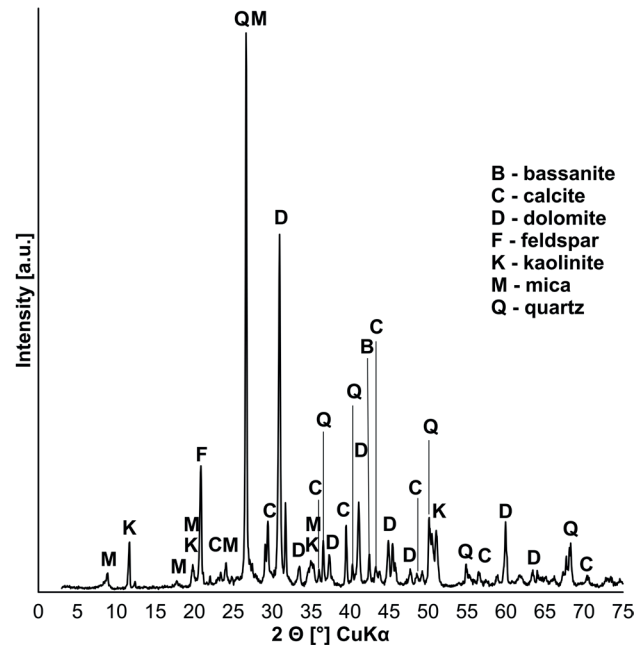


Fig. 1. XRD pattern of studied tailings

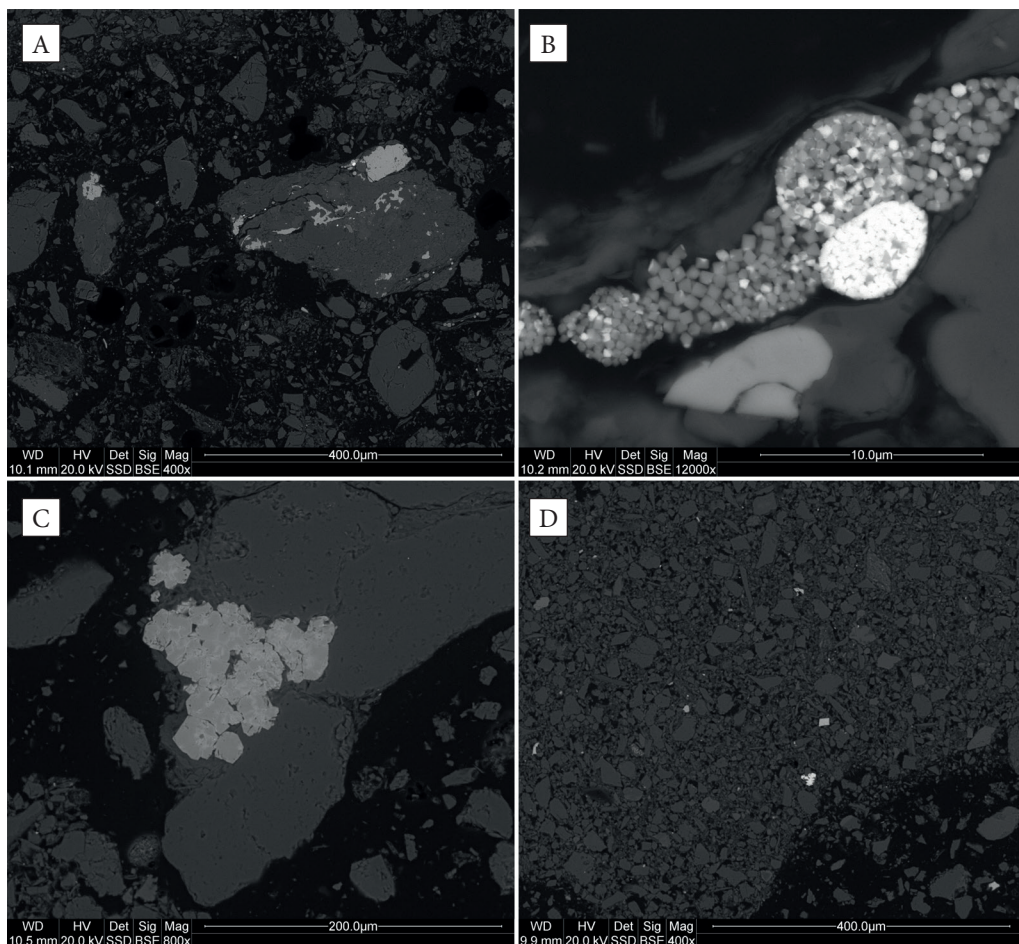


Fig. 2. SEM images of studied tailings: general overview of the sample (A), the specimen of framboidal pyrite (B), specimens of Cu-Fe sulfides (C) and overview with visible galena specimens (white) (D)

Table 2
Chemical composition of the studied tailings

Chemical components [wt.%]	Major elements				Chemical components [ppm]	Minor elements				Chemical components [ppm]	Rare earth elements			
	OP	OL	ORI	OR2		OP	OL	ORI	OR2		OP	OL	ORI	OR2
SiO ₂	25.8	50.1	50.0	53.2	Cu	1,551	1,311	1,267	1,505	Y	14.1	14.9	10.2	10.2
Al ₂ O ₃	6.69	7.61	4.22	5.19	Pb	280	919	393	339	La	17.2	15.3	12.1	11.3
Fe ₂ O ₃ *	1.32	1.38	1.11	1.00	Zn	31.0	126.0	64.0	51.0	Ce	32.4	28.5	22.8	20.7
MgO	9.53	5.35	6.89	5.59	Ni	14.90	35.40	10.90	9.70	Pr	4.18	3.96	2.85	2.77
CaO	22.7	12.3	14.4	13.2	As	11.1	120.0	13.5	15.5	Nd	16.5	16.7	12.0	11.3
Na ₂ O	0.70	0.87	0.70	0.91	Cd	0.20	0.70	0.30	0.20	Sm	3.35	4.15	2.45	2.63
K ₂ O	2.07	2.31	1.40	1.72	Sb	0.20	0.60	0.20	0.10	Eu	0.77	0.89	0.56	0.63
TiO ₂	0.30	0.25	0.20	0.19	Sn	2.00	1.00	1.00	<1.00	Gd	3.30	3.77	2.37	2.33
P ₂ O ₅	0.09	0.08	0.05	0.06	Bi	0.20	0.20	0.10	0.20	Tb	0.48	0.52	0.33	0.36
MnO	0.36	0.21	0.23	0.21	Ag	4.30	12.70	6.40	5.40	Dy	2.69	2.86	1.88	1.75
Cr ₂ O ₃	0.01	0.01	0.01	0.01	Au [ppb]	3.10	1.40	0.80	1.70	Ho	0.48	0.52	0.37	0.37
S total	0.76	0.41	0.96	1.23	Co	9.40	84.70	11.60	11.40	Er	1.38	1.45	0.99	1.02
LOI	29.8	18.9	20.2	18.1	Mo	7.80	28.50	8.60	9.60	Tm	0.18	0.19	0.15	0.15
					V	162.0	187.0	89.0	66.0	Yb	1.16	1.27	0.97	0.89
					W	1.30	1.10	0.90	0.90	Lu	0.18	0.18	0.13	0.14
					Sr	357	302	880	819	ΣREE	84.3	80.3	59.9	56.3
					Rb	85.2	82.1	52.6	57.4	ΣREE+Y	98.4	95.2	70.1	66.5

* total Fe

Explanations: OP – tailings from the concentrate with the biggest share of dolomite ore, OL – tailings from the flotation of the feed with the biggest share of shale fraction, ORI, OR2 – tailings from sandstone ore concentrate.

The OP sample is more abundant in carbonates and less in sandstone, which is reflected by high CaO and LOI, as well as higher MgO than other samples, whereas OL sample contains more shale, which is reflected in the high SiO₂, as well as highest content of Al₂O₃ and K₂O of all examined materials. The samples contain metals present in the orebody, such as Cu, Zn and Pb, as well as critical elements such as Co, V and REE (see Table 2). The composition of the examined flotation tailings is comparable to those described in literature. The research of Mikoda & Gruszecka-Kosowska (2018) shows that carbonate ore tailing can contain up to 45% of CaO (in the case of the OP sample from this study, CaO + LOI content is ca. 52%, which pretty much reflects carbonate content) and that it can also be rich in metals such as V (up to 395 ppm) (Mikoda & Gruszecka-Kosowska 2018). Several other studies have also characterized flotation tailings (Baran et al. 2013, Bakalarz 2019, Krawczyńska et al. 2020). The studied tailings are taken directly from the production chain. When deposited for longer, the proportions of constituents may vary, which can be caused by migration of some elements with infiltrating fluids (Duczmal-Czernikiewicz 2013, Kasowska et al. 2018).

Environmental risk posed by the disposal of tailings

Both leaching tests designed to replicate field conditions (field leaching test and SPLP) yielded results suggesting that all of the tailing samples are not prone to releasing metals both in quick water leaching of undisturbed samples, as well as in simulated rainfall conditions (Table A1 – Appendix). The amount of released metals was below the threshold limits present in Polish law (*Rozporządzenie...* 2019). In the case of the water leaching test, the results were virtually the same, meaning that the concentration of metals in leachates were below the permitted values. The only exception was Co leached from the OL sample, which exceeded the legal regulation value (Table A1 – Appendix) that was due to the initially higher content of this element in a bulk sample. Therefore, in the view of simulated field conditions that often reflect so-called worst-case scenarios, the tailings seem to be fairly inert for the surrounding environment which is in accordance with

several previous findings (Poling 1995, Drif et al. 2018). However, some studies have shown that tailing ponds contain more metals in the deeper parts of the deposits, which is proof of vertical metal migration to its lower layers (Duczmal-Czernikiewicz 2013, Kasowska et al. 2018).

The results of the sequential extraction of tailing samples are shown in Figure 3. The results show that the exchangeable fraction shares 10–21%, 6–10% and 23–36% of total Cu, Pb and Zn content, respectively. Most of the Cu, Pb and Zn are bound to sulfide and residual fractions, which is explicable since sulfides are the carriers of Cu, Pb and Zn in Kupferschiefer orebodies.

The fractionation of Cu, Pb and Zn in the tailing samples has been used to calculate the risk indices that have been found useful in environmental risk assessment (Miretzky et al. 2011, Pathak et al. 2014, Innocenzi et al. 2015, Mikoda et al. 2019). The indices calculated for tailing samples are shown in Table 3.

Table 3
Reduced partition indices (I_R) and risk assessment code (RAC) values of selected metals for different Kupferschiefer tailings samples

Indicator	Sample	Unit	Cu	Pb	Zn
I_R	OP	-	0.59	0.85	0.43
	OL		0.52	0.68	0.51
	OR1		0.51	0.75	0.39
	OR2		0.48	0.60	0.35
RAC	OP	%	14	7	31
	OL		21	8	23
	OR1		10	6	28
	OR2		16	10	36

The I_R indices calculated for tailing samples are lowest for Zn (0.35–0.51) and highest for Pb (0.60–0.85). These values correspond to the mobility of these metals expressed by exchangeable fraction, which showed that the biggest percentage of exchangeable fraction is given to Zn in all samples, whereas Pb holds the lowest exchangeable fraction among the analyzed metals. The RAC values calculated for tailings are in the following ranges: 6–10 for Pb, 10–21 for Cu and 23–36 for Zn, that are directly corresponding to exchangeable fractions of these metals.

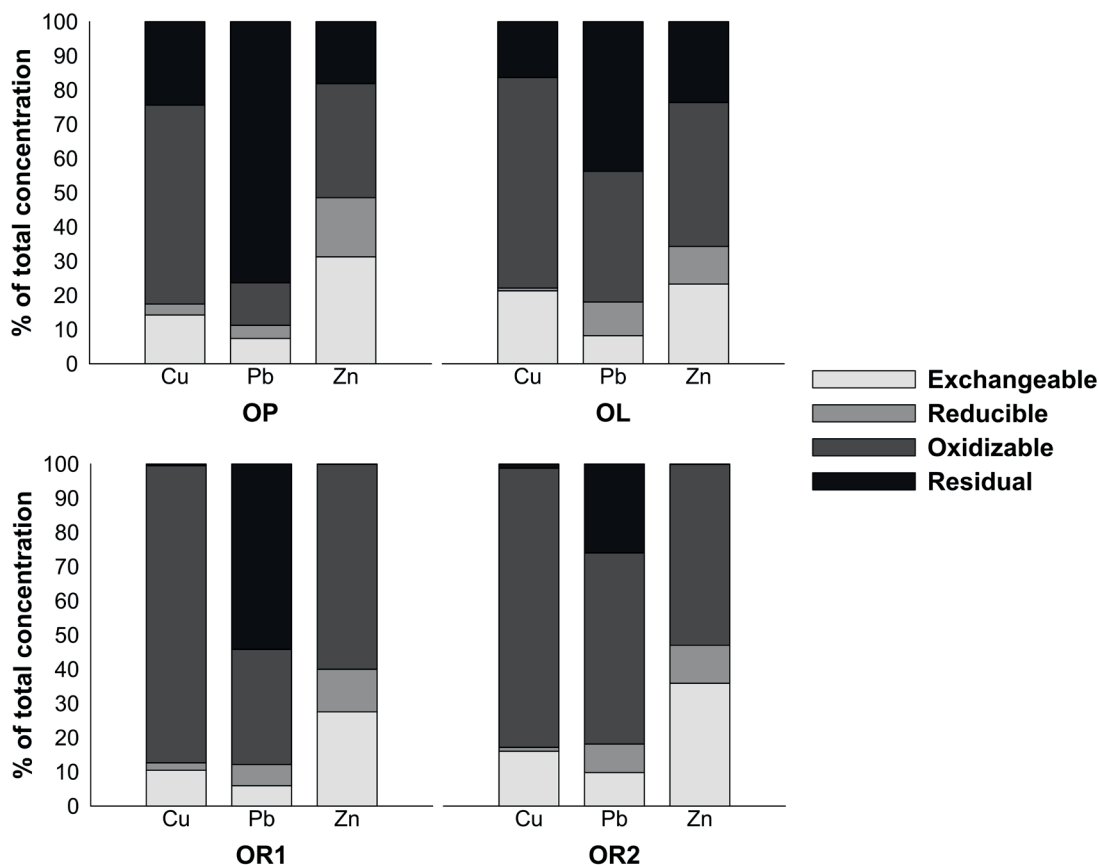


Fig. 3. Metal fractionation in flotation tailing samples determined by BCR sequential extraction

This means that the risks for Pb and Cu are assessed respectively as low and medium, whereas the risk for Zn is medium to high, indicating that Zn is the most mobile element. These values are also comparable to the results of Mikoda and Gruszecka-Kosowska (2018), which showed the lowest mobility for Pb (2%), intermediate mobility for Cu (18%) and highest for Zn (23%) among the analyzed metals in a sample of flotation tailings which were similar in composition to the OP sample.

Disposal of metal-bearing residues is the last-choice management option due to surface occupation and environmental risk posed during weathering. An organic rich solution (citric acid) was used to estimate both the potential environmental hazard and general susceptibility under exposure to such solution in the view of its potential application in the extractive industry. It has been demonstrated that as much as $22 \text{ mg}\cdot\text{kg}^{-1}$ (18%) of As and $0.2 \text{ mg}\cdot\text{kg}^{-1}$ (28.5%) of Sb could be released from OL tailings over the course of a 24 h period.

Likewise, 24 h long extraction at pH 2 gained 17.8 (14.8%) of As and 0.03 (6.07%) of Sb indicating that organic solution enhances the release of toxic compounds from the tailings. These values were compared with the legislation limits. However, it is worth mentioning that regulation is really unintuitive because according to them, hazardous character should be estimated based on extraction in water, while real dumping scenarios are exposed to many more aggressive dissolution agents and factors. Antonijević et al. (2008) emphasized that Cu can be leached from flotation tailings with water, especially if Cu is present in soluble copper forms. On the other hand, the flotation tailings are primarily characterized by their buffering properties (mainly due to the carbonates which are present), which impart a slightly alkaline pH to the flotation slurry (Bakalarz 2019, Costis et al. 2020). The risk of metal leaching for this material is generally low, as described by Kijewski (1995) and Łuszczkiewicz (2000). However, frequent rainfall episodes cause

the periodic washing of flotation tailings, potentially enhancing metal leaching. In addition, atmospheric oxygen also contributes to leaching intensification (Antonijević et al. 2008). Likewise, the native microbial consortia can either attach to the surface of the tailings and cause local leaching or generate organic agents that facilitate dissolution (Smith & Miettinen 2005). The finding of Antonijević et al. (2008) demonstrated the negligible impact of stirring on the element dissolution efficiency. This indicates that leaching is likely to occur under stationary conditions as those encountered in the disposal ponds. Of high importance is also the finding of Costis et al. (2020) who demonstrated that low temperatures and freeze-thaw episodes may also enhance element leaching from flotation tailings, mainly due to the higher solubility of carbonates at low temperatures and the fragmentation of fine particles which enhances their reactive surface area (Zhai et al. 2022).

Geoenvironmental evaluation of tailings

Two additional parameters were established for the proper assessment of environmental risk posed

by the examined tailings. The classification of the acid producing potential of tailing samples is presented in Figure 4. In addition to regular sample pH (grey) the NAG pH (purple) has been presented on the graph, and both values were compared to the total sulfur contents of the samples. Regular pH values of flotation tailings are in the range of 8.36–8.61, whereas NAG pH values are in range of 6.50–8.44. The lowest NAG pH values of 6.50 and 7.02 were noted for OR1 and OR2 samples, which are less abundant in carbonates and shale. Sulfur values for tailings are in the range of 0.41–1.23 mass%. The highest sulfur values (0.96 mass% and 1.23 mass%) are determined for OR1 and OR2 samples, respectively. The presence of sulfur in these samples is primarily due to the presence of residual sulfides, yet it also reflects low NAG pH values. It shows that these samples are more likely to generate acid when landfilled. Nonetheless, the combination of these parameters allowed the classification of tailing as potentially acid-producing (Fig. 4). The sulfur content of tailings converted to MPA shows that tailings can generate from 12.5 to 37.6 kg H₂SO₄ per 1 ton of waste.

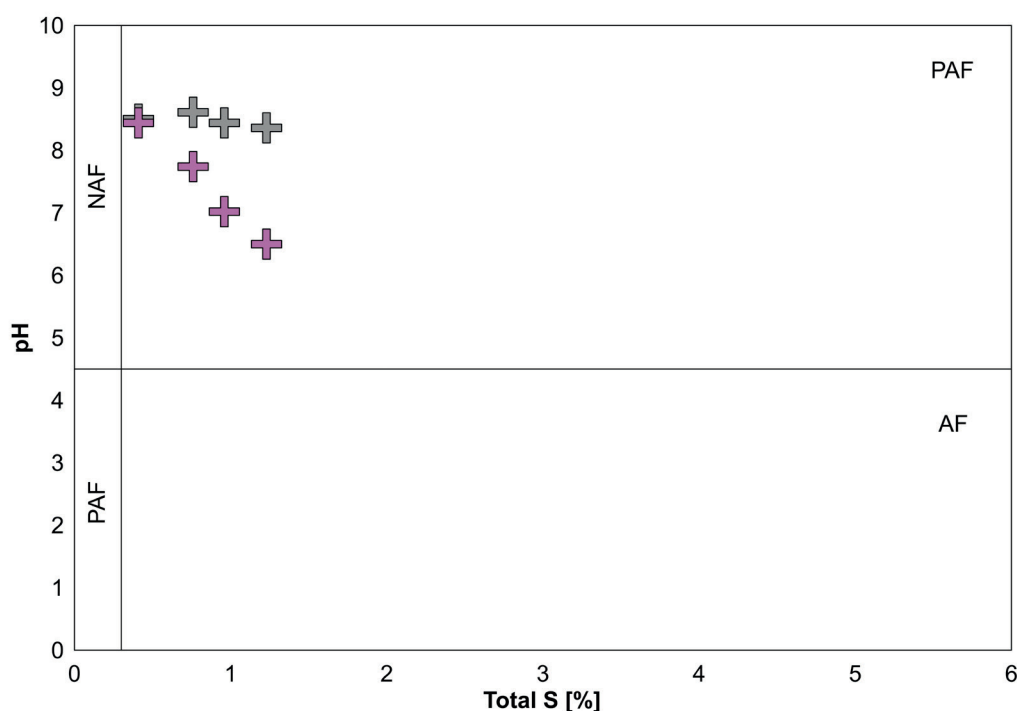


Fig. 4. Classification of acid forming potential for bulk composites of flotation tailings based on paste and net acid generation (NAG) pH versus total sulfur [mass%]. Abbreviations: AF – acid forming, NAF – not acid forming, PAF – potentially acid forming

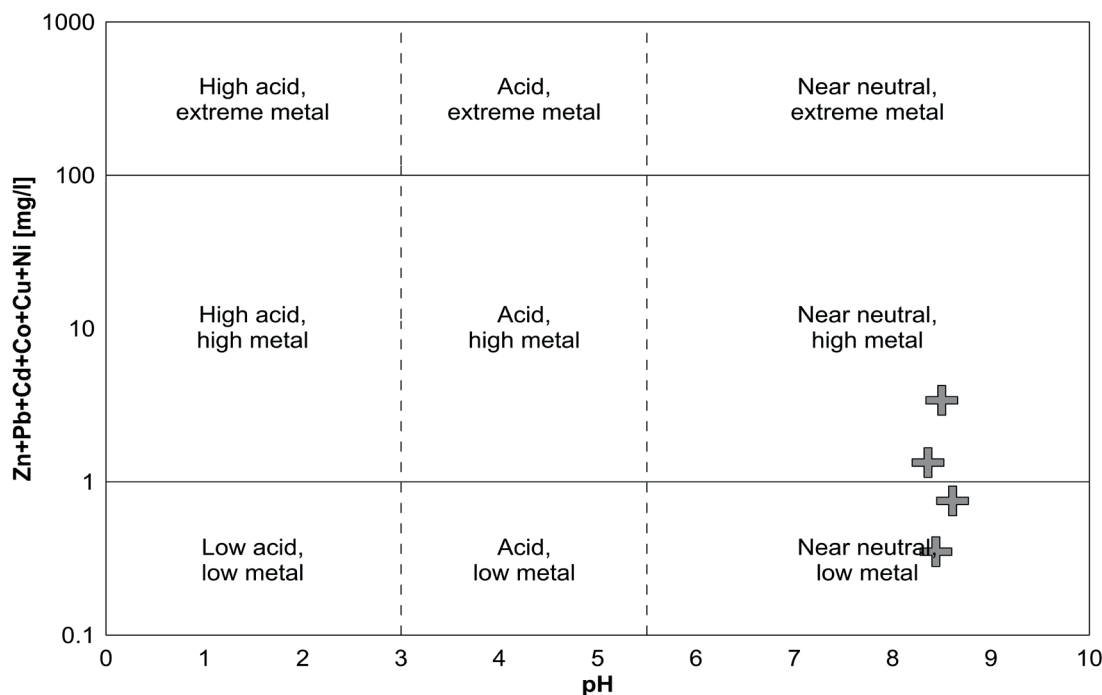


Fig. 5. Ficklin plot for tailing samples showing metals [mg/L] versus paste pH

The Ficklin plot for tailing samples is given in Figure 5. There is no clear connection between the leached amounts of metals and mineralogical properties. The highest value of leached metals (3.4 mg/L) was determined for the OL sample, whereas the lowest (0.35 mg/L) was determined for the OR1 sample. The other sample poor in shale and carbonates – OR2 – released as much as 1.33 mg/L of metals during the test procedure, whereas the carbonate-rich OP sample released 0.75 mg/L of metals. The high values of pH cause that the samples are considered as near-neutral, whereas the amount of leached metals below 1 mg/L allows to classify OR1 and OP samples as low-metal; OR2 and OL samples were classified as high-metal (Fig. 5).

The above-mentioned parameters lead to the conclusion that the tailings pose a threat to the environment. Although the amounts of released metals and sulfur content are relatively low, the amount of tailings produced per year (ca. 28 million Mg) makes the leachate enriched in metals and therefore dangerous to the surrounding environment. It must be emphasized that laboratory leaching enhances dissolution rates, thus leaching

dynamic and efficiency may differ in a real-time scenario. Nevertheless, the laboratory leaching test provides an insight into sample reactivity and the potential hazards that may be encountered when disposed.

Resource and utilization perspectives

It is important to note that the pyrometallurgical industry is associated with metal losses; a large number of reports have proven this based on mineralogical analysis (Bakalarz 2019, Zhang et al. 2021). The flotation tailings usually host metal-bearing phases indicating that complete process efficiency is not possible to achieve. The current understanding of the impact of tailings on ecosystems has led to increased urgency in the search for alternative management routes (Kossoff et al. 2014).

It is intuitive that most studies focus on extraction efficiencies related to the most concentrated metals in tailings. On the other hand, if we consider their economic potential, the elements that occur in the tailings at lower concentration levels, but having estimated a higher price on the market would be more reasonable to recover (Žibret et al. 2020).

Such comparative works are relevant to the development of standardized protocols useful for the treatment of such residues with a minor optimization tailored to specific solid of specific composition. Researchers dealing with the development of treatment strategies often face the problem of missing literature data. In other words, many studies concern several elements of interest – often those the most concentrated in the specific waste, while elements contained in lower amounts are often omitted. Additionally, it must be highlighted that the European Union is currently highlighting the need for a more sustainable and secure metals supply. Consequently, the list of critical raw materials has recently been updated and these elements occur in the studied tailings (see Table 2). There are numerous perspective treatment options including flotation, leaching, bioleaching, gravity and magnetic separation, and combinations of the above (Sagdieva et al. 2007, Hao et al. 2016, Falagan et al. 2017, Conić et al. 2020, Mackay et al. 2020, Yin et al. 2020, Drobe et al. 2021, Manca et al. 2021, Araujo et al. 2022, Chen et al. 2022).

However, given the specific green nature of bioleaching, its choice should be a priority (Kumar & Yaashikaa 2020). Previous studies undertaking the biohydrometallurgical approach to study flotation tailings in terms of metal extraction demonstrated that high recovery rates can be achieved if bioleaching conditions are appropriately designed. For example, Kisielowska & Kasinska-Pilut (2005) and Kisielowska et al. (2007) employed *Aspergillus niger* fungus producing organic acids to treat flotation tailings which resulted in a recovery yield reaching up to 88%.

The economic viability of bioleaching processes is an issue of utmost importance if these techniques are meant to pass from the laboratory and become the industry standard. Development of the bioleaching of flotation tailings requires the consideration of the following aspects: (a) Si content, (b) S content, (c) amount of target elements. First, the studied tailings contain 50.1% of SiO₂ (Table 2), while understanding the pH dependence in silicate dissolution is crucial for the development of optimally limited Si transport to the leachate. The understanding of how silicates contribute to pH buffering is essential for system performance. If silicate dissolution rates are

an upfront reaction to other acidifying phases (e.g. sulfides), then a strong buffering effect can be expected (Jambor et al. 2002). This process is desirable at disposal sites where the acid producing potential of sulfides can be counteracted by silicates. On the other hand, any changes of initially fixed pH are less desirable in extraction systems. Furthermore, the studied tailings contain sulfur levels of up to 1%, therefore one can assume that additional sulfur supplementation can be required in a bioleaching system where sulfur oxidizing microorganisms (e.g. *Acidithiobacillus thiooxidans*) are present. Sulfur oxidation results in acid production enhancing the effectiveness of the (bio)leaching process. The most desirable design conditions are those where microbial sulfur oxidation rates are faster than silicates dissolution (in this case mainly quartz). If the oxidation reaction of sulfur is more intense than the dissolution of silicates, then the silicate mediated buffering is also weaker and subsequently pH conditions in the leaching reactor are less variable. Given these considerations, a hybrid approach was undertaken in this study (Ilyas & Lee 2015); once H₂SO₄ production was achieved, supernatant was used as a leaching agent. Such an approach enabled avoid S supplementation in the reactor containing tailings. Furthermore, the studied tailings contain nearly 100 mg·kg⁻¹ of rare earth elements. As demonstrated previously, organic acids such as citric acid may be suitable for their recovery because it can leave major elements such as Al and Fe unextracted (Ujaczki et al. 2017).

The results of chemical and biological treatment of flotation tailings revealed that the concentration of H₂SO₄ has a marginal impact on extraction efficiency if PD 1% is used in the treatment. For example, as much as 14.3 mg·kg⁻¹ (11.3%) of Zn was extracted using 1M H₂SO₄, whereas 9.0 mg·kg⁻¹ (7.1%) of Zn was extracted using 0.1M H₂SO₄. A similar tendency was observed for other elements. Surprisingly, a higher extraction efficiency was achieved at higher pulp densities used; 20.7 mg·kg⁻¹ (16.5%) of Zn was extracted at 10% PD, whereas 14.3 mg·kg⁻¹ (11.3%) was extracted at 1% PD. On the other hand, citric acid concentration was found to have an influence on extraction efficiency even when PD 1% was used. The Zn extraction increased from 3.9 mg·kg⁻¹ (3.1%)

to $11.6 \text{ mg}\cdot\text{kg}^{-1}$ (9.2%) if acid concentration increased from 0.1 to 1 N. An increase of PD in citric acid extraction had a lower effect on efficiency when compared to that of sulfuric acid. For example, as

Zn extraction oscillated from $11.6 \text{ mg}\cdot\text{kg}^{-1}$ (9.2%) to $14.3 \text{ mg}\cdot\text{kg}^{-1}$ (11.3%) if PD ranged at 1–10% (Fig. 6). Overall recovery achieved in chemical treatment did not exceed 40%.

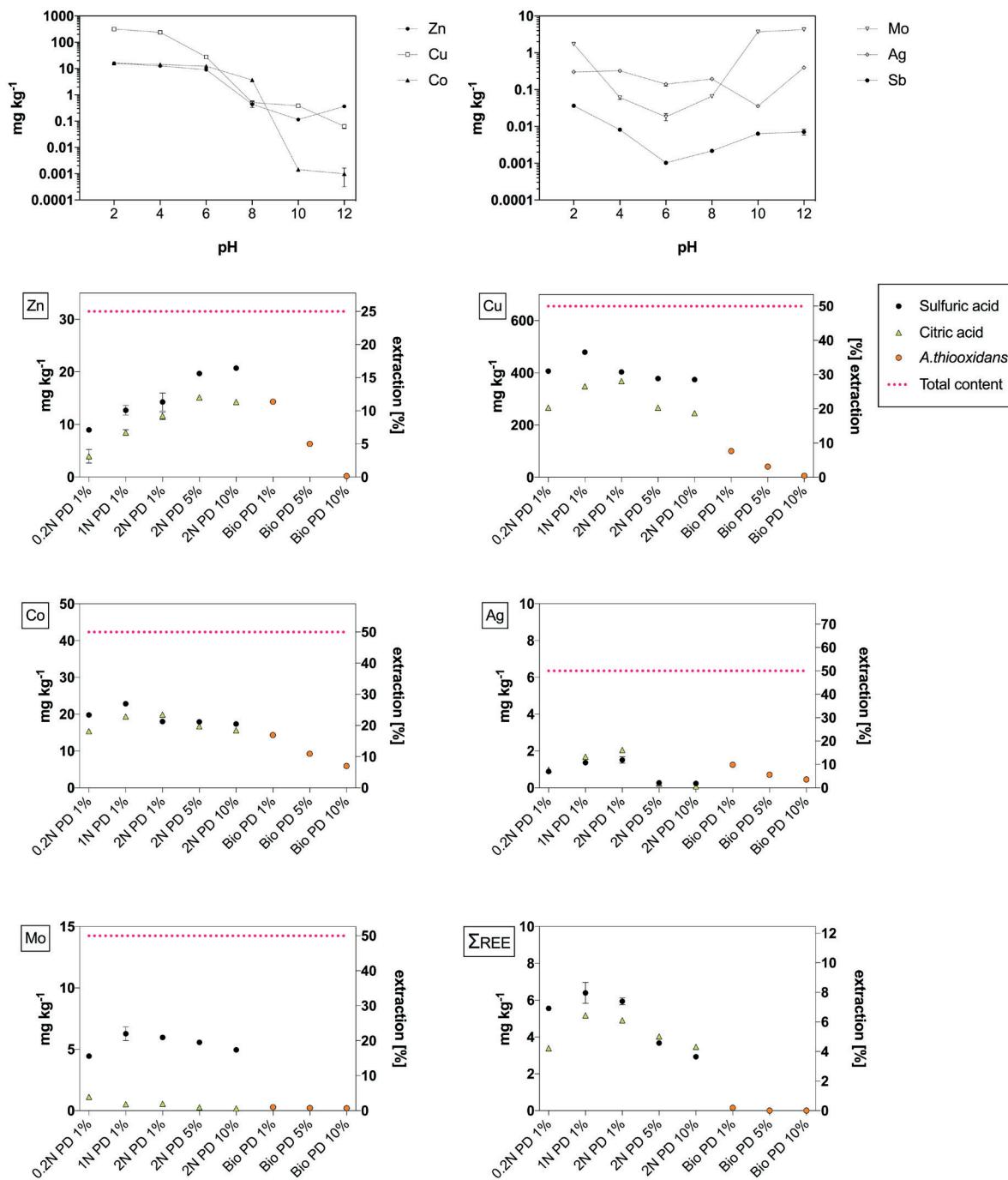


Fig. 6. Extraction of metals from flotation tailing samples using different lixiviants – effects of pH, leaching agent, concentration, and pulp density

In a hybrid process (i.e. H_2SO_4 produced by *A. thiooxidans*), an increase of PD led to lower extraction. What is important, the extraction in hybrid process was generally lower (not exceeding 20%) than that achieved in chemical treatment. For example, Zn extraction in hybrid process oscillated at 0.2–14.3 $\text{mg}\cdot\text{kg}^{-1}$ (up to 11.3%), whereas as much as 20.7 $\text{mg}\cdot\text{kg}^{-1}$ (16.5%) was achieved during chemical extraction. However, the biological approach is considered a “green technology” therefore further development of tailing treatments via biological and/or hybrid method require further efforts to establish environmentally sound technology.

Rare earth elements were also considered during the extraction process, and it has been demonstrated that chemical extraction with H_2SO_4 led to REE recovery up to 6.4 $\text{mg}\cdot\text{kg}^{-1}$ (8%). Similar, but slightly lower recovery level was reached using citric acid 5.2 $\text{mg}\cdot\text{kg}^{-1}$ (6.4%). The hybrid process was found to give unsatisfactory recovery rates not exceeding 0.2%.

Table 4
Theoretical economic potential of flotation tailings (for 1 kg of material)

Most efficient treatment	Element gained	Economic potential [USD]*
H_2SO_4 (PD 10%, 1 $\text{mol}\cdot\text{L}^{-1}$)	Zn 20.7 $\text{mg}\cdot\text{kg}^{-1}$	0.00007
H_2SO_4 (PD 1%, 0.5 $\text{mol}\cdot\text{L}^{-1}$)	Cu 479 $\text{mg}\cdot\text{kg}^{-1}$	0.00427
H_2SO_4 (PD 1%, 0.5 $\text{mol}\cdot\text{L}^{-1}$)	Co 23 $\text{mg}\cdot\text{kg}^{-1}$	0.00108
Citric acid (PD 1%, 2 N)	Ag 2.0 $\text{mg}\cdot\text{kg}^{-1}$	0.001264
H_2SO_4 (PD 1%, 0.5 $\text{mol}\cdot\text{L}^{-1}$)	Mo 6.3 $\text{mg}\cdot\text{kg}^{-1}$	0.000354
H_2SO_4 (PD 1%, 0.5 $\text{mol}\cdot\text{L}^{-1}$)	REE 6.4 $\text{mg}\cdot\text{kg}^{-1}$	0.000021**

* Element price taken from Shanghai Metal Market for 4th Nov 2022 (La 3583,49 USD/t, Mo 59,27 USD/kg, Ag 632.62 USD/kg, Cu 8909 USD/t, Zn 3363 USD/t, Co 47067 USD/t).

** For calculations of REE, the price of La was used.

Concerning the economic potential of the studied flotation tailings, at this point it is cost-inefficient (Table 4). The values of leached metals per 1 kg of solid are not satisfactory but given the total amount of flotation tailings produced annually (ca. 28 million Mg), development of an efficient treatment protocol is required to fit the concept of the circular economy. It must be emphasized that the studied flotation tailings are very complex in terms of their mineralogical composition and

specific mineral association with certain fraction particles as revealed by previous studies (Bakalarz 2019). Łuszczkiewicz et al. (2006). Therefore, the personalized treatment methodology aiming to enhance metal recovery yields from flotation tailings is also highly needed to reduce their potential negative environmental impact.

CONCLUSIONS

Based on the applied geochemical approach, the following conclusions can be drawn:

1. Studied flotation tailings are mainly composed of quartz and carbonates with sulfides occurring in minor volumetric proportions.
2. Flotation tailings were found to be fairly reactive when exposed to water leaching and rainfall conditions. However, laboratory tests serve only as a simplified approach for the assessment of element dissolution. Therefore, the reactivity of flotation tailings in genuine landfill conditions can be higher given prolonged solid exposure to weathering, several water inflow events during rainfalls and freeze-thaw episodes potentially contributing to solid fragmentation.
3. Results of sequential extraction revealed the highest metal release from sulfides and residual fraction. The environmental risk analysis demonstrated Zn to be the most susceptible element to liberation from the studied flotation tailings.
4. For most of the elements of interest, extraction conditions H_2SO_4 PD 1% 0.5 $\text{mol}\cdot\text{L}^{-1}$ were found to give satisfactory recovery rates, whereas Ag extraction was more efficient using citric acid. 24-hour extraction generally did not exceed 37% indicating that either a longer duration or a stronger leaching agent is required to improve recovery yield.

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APPENDIX

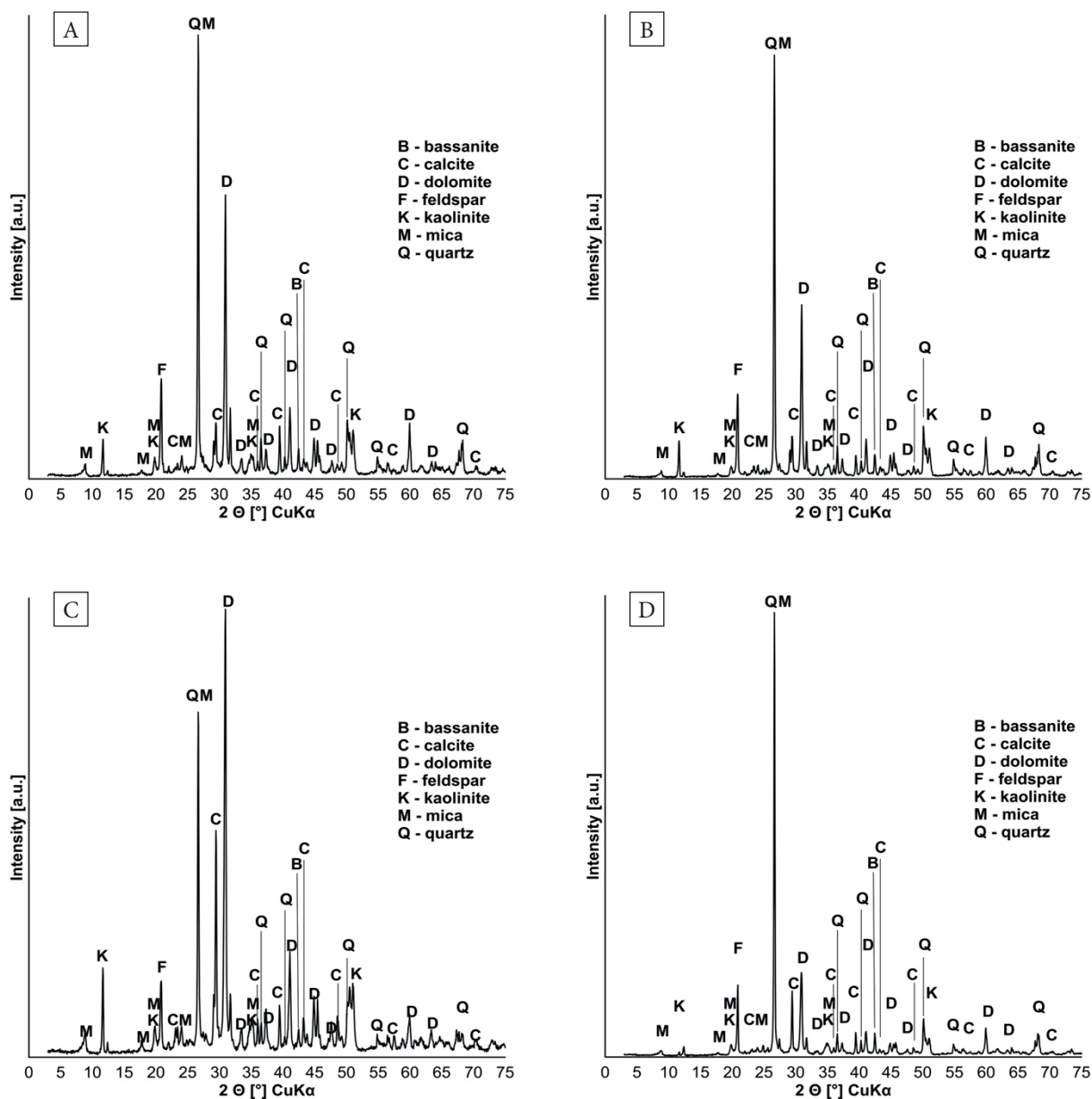


Fig. A1. XRD patterns of different samples of flotation tailings: A), B) the samples with most sandstone in the feed rock (OR1 and OR2); C) sample with most carbonates in the feed (OP); D) the tailing sample (OL) from the flotation of the feed with biggest share of shale fraction

Table A1

Results of leaching tests for selected elements of tailings samples and Polish regulatory values of these elements (Rozporządzenie... 2019)

Sample + test	Concentration [mg·dm ⁻³]					
	Cd	Co	Cu	Ni	Pb	Zn
OP FL	<0.01	<0.01	<0.005	<0.05	<0.01	<0.01
OP SPLP	<0.01	<0.01	0.065	<0.05	<0.01	<0.01
OP WL	0.015	0.137	0.316	0.169	0.061	0.053
OL FL	<0.01	<0.01	0.022	<0.05	<0.01	<0.01
OL SPLP	<0.01	0.013	0.011	<0.05	0.013	<0.01
OL WL	<0.01	1.68	0.514	0.544	0.043	0.618
OR1 FL	<0.01	<0.01	<0.005	<0.05	<0.01	<0.01
OR1 SPLP	<0.01	<0.01	0.064	<0.05	<0.01	<0.01
OR1 WL	<0.01	0.011	0.047	0.159	<0.01	0.118
OR2 FL	<0.01	<0.01	<0.005	<0.05	<0.01	<0.01
OR2 SPLP	<0.01	<0.01	0.051	<0.05	<0.01	0.015
OR2 WL	<0.01	0.358	0.297	0.284	0.064	0.327
Regulatory value	0.4	1	0.5	0.5	0.5	2

Explanations: FL – field leaching test, SPLP – simulated rainfall leaching, WL – water leaching.