Possibilities for Use of Vermiculite in Recultivation of Embankments Obtained as a Result of the Deposit of Mining Waste from the Extraction of Copper Ores

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Abstract. The present study examines the possibilities for vermiculite usage for recultivation of copper mining waste embankment. For this purpose, a laboratory study was carried out. The study which included the mixing of mining waste with different ratios of vermiculite and adds of other soil improvers (fertilizers and lime) with different norms. As a result is, it is observed that the vermiculite addition in larger quantities did not affect the pH of the substrate. The content of major pollutants in the waste - Cu and As, remains relatively high - over the maximum permissible concentrations. Independently of the added vermiculite, it is necessary to apply calcium materials and fertilizers to improve substrate properties.

1. Introduction
In the process of mining, spaces disturbed by direct extraction and occupied by embankments are formed and rapidly increase [1]. Embankments are characterized by heavy metals and metalloids content above the maximum concentration limits for the respective zonal soils, which poses a serious risk to the environment and human health due to the pollutant properties - toxicity, mobility, soil and plant accumulation ability and migration into the food chain [2-4]. In these cases it is necessary to introduce soil improvers to immobilize the pollutants.

In recent years, vermiculite has been a widely used mineral for the adsorption of metal cations [5-7]. Vermiculite is a three-layer clay mineral - hydrated magnesium-ferrous aluminosilicate. Its structure consists of two tetrahedral silicate layers and an interlayer space of an octahedral layer containing aluminum and iron. Vermiculite is characterized by: porous structure, high sorption capacity, high ion exchange capacity, low thermal conductivity and neutral pH. Many researchers believe that due to the content of elements such as calcium, magnesium, potassium, iron and silicon, vermiculite is a natural biostimulant for plant growth. Vermiculitis exhibits good adsorption capacity for heavy metal divalent ions [8], especially suitable for the adsorption and removal of potentially toxic cations such as Cu²⁺, Pb²⁺, Cd²⁺, Zn²⁺ и Ni²⁺ [9,10] due to its high cation exchange ability (120-150 meq/100g). The adsorption of metal ions from vermiculite decreases with decreasing pH and increasing ionic strength. An exception is arsenic, for which there is no evidence that it is adsorbed by vermiculite [11].

This study aims to determine the possibility of using vermiculite - alone and in combination with other ameliorants (NPK fertilizers and CaO) in biological recultivators of copper mining storage
facilities for the immobilization of copper and arsenic in substrates from embankments and changes in their fertility.

2. Materials and methods
The study materials and methods are closely aligned with the stated objectives. Those elements that we aim to eliminate or neutralize in soil-forming materials are investigated.

2.1. Materials
To achieve the purpose of investigation samples were taken from embankments for the storage of mining waste from the extraction of copper ores, which examined the elements and their properties, creating a harmful environment for flora and fauna.

2.2. Methods
The methods used in the study are analytical methods and methods of vegetation experience. Chemical characterization was investigated to characterize the mine waste and determine the state of the substrate after the vermiculite treatment. The analyzes include: potentiometric determination of soil acidity (ISO 10390); total nitrogen by the Kjeldahl method. (ISO 11261); K₂O and P₂O₅ - by the methods of Petko Ivanov; determination of copper and arsenic content by combustion in aqua regia and ICP-OES.

After clarifying the agrochemical properties of the substrates and vermiculite, a vegetation experiment was conducted with different amounts of vermiculite - 5, 10 and 20%, mixed with mineral fertilizers and CaO. In plastic cups with a capacity of 1.5 l for carrying out the vegetation experiment, 1 kg of substrate was filled with the appropriate amount of vermiculite (5%, 10% and 20%). For each vermiculite amount, 4 different variants were prepared - substrate + corresponding amount of vermiculite (%V), substrate + corresponding amount of vermiculite + NPK fertilizer (%V + F), substrate + corresponding amount of vermiculite + CaO (%V + CaO), substrate + corresponding amount of vermiculite, + NPK fertilizer + CaO (%V + F + CaO). A control sample was set up without the addition of vermiculite and other ameliorants. In each of them, Lolium perenne L. was sown and cultivated for 5 months, so as to allow sufficient time for contact and grass growth in each variant needed for the adsorption of heavy metals.

3. Results
3.1. Characteristics of vermiculite
The acidity data and the main elements characterizing the vermiculite were provided by the company owner of the vermiculite deposit as part of the internal control of the raw material. The silicate analysis of the raw material is presented in Table 1.

| Indicators | Value, % | Indicators | Value, % | Indicators | Value, % |
|------------|----------|------------|----------|------------|----------|
| pH         | 6.26     | TiO₂       | 0.35     | K₂O        | 0.92     |
| SiO₂       | 41.14    | Na₂O       | 0.23     | P₂O₅       | 8.34     |
| Al₂O₃      | 11.62    | MnO        | 0.10     | NiO        | 0.15     |
| CaO        | 2.56     | ZnO        | 0.14     | Cr₂O₃      | 0.26     |
| MgO        | 27.79    | CuO        | 0.01     |            |          |

Data from analyzes of vermiculite show that it does not contain dangerous substances in quantities above the limit values. Vermiculitis has a slightly acid reaction, and the value of the elements characterizing the cation-exchange capacity indicates that the vermiculite has a high levels of base saturation. The element of silicon is in the highest quantities, followed by magnesium, aluminum and phosphorus. The amount of calcium is much smaller than magnesium, while in natural soils, the amount of calcium is usually several times higher than magnesium. However, from a chemical point

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of view, it should be noted that imported into the soil or soil-forming substrate, it will not adversely affect them. In addition, it can be noted that the phosphorus content is much higher than in natural soils. The potassium content is also high in comparison to the average in the soil. The content of potassium absorbed by the plants is high, which would be beneficial for the plants. All other elements are in quantities that are relatively indifferent to soil formation and, through their chemical properties, do not adversely affect soils, vegetation and the environment. These data indicate that phosphorus and potassium fertilization may not be required when vermiculite is introduced into the soil. The data from the analyzes of the vermiculite raw material indicate the potential for its use in the reclamation of landfills.

3.2. Characteristics of mine waste from the embankments
Data on the chemical properties of the mine waste intended for vegetation experiment: acidity, electrical conductivity, nutrient content, content of copper and arsenic are presented in Table 2. The classification for salinity and content of nutrient and content of alkaline earth elements is made by Penkov (1996) [12].

| pH (H₂O) | Conductivity | N | P₂O₅ | K₂O | Mg | Ca | Na | Cu | As |
|----------|--------------|---|------|-----|----|----|----|----|----|
| -        | µS/cm | % | mg/100g | mg/100g | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| 3.6      | 136  | 0.089 | 0.51 | 2.0 | 734 | 4 | 384 | 599 | 19.20 |

As can be seen from the data in Table 2, the mining waste is characterized by an exterior acidic pH - 3.6. Low pH is a prerequisite for the mobilization of heavy metals contained in mining waste and can lead to a number of environmental problems [13]. Moreover, at these pH values, plant nutrition is characterized by an excess of micronutrient uptake [14]. Additional ameliorants are required to increase the pH value.

According to the value of the electrical conductivity, no salinity was observed in the samples tested, this is because, as the data in the table shows, the sodium content is scarce. The magnesium content is higher than that of calcium. However, the waste is poorly stored in calcium and very poorly stored in magnesium. The waste is poor in nitrogen, poorly stored in potassium and phosphorus. The analysis of the nutrient content implies the need for additional fertilization, since in vermiculite the content of P₂O₅ is 8.34% and the content of potassium is only 0.92%. The content of copper and arsenic exceeds the maximum permissible values (MPVs for industrial territories Cu - 500 mg/kg, As - 10 mg/kg according to Regulation 3 [15]). High levels of metals suggest toxicity to some microorganisms [16,17], as a result of which the mineralization of the soil and its ability for self-cleaning are impaired, the conditions for the development of vegetation also deteriorate.

3.3. Vegetation experience
The vegetation experience was conducted to identify the possibility of using vermiculite as a soil improver in the reclamation of embankments and the quantities required for the purpose, and more precisely, the most appropriate ratios of ameliorants to the basic soil-forming material and the corresponding ameliorations. At the end of the vegetation experience, analyzes of the substrates in the root habitat of the ryegrass were made. The vegetation experiment was carried out in closed containers, from which the water with which they are watered does not flow. Liming rate was determined by adding an aqueous solution of pure CaO to neutralization of the substrate - 0.5 g/ml. Based on the nutrient analysis, a fertilization rate of 0.05 g/ml was determined. The vegetation experiment is carried out for 5 months so as to allow sufficient time for contact between the vermiculite and the substrates.
3.4. Analyzes of soil-forming substrates at the end of the vegetation experiment

Figure 1 shows that the addition of vermiculite does not affect the pH value, despite the content of alkaline earth elements in it. The experiment also proves that the substrates need liming. The graph shows that in each of the variants, only in the case of CaO addition, an increase in pH from slightly acidic to neutral is observed, under which optimal conditions for plant nutrition are created.

![Figure 1. pH of the substrates at the end of the vegetation experiment.](image)

Figure 2 and Figure 3 show the contents of the basic nutrients in the studied substrates in the various applications of ameliorants. Figure 2 shows that, despite fertilization, the nitrogen stock is very small to small. The introduction of more vermiculite does not increase the amount of nitrogen. Compared to the control sample a decrease in the amount of total nitrogen was observed. The data (Figure 3) show that the uptake of nutrients from mineral fertilizers is not always dependent on the acidity of the substrates and is almost unaffected by the presence of vermiculite. Potassium remains in the highest amounts in the substrate, in most cases where the pH is completely in the neutral range. In a few variants, the phosphorus content is in greater quantities - probably the element is in a water-soluble form and is absorbed by the grass root system. Only in the samples with 20% vermiculite, fertilizers and liming concentrations of potassium and phosphorus exceed those in the control sample.

![Figure 2. Total nitrogen content of the substrates at the end of the vegetation experiment, %](image)

![Figure 3. Content of P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O substrates at the end of the vegetation experiment, mg/kg.](image)

Of the metals and metalloids, only the content of copper and arsenic was examined as indicators of the deposit. Data on their content at the end of the vegetation experiment are presented in Figure 4 and Figure 5. The amount of copper is reduced compared to the control sample. The lowest concentrations were observed in the samples treated with 20% vermiculite, however, the values were close to the
MPV – 500 mg/kg. In all substrates – control, with or without vermiculite, copper is above the maximum levels, except for samples with 10% vermiculite and liming. There is no direct correlation between copper content and meliorations. The likely decrease in Cu content is due to its extraction and accumulation in the plant mass. It is very likely that in samples that have created better conditions for the development of vegetation, the amount of Cu in the soil has decreased due to the development of more biomass.

The content of arsenic in all samples from the mine is between 15.23 and 23.71 mg/kg, with the highest amounts in the samples with 20% vermiculite and the smallest without vermiculite or 5% vermiculite. Whereas, that arsenic is absorbed by plants regardless of the acidity of the soil substrate, we can assume that larger amounts of vermiculite retain larger amounts of arsenic and prevent for arsenic absorption from the herbs. Although part of the samples shows a decrease in value compared to the control sample in all samples has an arsenic concentration exceeding the MPV – 10 mg/kg.

4. Conclusion
In conclusion from the vegetation experiment conducted, we can say that vermiculite does not affect the acidity of the substrates.

In limed and fertilized variants, the potassium and phosphorus content of the substrates is higher, while the nitrogen content is reduced. This suggests that from these variants the elements are absorbed more slowly by the plants. Regardless of the amount of vermiculite imported, it is necessary to bring in neutralizing calcium materials to raise the pH and immobilize the heavy metals. Fertilization with mineral fertilizers is also a necessary reclamation activity in biological reclamation.

The present study confirms that vermiculite has no effect on As content, despite additional meliorations applied. There is a decrease in Cu content, which is probably related to the development of vegetation in each of the samples. Further investigations are needed to determine the causes for the reduction of the copper content.

Through the vegetation experience conducted under controlled conditions, the overall role of vermiculite in the remediation of embankments with the acid reaction of bulk materials cannot be demonstrated. It is necessary to continue the experiments by testing the vermiculite and the reclamation applied to the vegetation experience through.

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