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Assessment of the possibilities of recovering Zn-Pb ore tailings located at former tailings dump site

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Abstract

Mining and metallurgical tailings represent a metal resource, but also a significant environmental problem. Depending on their properties, they can also be used in construction, road building, mining or land reclamation. The recovery of Zn and Pb from tailings dumped after ore processing is an example of the use of mineral wastes. This paper presents the results of a study on the possibilities of using post-flotation wastes deposited on old tailings disposal sites for land reclamation. The physical and chemical properties and ecotoxicity studies of the waste were carried out. The investigated waste is classified as silty sand, containing mainly carbonate and clay minerals and quartz. The chemical composition is mainly CaO, MgO, SiO_2, Al_2O_3, SO_3 and ZnO. Despite the presence of heavy metals, their leachability does not pose a threat to the groundwater environment. Only the leachability of sulphates from the tested waste exceeds permissible quantities. The results of toxicity tests carried out on the tested waste: the Lepidium sativum germination test in an aqueous extract of the waste and the Phytotoxkit for the solid phase in relation to *Sorghum saccharatum*, *Lepidium sativum* and *Synpis alba*. These tests showed no phytotoxicity.

Introduction

The waste accumulated over many years at tailings disposal facilities, metallurgical waste dumps, metal ore tailings dumps, or energy waste dumps can be anthropogenic deposits from which commercially usable raw materials can be obtained. Exploitation of such deposits contributes to the recovery of the waste stored therein, which is a substitute for natural resources, thus saving their resources and acquiring previously occupied land that can then be used in various ways. The recovery of raw materials from anthropogenic deposits, which has been ongoing for many years, nowadays fits into the model of a circular economy in force in the EU (European Commission 2017). The type of potential raw materials collected in an anthropogenic deposit, as well as the profitability of their extraction, depends on a number of factors related to the source of the waste (type and quantity of waste deposited), the effectiveness of the former processing methods carried out (raw material content), the method of storage (selective, non-selective), the age of the deposit or the physical and chemical changes that have taken place within the deposit. The risks to the environment and human health from the operation of landfills are also important. All these aspects have impacted on the economic assessment of landfill mining processes (Kieckhäfer *et al*. 2017; Quaghebeur *et al*. 2013).

Uncertainty of supply and, above all, the increase in the price of raw materials on world markets, are making it increasingly profitable to recover metals from other wastes in which their concentration is low, so that recovery for economic reasons has not yet been carried out on an industrial scale. These changes are resulting in mineral waste from the mining, processing, metallurgical and chemical industries becoming a source of critical raw materials (CRMs) or other valuable metals (e.g. Zn) not classified as critical raw materials (European Commission 2020 and 2023). Non-ferrous and ferrous metals, plastics and combustible fractions (as fuels) are recovered from the landfills of municipal solid waste (Rotheut and Quicker 2017; Wagner and Raymond 2015; Masi *et al*. 2014).

The extraction of metals from mineral landfills requires the use of technological operations known mainly from open-pit mining and processing operations used in the processing of metal ores. The result is metal concentrates and tailings that should be used as much as possible (Matusiak and Kowol 2016; Kudełko and Nitek 2011; Zee van der *et al*. 2004).

Base-metal tailings have been used as aggregates for mortars (Argane *et al.* 2015). Reuse of these tailings produces mortars with good mechanical and durability performance, and the risk of metals release from tailings mortars is low. Thomas *et al.* (2013) observed that copper tailing may be used as partial replacement of natural fine aggregates in cement concrete until 60% replacement is achieved. According to Onuaguluchi *et al*. (2016), the best tailings reuse based on corrosion performance and cost efficiency analyses was utilisation of 5% pre-wetted cooper tailings either as a cement replacement or an additive material. Because of grain composition, post-flotation waste cannot be used in underground mines as hydraulic backfill. However, it can be used as a component of suspensions (with binding materials such as fly ash after coal combustion or cement) designed for sealing longwalls with cavingsin underground mines (Kępys 2017).

In the case of reclamation works, the waste is used as a material or component of various blends in the technical phase to shape the relief and improve the physical and chemical properties of grounds, and in the biological phase, in the process of soil reconstruction (Śliwka *et al*. 2017a; Śliwka *et al.* 2017b). The application of waste in reclamation depends on fulfilling the requirements defined in legal acts, regarding the geo-mechanical effect of waste on terrestrial and aquatic environment and vegetation. Thus, a certain scope of research must be conducted, including, first of all, an assessment of the amount of chemical pollutants from waste which can get into the environment, and the assessment of the impact of waste on living organisms, especially plants (Baran *et al*. 2015).

Another way to use landfilled waste from metal ore mining is to recover metals from them. One of the developing directions for extracting metals from mineral (post processing) waste or poor ores is biomining, including phytomining. The use of biological methods allows metals to be extracted from waste or ores containing very low concentrations of these metals. The use of microorganisms to extract metals in practice has been known since the eighteenth century, when copper was extracted in this way from rocks in Rio Tinto, Spain (Kikis *et al*. 2024; Macaskie and Dean 1989).

The article presents the results of studies on the possibility of use of post-processing waste in land reclamation. This waste was created in the process of re-flotation of old post-flotation waste after the processing of zinc and lead ores. The purpose of re-flotation was to recover metals from storage waste. Because the age of the landfill is several dozen years, the landfill was partly reclaimed, a comprehensive approach to its exploitation is important. Recovery of useful components from deposited waste, such as zinc and lead sulphides used for metal production is important, but the issue of residue management (waste) after the processing, especially after flotation, is important too. To avoid the build of a new repository, it is necessary to carry out a series of tests to determine the possibilities of their use. Due to environmental as well as social aspects (society’s fear of exploitation of a disused landfill and construction of a new repository), it is necessary to develop methods for using this type of tailings. One of the considered possibilities of using this kind of waste is the use in engineering works. To determine the suitability of tested waste to the production of materials used for reclamation, tests of physical and chemical properties were carried out, as well as tests of their phytotoxic properties.

Experimental

The material of studies was post-flotation waste, formed in the process of metal recovery from waste deposited in old repositories of a zinc and lead metallurgy plant. To define the possibilities of the utilisation of the tested waste, their physical, chemical and phytotoxic properties were determined.
Grain composition was marked with the laser diffraction method using the Analysette 22 by Fritsch. Phase composition was determined using the Philips APD PW 3020 X'Pert diffractometer. Chemical composition was determined by the Inductively Coupled Plasma Spectrometry/Atomic Emission Spectroscopy (ICP-AES) and by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with the use of the Perkin Elmer Elan 6100 apparatus. Leachability tests were conducted according to the EN 12457-2 standard. The distilled water, with a liquid-to-solid ratio (L/S) of 10, was used as a leaching solution. The suspension was agitated in a plastic flask for 24 hours, then the mixture was filtered through a 0.45 µm membrane filter. The resulting leachate was analyzed for pH and trace elements using ICP-AES and ICP-MS methods. The amount of chlorides was analysed using the Volhard titration method.
Toxicity testing included a standard test of aqueous extract of waste in relation to the test plant (*Lepidium sativum*). The water extract was prepared from the waste (standard procedure: aqueous extract of waste in distilled water, 1:10, 24 hours mixed), and then a range of dilutions was prepared: 6,25, 12.5, 25, 50 and 100%. 3 ml of the prepared dilution was put to Petri dishes, lined with the filtration paper (three repetitions for each concentration); control dishes were also prepared. 10 seeds of *Lepidium sativum* were put to each dish and incubated for 72 hours. Then the length of roots was measured.

To assess the phytotoxicity of the waste, a Phytotoxkit test for the solid phase was also performed. The test is in accordance with ISO 18763. The Phytotoxkit test by Tigret is a 3-day microbioassay of soil and sediment (acute) toxicity, based on the assessment of root germination and inhibition. The test uses the monocotyledonous *Sorghum saccharatum* and the dicotyledons *Lepidium sativum* and *Sinapis alba*. Plants are grown on special test plates (3 replicates for each species) in reference soil (Tigret reference soil), as control samples and test soil or sediments. Seeds are incubated in the dark at 25°C. The special design of the test plate allows for simple measurement of the length of plant roots and assessment of the number of germinated plants.
After three days, germination (germination inhibition) and early growth of test plants were assessed.
The impact of wastewater extract on the germination of test plants was defined as the percentage of inhibition (*I*) and calculated according to the equation:

$$I = \left(\frac{A-B}{A}\right) \cdot 100\% \qquad (1)$$

where:
A – the number of germinated seeds in control object
B – the number of germinated seeds in experimental object

The results of the Phytotoxkit test were statistically evaluated to check whether the obtained differences in root lengths were significant. Since the means were compared in several populations, for this purpose one-way ANOVA analysis and Tukey's post hoc test were performed at a significance level of 0.05. These analyses were performed in Statistica, version 13.

Results and discussion

The studied waste has very fine granulation (Figure 1). The grain size composition is typical of post-flotation waste and results from grinding the waste before it is floated. Almost 50% of grains are below 100 µm, and the maximum size of grains is 550 µm. The waste in its composition contains 68%

sand fraction and 32% dust fraction and according to the soil classification guidelines in EN ISO 14688-2:2018 (2018), the tested waste is classified as silty sand (siSa).

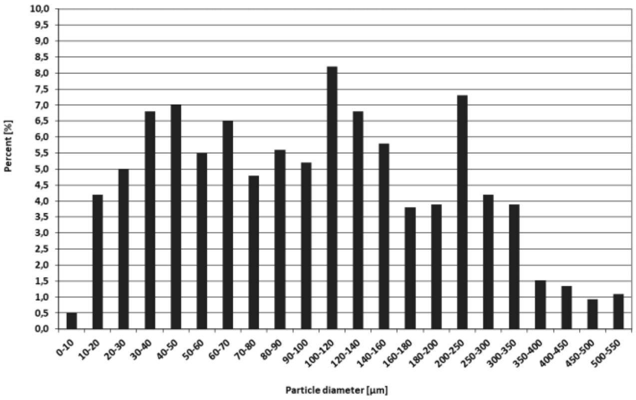

Figure 1. The grain size composition of the studied waste.

For waste, characteristic parameters of the particle size distribution were also determined, such as diameter: d10, d30, d50, d60 and d90 corresponding to 10, 30, 50, 60 and 90% of the volume of the set of particles passing through the sieve of a given diameter, the results are shown in Table 1.

Table 1. Waste-specific grain composition parameters.

Characteristic diameter [µm]				
d_{10}	d_{30}	d_{50}	d_{60}	d_{90}
29.4	61.5	98.1	121.9	279.7

The main mineral phases (Figure 2) are the common naturally occurring dolomite $CaMg(CO_3)_2$, calcite $CaCO_3$, quartz SiO_2 and kaolinite $Al_2Si_2O_5(OH)_4$.

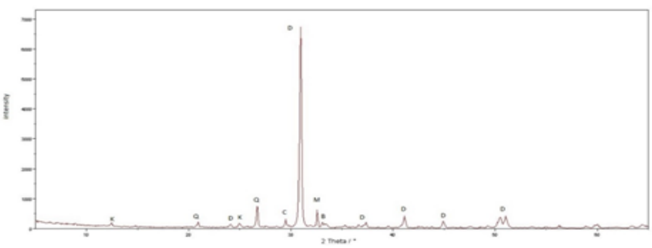

Figure 2. X-ray diffraction pattern of studied waste (dolomite – D, quartz – Q, calcite – C, kaolinite – K, bassanite– B, merwinite – M).

Figure 3 shows chemical composition of the studied post-flotation waste. The main compounds are CaO, MgO, SiO_2, Al_2O_3, which also occur in soils naturally. Note the content of ZnO and SO_3, which is obvious, as the waste represents the residue from processed Zn and Pb ores.

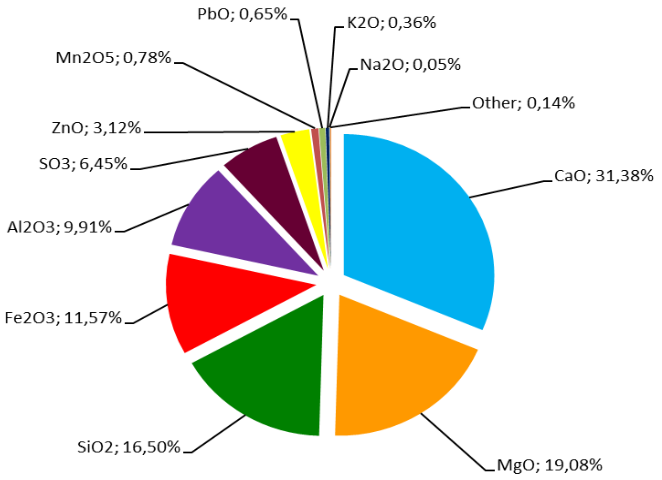

Figure 3. Major compounds content [% dry mass].

Important problem that can arise when re-using waste for reclamation is its impact on the aquatic environment through the dissolution and leaching of substances contained in the waste. The results of the tests of leachability of the tested waste are presented in Table 3.

The leachability results were compared with the upper limits of substances that are particularly harmful to the aquatic environment when introduced into soils and/or surface waters (Ordinance of the Minister of Environment 2016). The pH value of the water extract complies with the limits. In the case of biological reclamation, the pH value has a significant impact on the growth, development and yield of plants. The most advantageous level is in the range from slightly acidic to neutral (Boroń and Klatka 2009). The pH values in the samples are close to neutral. Despite the presence of heavy metals in the studied waste (Table 2), their leachability does not pose a threat to the aquatic environment. This is due to the occurrence of metals in bound forms, hardly soluble (Baic 2013). In addition, the low content of Zn and Pb ions in the aqueous eluate is a result of the neutral pH of the water associated with the presence of carbonate minerals, which significantly limits the mobility of trace elements (Motyka *et al.* 2019).

Table 2. Trace element content.

Element	Content [mg/kg]	Element	Content [mg/kg]
As	0.71	Li	16.36
Ag	0.19	Mo	0.13
Ba	237.56	Ni	33.94
Cd	0.10	P	46.94
Co	5.10	Sn	0.003
Cr	25.62	Sr	87.05
Cu	460.49	Ti	104.0
Hg	0.03		

Only the value of sulphates exceeds the acceptable one (1354 mg SO_4^{2-}/dm^3, while the accepted value is 500 mg SO_4^{2-}/dm^3). The high leachability of sulphates is a result of the weathering processes of metal sulphides, acidic solutions are formed which are neutralised in the carbonate rock environment, leading to the presence of sulphates and calcium and magnesium in the water (Motyka and Postawa 2013). Due to the concentration of sulphates, the direct addition of this waste to the ground is impossible. So, this waste cannot be used as the final product in a reclamation process. Its application will depend on whether it can be blended with other materials to lower the leachability of pollutants, which is practiced in engineering works and usually means mixing waste in proper quantities with the subsoil and other ingredients. On the other hand, sulphur is a biogenic element, essential for plant, which only takes it up from the soil solution in the form of sulphates. Therefore, the studied waste may have a positive effect on reducing the soil's sulphur deficit.
The results of the phytotest relative to *Lepidium sativum*, carried out on wastewater extracts, did not show any negative effect of the tested waste on the early growth of the test plants. In all the dilutions tested, the average root lengths in the water extracts from the tested soils were longer than in the control sample (Figure 4). This indicates that the tested wastes are not toxic to *Lepidium sativum*. The greater average root length in the test samples could indicate that the waste has stimulatory properties. The stimulating effect may be related to the presence of biogenic (fertilizing) elements in the waste, which are necessary for plant growth.
To confirm or reject this thesis, Anova analysis and Tukey's post-hoc test were performed This analysis did not show that the differences in root lengths between groups were significant.

Table 3. Leachability of chemical pollutants from post-flotation waste.

Kind of pollution	Post-flotation waste [mg/dm^3]	Acceptable value according to Ordinance of the Minister of Environment (2016) [mg/dm^3]
pH	7.85	6.5 - 9
Na	1.48	800
K	2.75	80
Ca	499.9	no requirements
Mg	33.2	no requirements
Sr	0.602	no requirements
Mn	2.039	no requirements
Zn	0.761	2
Cu	0.0017	0.5
Ni	0.006	0.5
Co	0.0044	1
Pb	0.0024	0.5
Hg	0.0001	0.03
Ca	0.0214	0.2
Se	< 0.02	1
Sb	0.00023	0.3
Al	0.002	3
Cr	0.004	0.5
Mo	0.015	1
Ti	< 0.002	1
As	0.0012	0.1
Cl^-	2.1	1000
SO_4^{2-}	1354	500

Based on the analysis of the Phytotoxkit test results, the inhibition of plant germination in the experimental objects relative to the control objects was calculated (Figure 5). A germination stimulation PE = -3.45% (PE - phytotoxicity effect) was found for *Sorgho saccharatum*, no effect (PE up to 20%) on the germination of *Sinapis alba* (PE = 20%) and a low risk (20% < PE ≤ 50%) of *Lepidium sativum* (PE = 25%). The different effects of the tested wastes on the germination and early growth of the test plants are related to the different environmental requirements of the species used in the Phytotoxkit test. However, no phytotoxicity of the tested wastes was found.

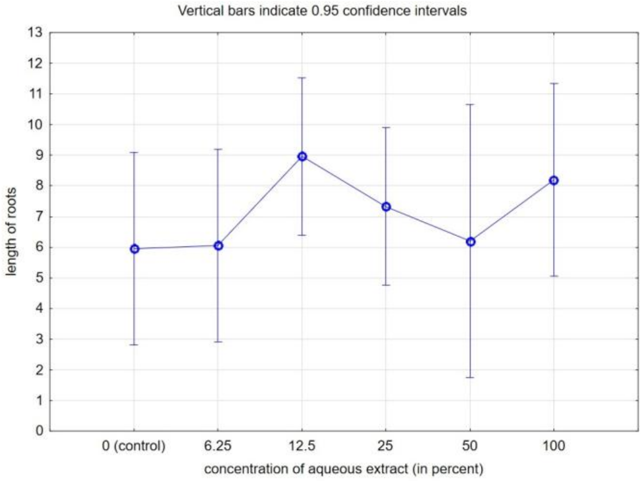

Figure 4. Expected marginal averages, results of ANOVA analyse (midpoints indicate average values, vertical bars indicate 0,95 confidence intervals).

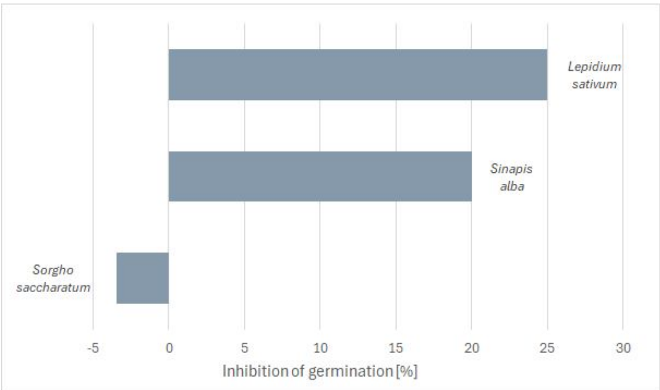

Figure 5. Inhibition of germination in the Phytotoxkit test.

Conclusions

The assessment of the properties of the tested post-flotation waste of lower content of metals was to identify the possibility of applying this waste for engineering purposes, including especially its ecological utilisation, e.g. in production a material (subsoil) for natural land reclamation. The analysis of the granulometric composition showed that the tested material of granulation corresponds to silty sands. The main elements are CaO, MgO, SiO_2, Al_2O_3, which also occur in soils naturally. Note the content of ZnO and SO_3, which is obvious, as the waste represents the residue from processed Zn and Pb ores. When comparing waste leachability with legal requirements for wastewater released to the ground, the excess of the load of sulphate ions was found. Based on the toxicity tests carried out, such as the germination test in the aqueous extract of the waste relative to *Lepidium sativim* and the standard Phytotoxkit microbiotest for the solid phase, no phytotoxicity of the mineral wastes tested was found. The analysis of the physicochemical and ecotoxicological properties of the metal-poor post-production Zn and Pb wastes showed that the tested mineral wastes could be used as an additive to improve soil properties in the reclamation of degraded areas.

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