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Evaluation of the Possibility of Using Post-Production Waste from Zn-Pb Ores as a Material for Natural Land Reclamation

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1. Introduction

In recent years, due to rapid technological development, the global need for natural resources has been growing. Mineral resources are limited, thus environmental protection becomes more and more important and in many countries circular economy is being introduced (EC 2017). The need to provide security in the supply of resources makes the recovery of waste a very important issue. This concerns not only waste formed right now, but also waste deposited in the past in various landfills.

Landfills for industrial waste (e.g. of mining or metallurgical origin) have for many years been a source of mineral resources, e.g. in the form of aggregates or waste containing coal. As we are facing changes to environmental, economic, technological and political conditions, more and more materials are being recovered from landfills of municipal and industrial waste. According to Bass et al. (2010) several aspects have to be solved before land mining: waste composition of landfills, efficiency of materials processing technologies, markets for materials recovered from landfills, and environmental and health risks from excavating landfills. All these aspects have impacted on the economic assessment of landfill mining processes (Kieckhäfer et al. 2017). Factors such as the age and type of the landfill and the country or region where the landfill is located might have an impact on the type of materials stored in the landfill and their valorization potential (Quaghebeur et al. 2013). According to Krook et al. (2012), landfill mining has primarily been seen as a way to solve traditional management issues related to landfills such as lack of landfill space and local pollution concerns, recovery of deposited resources, cover soil, produced waste fuel, recycling efforts have often been largely secondary. Obtaining raw materials from landfills of waste requires technological operations, mainly known from open cast mining, and the application of processing technologies (Matusiak & Kowol 2016, Kudełko & Nitek 2011, Van der Zee et al. 2004). In the literature, the majority of articles are devoted to the land mining of municipal solid waste landfill, with only a few overview articles on the land mining of mineral waste. Non-ferrous and ferrous metals, plastics and combustible fractions (as fuels) are recovered from the landfills of municipal waste, using mobile and stationary plants (Quaghebeur et al. 2013, Svetlov et al. 2015, Rotheut & Quicker 2017, Wanka et al. 2017). Wagner and Raymond (2015) reported the process of mining of municipal solid waste incineration ash landfill. Ash, having been fully processed for ferrous and non-ferrous metals, was then collected and returned to the ash landfill. As a result of landfill mining metal concentrates, construction materials or fuel are obtained; on the other hand often post-processing waste can be formed, which should be utilized.

Mostly mine tailings have been disposed, and according to Edraki et al. (2014) disposal methods include cross valley or hillside dams, raised, embankments/impoundments, dry-stacking of thickened tailings on land or disposal into rivers, lakes and the ocean, but tailings disposal may cause potential environmental problem. However, mine tailings depending on their physical and chemical properties can be reused, recycled and reprocessed. Reuse involves the new use or application of the total mine waste in its original form for a specific purpose directly, without any reprocessing. Recycling extracts new valuable resource ingredients or uses the waste as a feedstock and converts the entire mine waste into a new valuable product or application with some reprocessing. Reprocessing is designed to use the waste material as a feedstock for producing a valuable product, such as recovered minerals and metals (Lottermoser 2011).

Depending on their physical and chemical properties, mine tailings can be used in the construction of buildings and roads, mining, and reclamation, according to the European Waste hierarchy. Argane et al. (2015) proposed the use of mine tailings as aggregates for mortars. Reuse of base-metal tailings generates mortars with good mechanical and durability performance, and the risk that metals release from tailings mortars is minor. 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 & Eren 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, b). 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).

The article presents the results of studies on the possibility of use of post-processing waste in land remediation. 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. In order 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. In order 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.

2. Materials and methods

The subject of studies were 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 examined waste, their physical, chemical and phytotoxic properties were determined.

In the analysis of the physical and chemical properties of waste the following tests were carried out:

- grain composition was marked with the laser diffraction method using the Analysette 22 by Fritsch,
- determination of the natural concentrations of radioactive elements: ^{40}K, ^{226}Ra, and ^{228}Th was carried out with the use of gamma-ray scintillation and semiconductor spectrometry and two coefficients f_1, f_2 to establish whether

building material or waste are, acceptable for use. F_1 and f_2 coefficients were calculated according to (Ordinance of the Council of Ministers of 2 January 2007).

Coefficient f_1 determines the limit of exposure of the body to gamma radiation and is defined as:

$$f_1 = 0.00027S_K + 0.0027S_R + 0.0043S_T \quad (1)$$

where:
S_K, S_R, S_T – the contents of potassium K-40, radium Ra-226 and thorium Th-232 in a sample in $Bq \cdot kg^{-1}$

Coefficient f_2, which determines the limit of the concentration of radium Ra-226 in a building material and waste with reference to emanation of radon Rn-222 from the walls, ceilings and ground is defined as:

$$f_2 = S_R \quad (2)$$

- chemical composition analysis, post-flotation waste was digested using a mixture of HNO_3/HCl in a microwave oven. The obtained solution was analysed after dilution 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.

The phytotoxicity of waste of the lower content of metals was examined to define their impact on the germination, growth and condition of plants. The toxicity of waste was defined with regard to two selected test species: white mustard (*Sinapis alba*) and garden cress (*Lepidium sativum*). These are standard procedures used to assess germination and plant growth (e.g. Test No. 208: Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test; PN-EN ISO 11269-2:2013-06; microbiotest Microtox procedure).

The first stage of the study involved a standard toxicity test of the aqueous extract from waste in relation to a test plant (*Lepidium sativum*). The water extract was prepared from the waste (standard procedure), and then a range of solutions was prepared: 12.5, 25, 50, and 100%. 3 ml of the prepared solution 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 number of germination seeds was determined and the length of roots and aerial parts was measured. The impact of wastewater extract on the germination of test plants was defined as the percentage of inhibition and calculated according to the formula:

$$\left(\frac{A-B}{A}\right) \cdot 100\% \qquad (3)$$

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

The second stage involved pot observations. Both species of test plants were cultivated on a universal medium (peat substrate, pH 5.5) mixed with the examined waste. The same substrate was used in each experimental object. In every pot, 10 seeds of test plants were placed (selected). Experimental groups were differentiated in terms of the waste content in the medium (content: 10, 20, 30, 40 and 50% – of the volume). For comparison reference (control) pots were prepared, without the addition of waste.

All the observations were carried out in four repetitions, for each experimental object. Plant were cultivated in controlled laboratory conditions (humidity, access to light). Observations of germination and early growth of plants continued for seven days (to grow two leaves, standard procedure). Non-parametric Kolmogorov-Smirnov test in Statistica software was used to assess the significance of results.

3. Results

The studied waste has very fine granulation (Fig. 1). Almost 50% of grains are below 100 µm, and the maximum size of grains is 550 µm.

The analysis of the granulometric composition, according to EN ISO 14688-1:2018 and EN ISO 14688-2:2018, showed that the granulation in the studied material corresponds to silty sands (siSa). The values of the coefficient of graining non-uniformity and grain-size distribution curve allow us to classify the analysed waste as grain-uniform material.

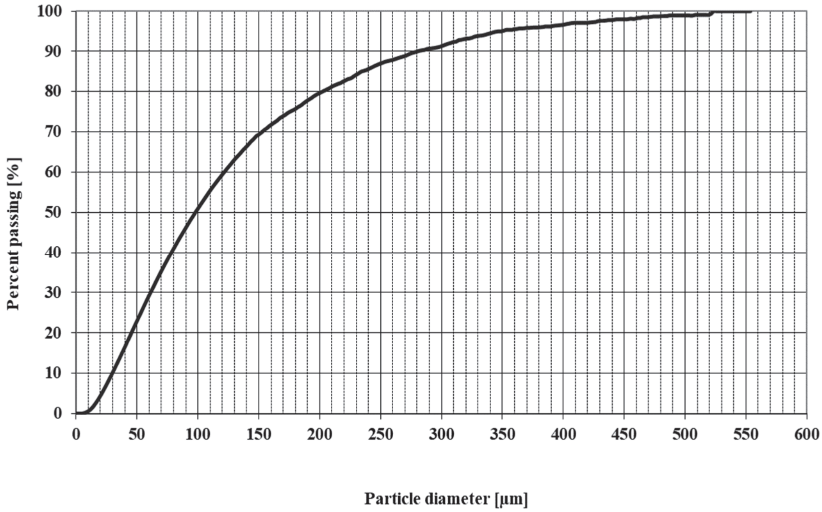


Fig. 1. The curve of the grain composition of the studied waste

In terms of the content of radioactive isotopes, indexes f_1 and f_2 defined for post-flotation waste (Table 1), fulfill the requirements for Poland (Polish legal act: Ordinance of the Council of Ministers of 2 January 2007). According to these regulations, the indexes f_1 and f_2 cannot exceed the values f_1 = 2 and f_2 = 400 Bq·kg^{-1} by more than 20% in the case of waste applied for the levelling of areas allocated for development, and f_1 = 3.5, f_2 = 1000 Bq·kg^{-1} in the case of other areas.

Table 1. The content of natural radioactive isotopes in post-flotation waste

Specification		Post-flotation waste
Specific Reactivity	K-40 [Bq·kg^{-1}]	102±6
	Ra-226 [Bq·kg^{-1}]	27±2
	Th-228 [Bq·kg^{-1}]	9±2
Reactivity Indexes	f_1 [-]	0.17±0.01

Table 2. Chemical composition of post-flotation waste

Chemical composition [% dry mass]											
P_2O_5	Mn_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	ZnO	PbO	K_2O	Na_2O	SO_3
0.01	0.78	16.5	9.91	11.57	31.38	19.08	3.12	0.65	0.36	0.05	6.45
Trace element content [$mg \cdot kg^{-1}$]											
As	Cd	Cr	Cu	Co	Mo	Hg	Ni	Sn	Sr	Ti	V
0.711	0.109	25.621	460.499	5.097	0.134	0.027	33.937	0.003	87.056	104.092	59.96

Table 2 shows chemical composition of the studied post-flotation waste. The main elements of the studied waste are CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3, these components also occur naturally in soils.

The results of the studies on the leachability of chemical pollutants from the analysed waste are presented in Table 3. Substances leached out from waste can pollute the soils and ground waters. However, in Poland there is no legal act that clearly defines the load of pollutants that can be introduced into the environment with leachate. Consequently, the results were compared with maximum (accepted by Polish law) contents of pollutants introduced to the ground with the released sewage (Polish legal act: Ordinance of the Minister of Environment of 18 November 2014). Such a comparison results from the assumption that if the permissible amount of pollutant load, which is introduced into the ground with sewage is safe for the environment, then also the same amount of pollutant load introduced into the ground with leachate is safe (Klojzy-Karczmarczyk & Mazurek 2015). The obtained results show that the value of the pH of the aqueous extract and its content of heavy metals is lower than the one acceptable in sewage. Only the value of sulphates exceeds the acceptable one (1,354 mg $SO_4 \cdot dm^{-3}$, while the accepted value is 500 mg $SO_4 \cdot dm^{-3}$).

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

Kind of pollution	Post-flotation waste [mg·dm^{-3}]	Acceptable value according to [23] [mg·dm^{-3}]	Kind of pollution	Post-flotation waste [mg·dm^{-3}]	Acceptable value according to [23] [mg·dm^{-3}]
pH	7.85	6.5-9	Cadmium	0.0214	0.2
Sodium	1.48	800	Selenium	< 0.02	1
Potassium	2.75	80	Antimony	0.00023	0.3
Calcium	499.9	no requirements	Aluminium	0.002	3
Magnesium	33.2	no requirements	Chromium	0.004	0.5
Strontium	0.602	no requirements	Molybdenum	0.015	1
Manganese	2.039	no requirements	Titanium	< 0.002	1
Zinc	0.761	2	Arsenic	0.0012	0.1
Copper	0.0017	0.5	Chlorides	2.1	1,000
Nickel	0.006	0.5	Sulphates	1,354	500
Cobalt	0.0044	1	Cyanides	< 0.01	0.1
Lead	0.0024	0.5	Sulphides	< 0.05	0.2
Mercury	0.0001	0.03	COD	< 100	125

Because the concentration of sulphate ions in the leachate has been exceeded, direct addition of this waste to the ground in the process of biological reclamation is impossible. Therefore, it was checked whether reduction in the concentration of sulphate ions by blending waste with soil is possible. In the blend with soil, waste accounted for 10-50% of the mass; the results of leachability of sulphates are presented in Table 4. For the blend of soil with 10% of waste the concentration of sulphates is within the required limits. Importantly, in soil alone the leachability of sulphates was almost half of the acceptable value – 241 mg·dm^{-3}, the maximum acceptable level is 500 mg·dm^{-3}.

Table 4. The concentration of sulphate ions in the blend with waste with soil [mg·dm^{-3}]

Pollution	Blends of waste with soil					
	100% soil	90% soil + 10% waste	80% soil + 20% waste	70% soil + 30% waste	60% soil + 40% waste	50% soil + 50% waste
Sulphates	241	439	636	782	876	972

Pursuant to the Ordinance of the Minister of Environment of 1st September 2016 on the manner of conducting soil surface pollution assessments (Journal of Laws of 2016, item 1395), the concentration of substances causing particular risk for the soil surface should not be exceeded. For zinc, lead, and copper, the maximum allowed concentrations were exceeded in waste (Table 5). Due to high levels of these metal concentrations, detailed studies of their impact on plant growth were carried out.

Table 5. Acceptable content of elements in soil (Journal of Laws of 2016 item 1395) and in waste

Substance	Soil – maximum acceptable value [mg·kg^{-1}] (Journal of Laws of 2016, item 1395)						The studied waste [mg·kg^{-1}]
	Group I	Group II-1	Group II-2	Group II-3	Group III	Group IV	
Arsenic (As)	25	10	20	50	50	100	0.711
Barium (Ba)	400	200	400	600	1,000	1,500	237.6
Chromium (Cr)	200	150	300	500	500	1,000	25.6
Tin (Sn)	20	10	20	40	100	350	0.003
Zinc (Zn)	500	300	500	1,000	1,000	2,000	25,084
Cadmium (Cd)	2	2	3	5	10	15	0.109

Table 5. cont.

Substance	Soil – maximum acceptable value [mg·kg^{-1}] (Journal of Laws of 2016, item 1395)						The studied waste [mg·kg^{-1}]
	Group I	Group II-1	Group II-2	Group II-3	Group III	Group IV	
Cobalt (Co)	50	20	30	50	100	200	5.097
Copper (Cu)	200	100	150	300	300	600	460.5
Molybdenum (Mo)	50	10	25	50	100	250	0.134
Nickel (Ni)	150	100	150	300	300	500	33.937
Lead (Pb)	200	100	250	500	500	600	6,064
Mercury (Hg)	5	2	4	5	10	30	0.027

First, the test of the phytotoxicity of aqueous extract of waste towards *Lepidium sativum* was carried out. It did not show any toxic impact on the plants. A stimulation of the development of the aerial parts of plants was observed with an increase in the concentration of aqueous extract in the medium, as compared to control objects (Fig. 2a). In the case of assessment of the rhizosphere, stimulation of the growth of roots was also found. The highest mean growth value was observed in concentration equaling 12.5%. Then a slight decrease of the roots growth with the growth of the concentration of aqueous extract from waste was observed, but the mean values were higher than the mean value in control (Fig. 2b). One should emphasize that the development of roots in all the experimental objects was significantly higher than in control objects without the addition of the aqueous extract (Fig. 2b and 3), and the rhizosphere was more developed.

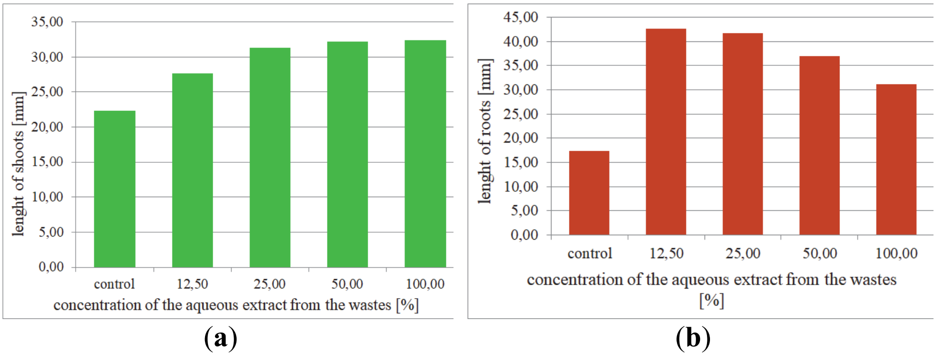


Fig. 2. Mean growth of *Lepidium sativum* in subsequent experimental objects (various concentrations); (a) aerial parts, (b) roots

In experimental objects in the concentration of aqueous extract equalling 25% or higher, the length of stems was significantly different than in control objects, as 3. presented in Fig. 3.

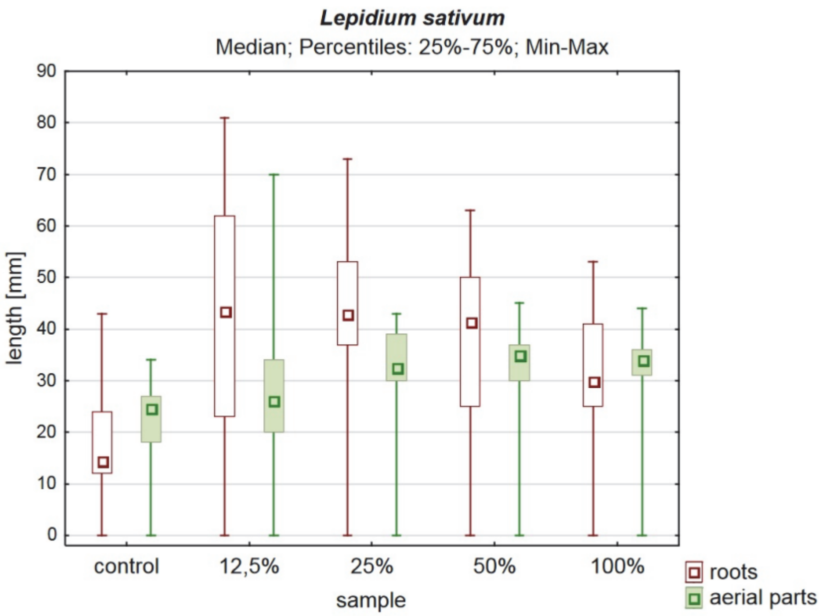


Fig. 3. The growth of *Lepidium sativum* after 72 hours of incubation of subsequent objects (for the studied concentrations)

The mean value and standard deviation for control sample and all dilutions are presented in Fig. 4. The highest values of standard deviation (25.7 for roots and 15.1 for steams) occur in the 12.5% aqueous extract concentration.

Because toxicity assessment should not be based on only one test type, pot tests were also carried out. Assuming that waste would not be a good substrate for plants, we carried out all experiments on different blends of this waste with the soil. Pot experiments revealed that the addition of waste to the medium in an amount of up to 30% caused the stimulation of germination in both species of test plants, while for higher concentrations (above 30%) seed germination in *Sinapis alba* and *Lepidium sativum* was observed to halt (Fig. 5 and Fig. 6).

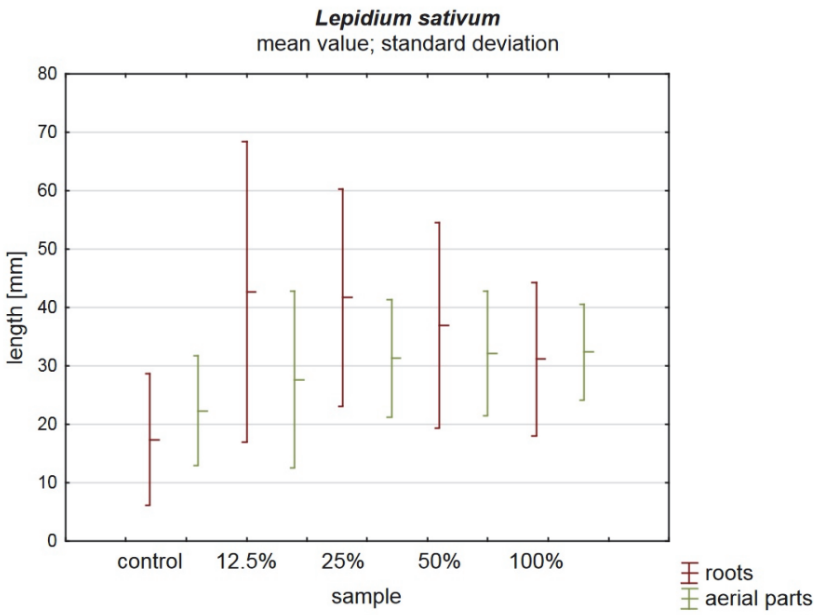


Fig. 4. Standard deviation of the growth of *Lepidium sativum* after 72 hours of incubation of subsequent objects (for the studied concentrations)

The addition of the examined waste to the medium in the amounts of 10, 20 and 30% was significantly beneficial for the development of the aerial parts of *Sinapis alba* compared to control objects cultivated on the universal medium. The limitation of the plant growth was observed for waste concentrations 40-50% in the medium, as was shown in Fig. 7a.

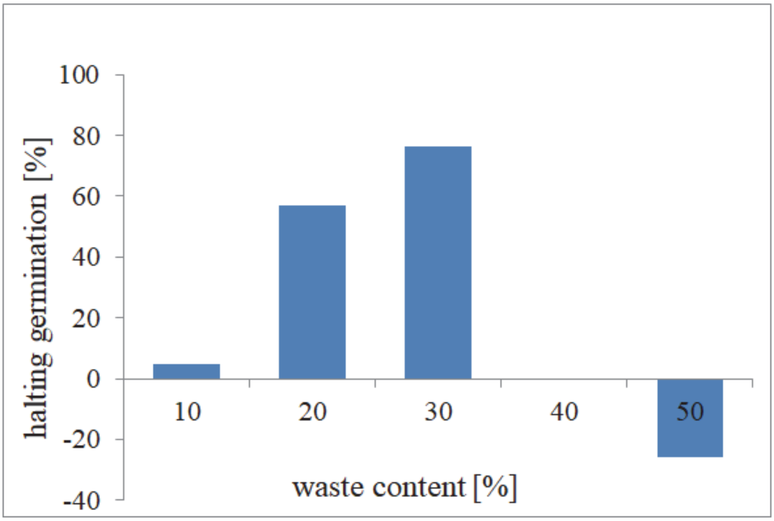


Fig. 5. Halting germination of *Lepidium sativum* in subsequent experimental objects (the percent of inhibition)

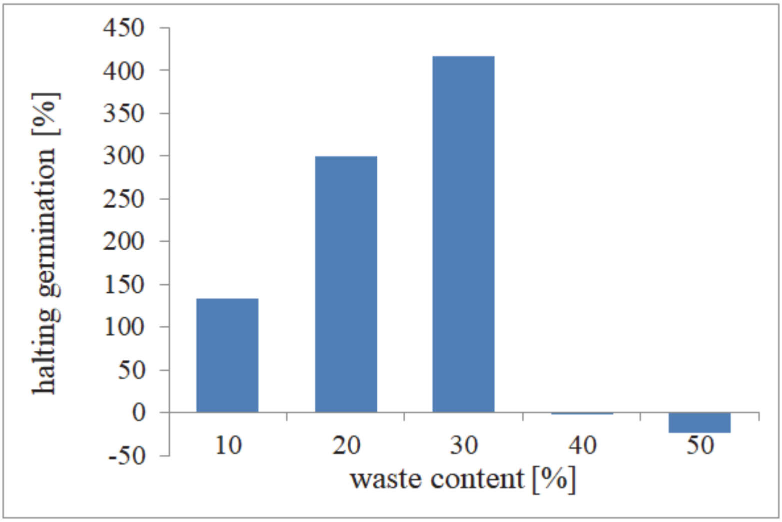
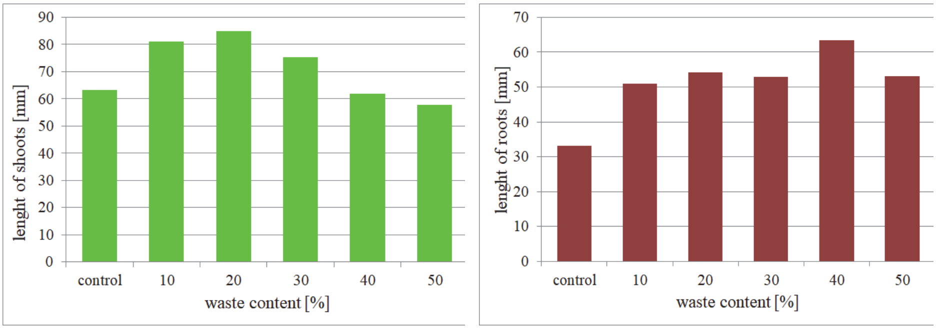


Fig. 6. Halting germination of *Sinapis alba* in subsequent experimental objects (the percent of inhibition)



(a) **(b)**

Fig. 7. Mean growth of *Sinapis alba* in subsequent experimental objects: (a) aerial parts; (b) roots

The addition of the examined waste to the medium was also beneficial for the development of the rhizosphere of *Sinapis alba*, the roots of test plants were longer (mean value) and more developed compared to plants from control objects (Fig. 7b). However, the Kolmogorov–Smirnov test did not show any significant differences between control objects and objects with 20% and 30% waste addition (Fig. 8). Significant differences were observed between the control and remaining objects.

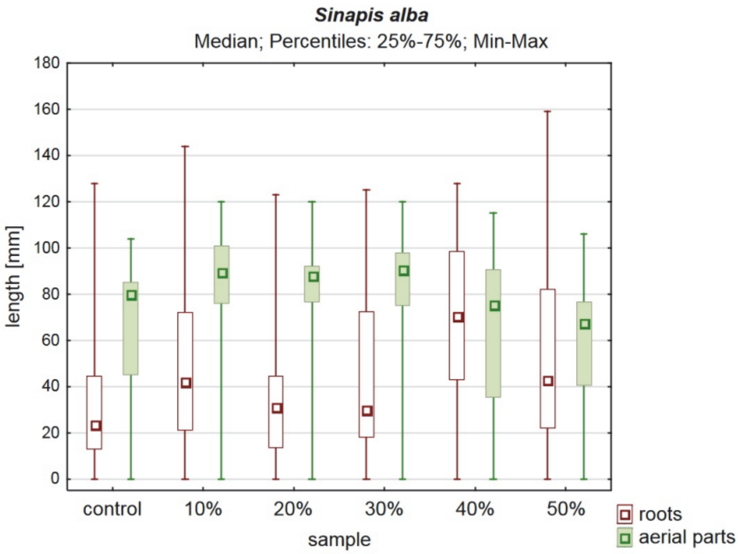


Fig. 8. The growth of roots and stems of *Sinapis alba* on the 7th day of the experiment on the medium with various additions of waste

Mean value and standard deviation for the control sample and all concentrations of waste in the medium are presented in Fig. 9. The highest values of standard deviation (42.5 for roots and 38.0 for steams) occur in concentrations of waste equaling 40% and 30% respectively.

A significant impact of the media containing the addition of waste on the biomass growth was observed (summary length of the aerial parts and roots) in *Sinapis alba* in the amount of up to 40% (Fig. 7 and 8). As already mentioned, the higher content of waste in the medium halted the germination of plants (after three days from sowing), but the growth of plant biomass, also for the concentration of 50%, was comparable with control objects.

In the case of the second test plant, *Lepidium sativum*, a beneficial impact of the content of waste in the medium on the development and growth of plants was found. For the content of 30% of waste in the medium, a significant stimulation of the growth of aerial parts was observed (Fig. 10a and 11), and the development of the rhizosphere was significantly higher in the objects with greater participation of waste (30% and 40%) than in control objects (Fig. 10b and 11).

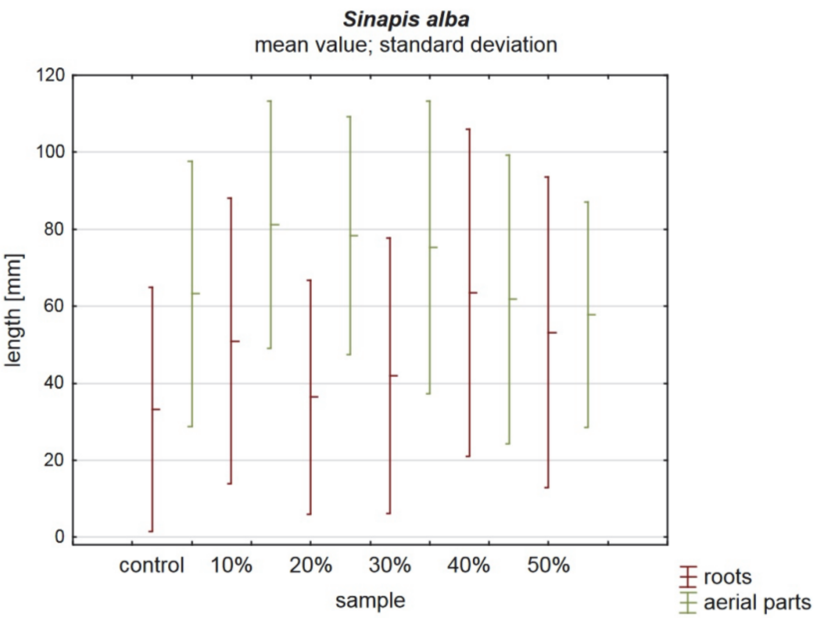
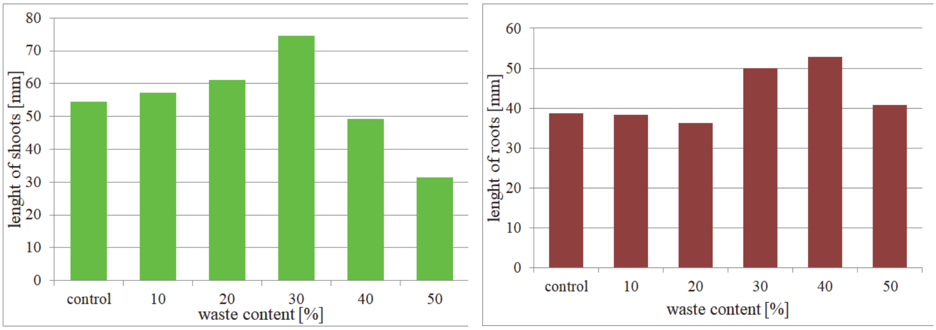


Fig. 9. Standard deviation of the growth of *Sinapis alba* on the 7th day of the experiment on the medium with various additions of waste



(a) (b)

Fig. 10. Mean growth of *Lepidium sativum* in subsequent experimental objects: (a) aerial parts, (b) roots

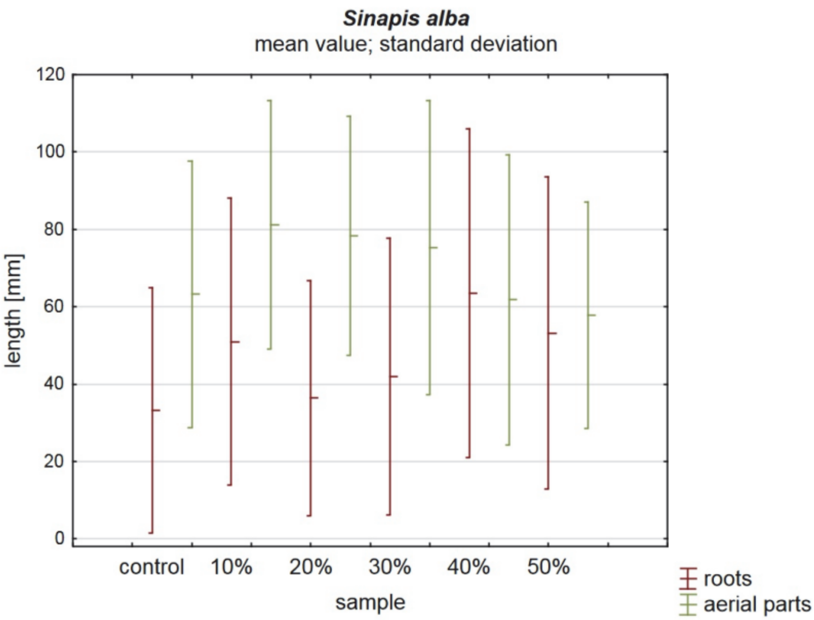


Fig. 11. The growth of roots and stems of *Lepidium sativum* on the 7th day of the experiment on the medium with various additions of waste

The mean value and standard deviation for the control sample and all concentrations of waste in the medium are presented in Fig. 12. The highest values of standard deviation (31.9 for roots and 32.2 for steams) occur in concentrations of waste equaling 40% and 10%, respectively.

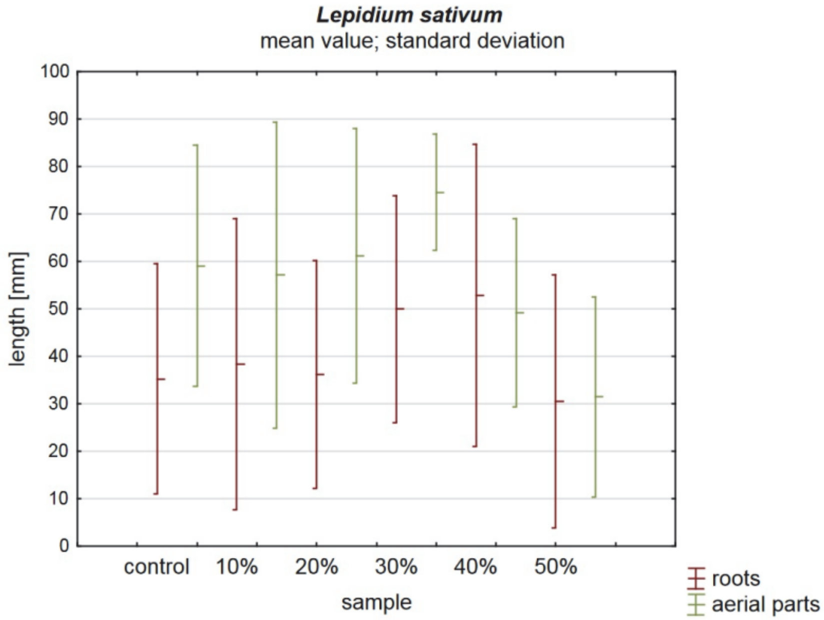


Fig. 12. Standard deviation of the growth of *Lepidium sativum* on the 7th day of the experiment on the medium with various additions of waste

The mean growth of the aerial parts and roots of *Lepidium sativum* was the highest in the group with 30% content of waste in the medium (the Kolmogorov-Smirnov test showed significant differences between this group and the control sample). The addition of 50% waste caused a marked decrease in the plant biomass growth, compared to the control of objects and objects of the lower content of waste.

4. Discussion

The studied waste is a fine-grained material. Its granulation is typical for post-flotation waste. It is the result of grinding of the waste before the flotation process. Considering grain composition, this waste can be used to produce a blend added to the soil during the biological reclamation process. The content of radioactive isotopes is also low and does not exceed the admissible values specified in Polish law for materials used for surface levelling.

When analyzing the results of ion concentrations in the leachate, it was found that only concentration of sulphates exceeded the acceptable values (1,354 mg $SO_4 \cdot dm^{-3}$, while the accepted value is 500 mg $SO_4 \cdot dm^{-3}$) according to Polish law. Other parameters were within the range of permissible standards.

However, 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. It should be stressed that the level of sulphate ion concentration in the blend also depends on the concentration of these ions in the subsoil. Therefore, one should carry out studies with the ground, which will be applied in engineering works, to select a proper proportion of the blend. If such a blend meets all the quality requirements, it can become a product that will be used in reclamation. In our case, for the blend of soil with 10% of waste, the concentration of sulphates in the leachate was within the required limits. It may seem that a 10% waste addition is low, but it should be mentioned that in soil alone the leachability of sulphates was almost half of the acceptable value – 241 $mg \cdot dm^{-3}$. The concentration of metals in the leachate was within acceptable limits also, despite the high content of these metals in the waste. It should be noted that the studied waste had a high pH value, which can inhibit metals from being discharged into aqueous solutions. Excessively high metal concentrations in the analysed waste (according to Polish law) are also the reason why this waste (without dilution) cannot serve as the final product in the reclamation process - it may be toxic for the environment, including plants.

The phytotoxicity test with *Lepidium sativum* did not show any toxic impact of the waste aqueous extract on plants. Stimulation effects were observed in all samples with the addition of aqueous extract, as compared to control objects. In experimental objects, where the concentration of aqueous extract was 25% or higher, the lengths of roots and stems were significantly different from those in control objects. The highest mean value of root lengths was recorded for concentration 12.5%, while the highest mean value of stem lengths was recorded for concentration 100%. Pot experiments with *Sinapis alba* and *Lepidium sativum* showed that a small addition (up to 30%) of waste to the medium caused stimulation of seed germination, but higher concentrations (above 30%) halted germination. Similarly, in the case of early plant growth, beneficial effects were observed when the concentration of waste in the substrate did not exceed 30%. In experimental objects with higher waste concentrations, the shoots were shorter than in the control objects. Based on the toxicity tests carried out, we can assume that the waste addition to the subsoil in the amount of up to 30% will be beneficial for plant growth.

5. Conclusions

The assessment of the properties of the examined flotation waste of lower content of metals was to identify the possibility of applying this waste for engineering purposes, including especially its ecological utilization, e.g. in production a material (subsoil) for natural land reclamation. The obtained results were referred to the requirements defined in the legislation connected with the proposed direction of the utilization of this waste.

The conclusions from conducted research are as follows:

1. The analysis of the granulometric composition showed that the examined material of granulation corresponds to silty sands. In terms of the content of radioactive isotopes, this waste can be used in area levelling for development.
2. When comparing waste leachability with legal requirements for wastewater released to the soil, the excess of the load of sulphate ions was found. However, selecting a proper participation of waste in the blend with the ground, the required level of content could be obtained. In a similar way the decrease in the concentration of zinc, lead and copper can be obtained in the blend of waste with the ground.
3. The phytotoxicity test of aqueous extract with waste towards the test plants showed the stimulation of their growth compared to control objects. One should notice, however, that at the concentration of aqueous extract with waste of the values of 50% and higher, the development of the plant rhizosphere was slightly limited, compared to lower concentrations.
4. As a result of the pot experiments, it was found that the content of waste in the amount of 10-30% in the medium stimulated the germination of plants, as compared to the control objects, while the higher participation of waste in the blend caused the halting of the plant germination. Similar reactions were observed in the case of both species of test plants.
5. Observations of early growth revealed the stimulation of the growth of the aerial parts in test plants in experimental objects up to the content of 30% of waste in the medium. In the case of the rhizosphere, no halting effect was observed in roots.
6. Despite a relatively high level of the concentration of metals in the waste and a high leachability of sulphate ions, it is possible to select such a dose of waste for release to the ground, which will stimulate plant development.
7. The waste tested can be used in production of material (subsoil) for natural land reclamation.

Test plant species used in the experiments are species recommended for the tests of the phytotoxicity assessment (Traczewska 2011). It is reasonable to continue vegetation experiments based on plant species applied in biological reclamation (with the exception of agricultural remediation), biological lining of engineering objects or native species accustomed to local habitat conditions.

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Abstract

Rapid technological development in the second half of the 20th century has led to the production of large amounts of waste, which have been collected for years in landfills. The municipal solid waste deposited in landfills and waste from the mining and metallurgical industries constitutes a major environmental problem, but on the other hand these types of waste serve as a reservoir of raw materials, therefore, they are becoming more and more popular as a source of raw materials. Obtaining raw materials from landfills of waste requires technological operations, mainly known from open cast mining, and the application of processing technologies. As a result of landfill mining metal concentrates, construction materials or fuel are obtained; on the other hand often post-processing waste can be formed, which should be utilized, to reduce their nuisance to the environment.

Depending on their physicochemical properties, they can be used, e.g. in construction, road engineering, mining or land reclamation.

This paper presents research on the possibilities of using post-flotation waste from zinc and lead ores, deposited in old repositories, for land reclamation after waste reflotation. For this purpose, the physical and chemical properties of waste were examined, such as: grain composition, chemical composition, content of radioactive isotopes and leaching. To determine the ecotoxicity of the investigated wastes, vegetative experiments were carried out. These studies allowed the assessment of the impact of the tested wastes on selected test plant species. Among other things, the impact of waste on such physiological processes as germination of seeds and the growth of plants (roots and above-ground parts) were investigated. Despite relatively high metal concentration levels in waste and a high leachability of sulphate ions, a small dose of waste, which will be added to soil will stimulate plant growth. It was found, that the addition of waste to the substrate in quantities of 10-30% have accelerated germination of plants compared to control objects. In the case of higher waste content (over 30%) germination inhibition was observed. Similar reactions were observed for both test plant species. It was found that it is possible to select such a dose of waste for release to the ground, which will stimulate plant development. So, there is a possibility of using the tested waste to produce material (substrate) for natural land reclamation. The natural use of industrial waste can substantially contribute to solving the problem of the negative impact of deposited waste on natural environment.

Keywords:
ore processing waste, post-flotation waste, reclamation, raw material recovery, phytotoxicity, waste utilisation

Ocena możliwości wykorzystania odpadów poflotacyjnych z rud Zn-Pb jako materiału do naturalnej rekultywacji gruntów

Streszczenie

Szybki rozwój technologiczny, który nastąpił w drugiej połowie XX wieku, doprowadził do powstania dużych ilości odpadów, które gromadzone były przez lata na składowiskach. Stałe odpady komunalne, odpady z przemysłu wydobywczego i metalurgicznego zdeponowane na składowiskach stanowią poważny problem środowiskowy, ale jednocześnie są także istotnym rezerwuarem surowców i cieszą się coraz większym zainteresowaniem. Pozyskanie surowców ze składowisk wymaga stosowania operacji technologicznych z zakresu górnictwa odkrywkowego, a także zastosowania procesów przeróbczych. W efekcie tych procesów otrzymywane są koncentraty metali, materiały budowlane lub paliwo. Niestety, w procesach tych mogą także powstawać odpady przeróbcze, które należy w odpowiedni sposób zagospodarować, tak, żeby zmniejszyć ich uciążliwość dla środowiska. W zależności od właściwości fizykochemicznych odpadów wydobywczych i przeróbczych, można je stosować, np. w budownictwie, drogownictwie, górnictwie lub rekultywacji gruntów.

W pracy przedstawione zostały wyniki badań związanych z oceną możliwości przyrodniczego wykorzystania odpadów poflotacyjnych z rud cynku i ołowiu, zdeponowanych na starych składowiskach, po poddaniu ich przeróbce w celu odzysku z nich metali. Zbadano właściwości fizyczne i chemiczne odpadów, takie jak: skład ziarnowy, skład chemiczny w tym zawartość izotopów promieniotwórczych oraz wymywalność. W celu określenia ekotoksyczności badanych odpadów przeprowadzono doświadczenia wegetacyjne, które pozwoliły na ocenę wpływu badanych odpadów na wybrane gatunki roślin testowych. Badano między innymi wpływ odpadów na takie procesy fizjologiczne jak kiełkowanie nasion oraz wzrost roślin (korzeni i części nadziemnych). Wyniki przeprowadzonych doświadczeń wykazały, że pomimo stosunkowo wysokich poziomów stężenia metali w odpadach oraz wysokiej wymywalności jonów siarczanowych, niewielki dodatek odpadów do podłoża, na którym uprawiane były rośliny, miał korzystny wpływ na kiełkowanie roślin i przyrost ich biomasy. Stwierdzono, między innymi, że dodatek do podłoża odpadów w ilości 10-30% stymulował kiełkowanie roślin w porównaniu z obiektami kontrolnymi. W przypadku większej zawartości odpadów zaobserwowano zahamowanie kiełkowania. Podobne reakcje obserwowano w przypadku obu gatunków roślin testowych. Stwierdzono, że możliwe, jest dobranie takiej dawki odpadów w podłożu, która nie spowoduje wprowadzenia do gleby nadmiernych ilości zanieczyszczeń, natomiast korzystnie wpłynie na rozwój roślin. Istnieje więc możliwość wykorzystania badanych odpadów do produkcji materiału (podłoża) do naturalnej rekultywacji gruntów. Naturalne wykorzystanie odpadów przemysłowych może znacząco przyczynić się do rozwiązania problemu negatywnego wpływu składowanych odpadów przemysłowych, po przeróbce rud metali, na środowisko.

Słowa kluczowe:
odpady z przeróbki rud metali; odpady poflotacyjne, rekultywacja,
odzyskiwanie surowców; fitotoksyczność; utylizacja odpadów