Vermiculite-lizardite ameliorants from mining waste

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Abstract. Beneficiation products of phlogopite mining waste have been studied in terms of their use in soil engineering to improve soil hydro-physical and physicochemical properties. Vermiculite and lizardite minerals, parts of the obtained products, can interact with acid solutions and can be used to reduce the acidity of agricultural soils as well as to rehabilitate acidified industrial landscapes. The plant testing results indicate a positive effect of vermiculite-lizardite materials on plant growth and development.

1. Introduction

The negative effects of deposit development include disturbance of natural landscapes resulting from the displacement of large amounts of overburden rocks, alienation of territories for waste storage, and pollution of adjacent water and soil objects due to particles from the disintegrated rock mass.

On the other hand, overburden rocks can be recycled if their composition allows effective use in the national economy. The given paper suggests the use of products of phlogopite mining waste processing in Kovdor in the Murmansk region that contains vermiculite and serpentine minerals as components of soil structures.

Ameliorants improve and condition degraded, including polluted, soils. The products containing vermiculite and serpentine mineral lizardite can be used for land-improvement purposes because of their main mineral components’ ability to interact with acidic solutions; to adsorb copper, nickel, and other metals [1, 2]; and to increase the amount of magnesium and silicon available for plants [3].
2. Materials and methods

Deposited vermiculite-lizardite waste from the open-pit phlogopite mine LLC “Kovdorsljud” located in the town of Kovdor in the Murmansk region of Russia (67°35′32.2″ N 30°26′51.1″ E) occupies an area of about 70,000 m² and contains several hundred thousand tons of vermiculite and lizardite [4].

The vermiculite-lizardite products were obtained by a gravitational scheme of processing vermiculite-lizardite raw materials - phlogopite mining waste. The gravitational beneficiation scheme included using a hydro separator, a spiral separator, and concentrating tables.

The granular vermiculite-lizardite product was roasted at a temperature of 700°C in an electric modular launching furnace designed by A.I. Nizhegorodov of Irkutsk National Research Technical University [5, 6].

Chemical analysis was performed using an inductively coupled plasma mass spectrometer, ELAN 9000 DRC-e (Perkin Elmer). The acid-neutralizing ability (B, mg-eq g⁻¹) of vermiculite-lizardite products was evaluated according to a previously developed method for determining the activity of thermally activated serpentine minerals [7]. The method is based on acidimetric titration of samples, which were placed in a hydrochloric acid solution with a concentration of 0.02 mg-eq l⁻¹, stirred for 3 hours, and then kept without stirring. The standard total duration of interaction is 24 hours. Because the interaction of powders with an acid solution is influenced by the particle’s size, the dynamics of the change in the system’s state were observed for 30 days. The suspension was filtered through a “blue ribbon” filter; the acid remaining in the solution was titrated with a Na₂CO₃ solution with a concentration of 0.01 mg-eq g⁻¹.

The authors performed plant testing of the slime product, characterized by a high content of fine-dispersed fraction. The studies were carried out under the conditions of a short-term (9 days) laboratory experiment using tablet test systems [8] and the seeds of three plant species. The standard test cultures—Lepidium sativum, Brassica juncea, and Festuca rubra—were used. In the reference option, seeds contacted with distilled water; in the experimental version, seeds were watered with an aqueous extract from the slime product, obtained at a ratio of 20 g of material per 100 ml of water. The authors determined the germinating ability of seeds, their energy and seedling vigor, and the length of the primary root to be indicators of toxicity.

3. Results and discussion

3.1. Mineral composition of obtained materials

The initial mining waste was divided into three products: granular, slime, and offgrade (so-called processing “tailings”). Figure 1 shows a general view of the products. The distribution of the main minerals in the processing products is presented in table 1. The mineral content in the products is indicated in mass percent.

![Figure 1. A general view of final processing products at 15x zoom: a) granular product, b) slime product, and c) tailings.](image-url)
The granular product is a material with a particle size up to 2 mm and is mostly white (the color of lizardite). The content of target lizardite and vermiculite minerals is 31% and 33%, with an extraction of 52% and 60%, respectively (table 1). The product contains about 36% impurities, predominantly particles of olivine-pyroxene rocks and fine-crystalline phenites or syenites as well as diopside, quartz, and feldspar particles. The yield of granular product is 34.4%.

The slime product is a fine-grained material with a particle size up to 0.3 mm. The content of lizardite and vermiculite is approximately the same and amounts to about 30% each. In this product, vermiculite does not contain packs and is represented by small thin leaves. The yield of the slime product is 22%, with the recovery of lizardite and vermiculite 32–35%.

The tailings contain a small amount of lizardite and vermiculite (7% and 2%, respectively) and are not of interest in terms of a substrate that can change the soil’s chemical composition; however, they can be used to adjust the hydro-physical soil properties. The tailings can be used to increase the proportion of physical sand (particles greater than 0.01 mm in size), which increases the water permeability of the soil and changes its hydrological characteristics [9].

Besides initial granular material, the authors studied a thermally activated (expanded) granular product. The roasting was performed with the aim of obtaining material containing expanded vermiculite, which is widely used in agricultural engineering.

### Table 1. Parameters of gravity processing of vermiculite-lizardite waste from Kovdorsluda LLC.

| Product      | Yield | Mineral content, mas.% | Mineral recovery, % |
|--------------|-------|-------------------------|---------------------|
|              |       | Lizardite | Vermiculite | Other | Lizardite | Vermiculite | Other |
| Granular product | 34.4  | 31        | 33        | 36    | 52.5      | 60.3       | 20.3  |
| Slime product  | 22.2  | 30        | 30        | 40    | 32.5      | 35.1       | 14.5  |
| Tailings      | 43.6  | 7         | 2         | 91    | 15.8      | 4.6        | 65.2  |
| Total         | 100.0 | 20        | 19        | 61    | 100.0     | 100.0      | 100.0 |

The chemical composition of vermiculite-lizardite products is presented in table 2. The main components are magnesium and silicon (24–42%) as well as iron and calcium (4–14%). Titanium, manganese, and nickel are present as microcomponents. The chemical analysis has shown the presence of carbonates in the vermiculite-lizardite sample; the CO₂ content is about 3.8–4.8%.

### 3.2. Physical and chemical properties of obtained materials

Figure 2 presents data on the granulometric composition of vermiculite-lizardite products. The linear nature of cumulative dependence for the granular product (figure 2a), which indicates the uniform distribution of particle sizes, draws the attention. Compared to the granular product, slime product and tailings are characterized by a higher content of fine particles.

Figure 2b presents the differential curves for the granulometric composition. The data analysis shows the domination of pulverescent particles with a size of less than 0.05 mm in the slime product and the domination of fine sand (particle size 0.05–0.25 mm) in the tailings.

The moisture retaining power of the products was evaluated by such a practically important indicator as the field capacity [9]. The field capacity is the moisture of pre-saturated soil that is established after draining excess water. Field capacity of the slime and granular products is almost the same and amounts to 43–45% (table 2). Expanded vermiculite doubles field capacity of the roasted granular product up to 90%.

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### 3.3. Acid neutralization ability of obtained materials

Carbonates are minerals that are the least resistant to acidic solutions. A well-known property of serpentine minerals, including lizardite, is an ability to interact with acidic solutions. Figure 3 presents the results of the determination of the samples’ acid-neutralizing ability B (mg-eq g⁻¹).
Figure 2. Integral (a) and differential (b) curves of granulometric composition of granular (—), slime (···), and tailings (-----) products

Table 2. Properties of vermiculite-lizardite products.

| Characteristics                        | Slime product | Granular product | Granular product roasted at 700 °C |
|----------------------------------------|---------------|------------------|-----------------------------------|
| Component content (%)                  |               |                  |                                   |
| SiO₂                                   | 39.94         | 41.96            | 42.37                             |
| MgO                                    | 27.69         | 24.45            | 24.75                             |
| Al₂O₃                                  | 0.38          | 3.25             | 4.20                              |
| Fe₂O₃                                  | 14.18         | 8.81             | 8.46                              |
| CaO                                    | 4.58          | 5.96             | 6.44                              |
| TiO₂                                   | 0.15          | 0.20             | 0.36                              |
| MnO                                    | 0.49          | 0.38             | 0.20                              |
| NiO                                    | 0.25          | 0.21             | 0.14                              |
| Cr₂O₃                                  | 0.00          | 0.05             | 0.05                              |
| S                                      | 0.05          | 0.03             | 0.01                              |
| CO₂                                    | 3.81          | 4.77             | 4.03                              |
| H₂O                                    | 8.31          | 9.40             | 8.26                              |
| Physico-chemical characteristics       |               |                  |                                   |
| aB max, mg-eq g⁻¹                      | 15.48         | 14.35            | 14.68                             |
| bB 20 / B max, %                       | 86            | 71               | 78                                |
| Field capacity, mas. %                 | 45            | 43               | 90                                |

aB max - maximum value of acid-neutralizing ability estimated by the content of magnesium oxide of vermiculite-lizardite products

bB 20 - results of the experimental determination of the samples’ acid-neutralizing ability after 20 days of interaction with an acid solution
The data obtained indicate that all vermiculite-lizardite products interact with the acid solution, and the reaction proceeds slowly; equilibrium is reached within 20 to 30 days. The initial granular product is less active compared to the other two products. The relatively high activity of the slime product is explained by its high dispersion. The more intense release of the alkaline potential by the thermally activated granular product may be due to both partial amorphization of lizardite and dehydroxylation of the vermiculite surface.

Theoretically, the maximum value of acid-neutralizing ability can be estimated by the content of magnesium oxide. The degree of interaction of the reagent with the acid solution was calculated as the percentage ratio of the amount of the alkaline component that entered the neutralization reaction after 20 days to the maximum amount of the alkaline component. The calculated data are given in table 2. The highest degree of interaction of alkaline components with acid is 86%; it was fixed for a fine-dispersed slime product. With an increase in particle size, this indicator decreases to 71% for the initial granular product. Roasting the granular product results in a regular increase (up to 78%) of the interaction degree.

Table 3. Results of plant testing of the slime product.

| Indicator                  | Testing culture | Reference | Test     | Effect |
|----------------------------|-----------------|-----------|---------|--------|
| Germination energy, %      | Lepidium sativum| 32        | 44      | +12    |
|                            | Brassica juncea | 14        | 18      | +4     |
|                            | Festuca rubra   | 32        | 44      | +12    |
|                            | Lepidium sativum| 8.4       | 9.3     | +0.9   |
| Seedling vigor, unit/day   | Brassica juncea | 3.8       | 5.1     | +0.3   |
|                            | Festuca rubra   | 8.9       | 9.6     | +0.7   |
|                            | Lepidium sativum| 76        | 84      | +8     |
| Laboratory germination, %  | Brassica juncea | 34        | 46      | +12    |
|                            | Festuca rubra   | 80        | 86      | +6     |
|                            | Lepidium sativum| 3.2±2.0   | 7.7±4.8 |        |
| Root length, cm            | Brassica juncea | 2.3±1.6   | 2.6±1.9 | *      |
|                            | Festuca rubra   | 4.2±1.9   | 5.4±1.6 |        |

*Statistically significant differences between the reference and testing variants have not been established.
3.4. **Plant testing of obtained materials**

An important feature of ameliorative vermiculite-lizardite products is their impact on plant growth and development. Plant testing was performed for a slime product, which is advisable to use as an additive that improves the soil chemical composition. The observations showed that the aqueous extract from the slime product accelerated the appearance of both the first and mass plantlets. Seeds of all test cultures used in the laboratory experiment germinated in experimental variants a day earlier compared to the reference (table 3).

The results of the plant testing of the slime product indicate the beneficial effects of its components at the early stages of plant growth and development. In the experimental version, germination, energy, and vigor of seed germination increased. As for the length of the roots, statistically significant differences between the reference and experimental variants have not been established for this indicator; however, there is a positive trend in the increase of this indicator in the experiment with the aqueous extract of the slime product when compared to distilled water.

4. **Conclusion**

1. The mineral composition of the processing products of vermiculite-lizardite waste allows them to be used to improve the quality of the soil. The slime product plant testing results confirm the hypothesis on the positive effect of vermiculite-lizardite-type materials on plant growth and development.

2. The fraction composition of slime, granular and substandard products differs in the content of pulvcraceous particles and fine sand. The resulting products can be used to adjust the granulometric composition and moisture capacity of soil, and the choice of a particular product and its amount will depend on the texture of the base material.

3. The products with vermiculite-lizardite composition can interact with acid solutions. Neutralization reaction proceeds at a low rate with the establishment of equilibrium within 20-30 days. The obtained materials can be used to reduce the acidity of agricultural soils and to rehabilitate acidified landscapes affected by nonferrous industrial facilities.

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