Expanded vermiculite-reached product obtained from mining waste: the effect of roasting temperature on the agronomic properties

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Abstract: This article explores the possibility of using the vermiculite-lizardite granular product with 30 % of vermiculite content for the potential agronomic application. The vermiculite-lizardite product was obtained by beneficiation of phlogopite mining waste (Kovdor, Murmansk region, Russia). The beneficiation scheme included a hydro separator, a spiral separator, and concentrating tables. The output of vermiculite-lizardite product was about 35 %. The effect of roasting temperature on the hydrophysical and agrochemical properties of the vermiculite-lizardite material and the mono-mineral vermiculite was studied. Heat treatment of materials was performed in the laboratory shaft furnace. Based on the differential thermal analysis results, a temperature of 700°C was selected as the upper limit and the temperature of 400°C - as the lower limit of the temperature range in order to obtain an expanded vermiculite-reached product containing lizardite. For samples obtained in this temperature range with a step of 25°C, a set of data such as bulk density, water saturation, surface area, volume and average pore diameter, Eh, pH suspensions in water and KCl solution, chemical resistance in ammonium acetate solution buffered at pH 4.65 were obtained. The temperature range of 500-600°C of the vermiculite-lizardite granular product was determined as favorable for agronomic application.

Keywords: recycling, beneficiation, vermiculite, lizardite, differential thermal analysis

1. Introduction

Vermiculite is widely used for various purposes such as a hydroponic substrate (Marwa et al., 2009), soil conditioning (Antoniadis et al., 2017), cleaning up of oil (Mesyats et al., 1984; Gunatilake, Bandara, 2017) and trace metals (Raval et al., 2016) pollution. Some mining wastes contain vermiculite, for example, phlogopite mining waste from the Kovdorsky field (Murmansk region, Russia). Obtaining high-quality products from waste is usually unjustified and impractical because vermiculite in waste may be represented by a non-removable form. Besides, the cost of the ultimate product in the case of using a complex beneficiation technology may be higher in comparison to the standard ore processing scheme. At the same time, recycling of such waste will contribute to the restoration of disturbed natural landscapes (Gruszecka-Kosowska et al., 2017; Slukovskaya et al., 2018). Low-quality vermiculite products can be used in remediation technologies for areas with high levels of pollutants, such as trace metals (Kremenetskaya et al., 2015).

The expanded vermiculite showed sorption properties, essential for the detoxification of solutions during reclamation in areas with high levels of acidification and contamination with trace metals (Lee, 2012). Numerous studies addressed the following issues: the dependence of the adsorption properties

of vermiculite on trace metals (Dos Anjos et al., 2014), the effect of organic compounds on the cleaning efficiency of solutions (Malandrino et al., 2006), the sorption properties of natural sorbents, e.g. vermiculite for trace metals remediation (Malamis, Katsou, 2013).

In addition to cleaning solutions, vermiculite can be used to improve the properties of contaminated soil. Malandrino et al. (2011) showed that in the presence of vermiculite, the intake of trace metals into plants decreased. Expanded vermiculite not only reduced the toxicity of the soil but can also serve as the basis for the accelerated formation of artificial plant communities in cold climate conditions (Slukovskaya et al., 2017).

The remediation of highly contaminated soils in northern latitudes requires a particular approach. In 2004-2016, researchers created methods of intense development of plant communities that resulted in four patented hydroponic technologies based on the creation of favourable conditions for plant growth (Kotelnikov, Ivanova, 2011; Ivanova et al., 2017). The developed technologies have been successfully used to create grass cover on highly contaminated areas within the impact zones of copper-nickel enterprises located in the Subarctic and Arctic (Slukovskaya et al., 2017). Expanded vermiculite plays an essential role in ecosystem rehabilitation. It serves as a hydroponic substrate, neutralizes high acidity, and decreases trace metals concentration due to its sorption-active properties.

The primary condition of the wide-scale use of the developed technologies is accessibility and low cost of the materials including expanded vermiculite. This research aims to develop production technology of vermiculite-reached material obtained from phlogopite mining waste and to determine conditions of its thermo-expansion. It was previously established that the optimal agronomic properties of expanded Kovdor vermiculite could be obtained at temperatures of 600-650°C (Ivanova et al., 2006). However, the presence of serpentine minerals in the vermiculite material may affect the properties of the product obtained during thermal treatment.

The purpose of this work was to develop the beneficiation scheme of phlogopite waste with a vermiculite-lizardite product and to study the effect of the thermal treatment temperature on the agronomic properties of the obtained material.

2.   Materials and methods

2.1. Description of vermiculite-lizardite waste

Deposited vermiculite-lizardite waste from the open-pit phlogopite mine (LLC "Kovdorsljuda") located in the town of Kovdor in the Murmansk region of Russia occupies an area of about 70 000 m2 and contains several hundred thousand tons of vermiculite and lizardite (Kremenetskaya et al., 2015). Currently, this waste is not processed by either the mining enterprise or government agencies. A trial consignment of vermiculite-lizardite waste (5 tons) was sampled in the deposit area and transported to the Kola Scientific Centre of Russian Academy of Sciences for further investigation. The material consists of small size particles with the granulometric fraction of less than 10 mm comprising 80 % of the initial sample mass (Kremenetskaya et al., 2015). The waste with white lizardite inclusions is shown in Fig. 1.
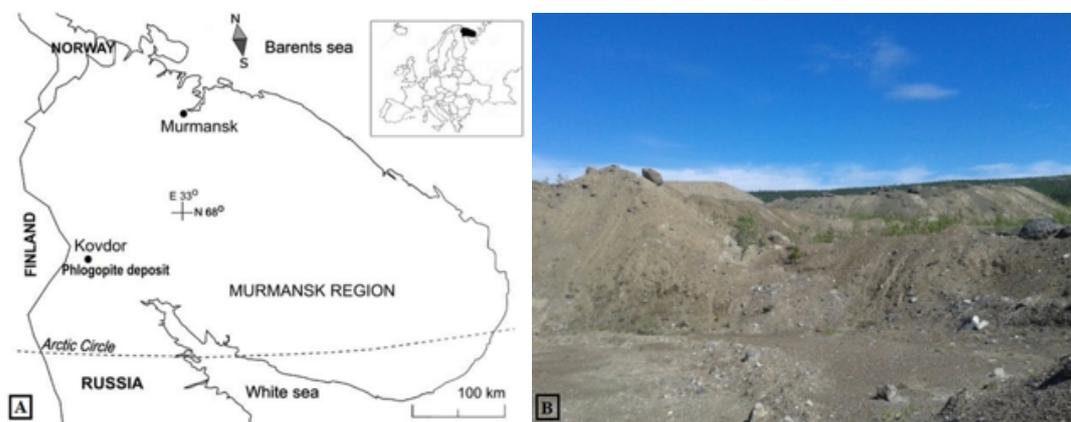

Fig. 1. (a) Location of the phlogopite mine in Kovdor, the Murmansk region and (b) photo of vermiculite-lizardite waste in the open-pit

An assessment of mineral composition showed an equal proportion of lizardite and vermiculite, 19-21 % for each mineral. Other minerals such as pyroxene, olivine, iron oxides and hydroxides, titaniferous magnetite, feldspar, quartz, nepheline, zeolite, and calcite made up 60 % of the material. The fraction of 10-40 mm was used to produce beneficiated vermiculite-lizardite material. The content of this fraction was 20 % of the total sample mass.

2.2. Beneficiation scheme of vermiculite-lizardite waste

Grinding of raw material to a fraction of minus 2 mm was performed using a jaw and roll crusher. The gravitational beneficiation scheme included using a hydroseparator, a spiral separator, and concentrating tables.

The technological scheme of the beneficiation is shown in Fig. 2. The best results for vermiculite production were obtained when the hydro separator was used at the initial stage of beneficiation. The raw material of minus 2-mm size was sent to the hydroseparator to produce a slime product.
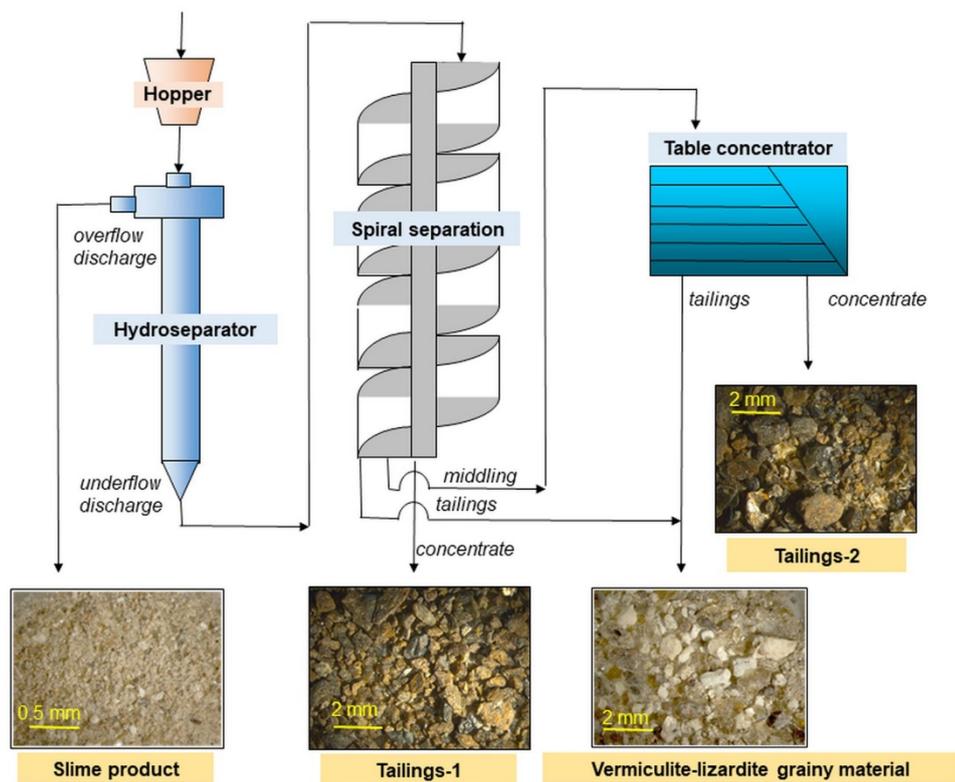

Fig. 2. Technological scheme of beneficiation of vermiculite-lizardite fragments

The sands of the hydraulic classifier were further sent to the spiral separator. The resulting concentrate from the spiral separator consisted of tailings from the beneficiation of vermiculite-lizardite waste because the material that passed into this concentrate were predominantly massive rock particles. The lightest and smallest particles remained on the outer side of the separator and were joined with a slime product. The obtained product was then sent to purification at the concentrate tables. Tailings were extracted in a concentrating zone of the table because more massive dark-colored particles concentrated here. Moreover, the product containing vermiculite and lizardite was formed in a tail zone of the table. Tailings, slime product and vermiculite-lizardite material were obtained as a result of gravitational beneficiation (Table 1).

Tailings obtained after the beneficiation of vermiculite-lizardite wastes can be used as a part of heat-resistant concrete (Bastrygina et al., 2014). The hydroseparator slurry is a fine-grained product with mineral composition beneficiated by vermiculite and lizardite compared with vermiculite-lizardite wastes. This product can be used as silicon fertilizer and macronutrient amendment for plant growth (Mikhaylova et al., 2019).

The vermiculite-lizardite material can be used for the expanded vermiculite obtainment. It is a 2 mm sized grainy material with the lizardite and vermiculite content of 31 and 33 % and with the extraction of 52 and 60 %, respectively. The product contains about 36 % of impurities among them there are olivine-pyroxene rocks, fine crystalline fenites or syenites, as well as particles of diopside, quartz, and feldspar. The output of this product was about 35 %.

Table 1. Characteristics of products of vermiculite-lizardite mining wastes' gravitational beneficiation (%)

Product	Output	Mineral content			Mineral extraction		
		Lizardite	Vermiculite	Others	Lizardite	Vermiculite	Others
Vermiculite-lizardite	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

2.3. Specification of raw beneficiated vermiculite-lizardite product and monomineral materials

The vermiculite expansion was studied using vermiculite and vermiculite-lizardite samples. The samples of vermiculite and lizardite were isolated from the geological samples of the Kovdorsky field of vermiculite. Vermiculite represents a typical variety for the Kovdor deposit with a sufficient phlogopite impurity determined by X-ray analysis. The content of the main components was determined using X-ray fluorescence spectrometry (Spectroscan MAKC-GV, Spectron, Russia) (Table 2).

The main difference between vermiculite-lizardite material and mono-mineral vermiculite is the presence of the two components (serpentine mineral lizardite and vermiculite) with an ability for thermic activation. The well-known property of serpentine minerals is the formation of an intermediate active metastable phase (meta-serpentine) in a temperature range limited by the onset of structural destruction (600-650°C) and the formation of a stable forsterite phase (810-850°C) (Kremenetskaya et al., 2010). Meta-serpentine actively interacts with acidic solutions and causes an alkaline medium, which can be unfavorable for plant growth.

The purpose of thermal activation of the vermiculite-lizardite material is an expansion of the vermiculite, i.e. obtaining such properties that ensure its successful use in hydroponic technologies (sub-neutral pH of water solution, low bulk density, high air, and moisture capacity) (Marwa et al., 2009). In our previous studies, the optimal agronomic properties of the expanded Kovdor vermiculite was obtained at a roasting temperature of 600-650°C (Ivanova et al., 2006). However, the presence of the thermally activated serpentine mineral in vermiculite-lizardite may affect the properties of the product after roasting. Therefore, the thermal effects of vermiculite, lizardite and vermiculite-lizardite products, as well as the influence of temperature on the physicochemical properties are discussed in this paper. The main goal of the current research was to determine the optimal roasting temperature considering the characteristics of the components of the vermiculite-lizardite material.

2.4. Expanded products research methods

The roasting of the samples was performed in a laboratory shaft furnace designed and manufactured at the "Tula-Therm" LTD (Russia). The design of the furnace and the use of digital control ensures the stability of the temperature regime with a deviation from the set temperature of 5°C. The heat treatment by a thermal shock method was also used. The samples were heated at 400, 425, 450, 475, 500, 525, 550, 575, 600, 625, 650, 675 and 700°C with the dwell time of 3 min.

The duration of roasting in shaft furnace corresponds to the length of stay of the material in the electric modular-trigger furnace (Nizhegorodov, 2015), which will be used for further large-scale production of expanded vermiculite-reached product.

Table 2. General characteristics of the raw vermiculite and/or lizardite-enriched products

Characteristics	Vermiculite	Lizardite	Vermiculite-lizardite
Particle size, mm	1-2	< 0.08	1-2
Bulk density, g sm^{-3}	0.89	-	1.15
Mineral composition, weight percentage, %			
Vermiculite	95	-	33
Lizardite	-	91	31
Olivine, pyroxene	5	9	36
Chemical composition, weight percentage, %			
SiO_2	34.59	50.44	41.96
MgO	18.71	26.20	24.95
K_2O	1.03	0.13	-
Al_2O_3	9.97	2.09	2.25
Fe_2O_3	9.67	1.78	10.81
CaO	5.70	2.60	4.96
TiO_2	0.70	0.19	0.20
MnO	0.14	0.05	0.38
NiO	0.07	0.12	0.21
Cr_2O_3	0.10	0.03	0.05
CO_2	3.85	0.63	4.77
H_2O	15.45	15.73	9.40

Differential thermal analysis (DTA) results were obtained using a thermal microanalyzer STA409 (Germany) by heating the samples from 25 to 900°C at a rate of 10°C min-1. Physical and chemical properties affected by temperature were also determined.

The bulk density was measured by weighing a known volume of the sample determined by tipping the loose fragments into a measuring cylinder without compaction. The difference in weights between the water saturated and dry sample gave the water saturation characteristic.

The textural properties of the vermiculite (surface area, average pore diameter, and pore volume) were assessed by interpreting the experimental adsorption–desorption data of N2, which was obtained using physisorption by porosimetry analyzer TriStar 3000 (USA).

Values of pH and Eh were measured using laboratory ion meter I-160 in soil/water and soil/1 mol ·L-1 KCl (1:10) suspensions. All analyses were carried out in three replications.
Chemical resistance was determined by the ammonium acetate saturation method buffered at pH 4.65 (Hojati, Landi, 2015). Solutions were analyzed with an inductively coupled plasma mass spectrometer ELAN 9000 DRC-e (Perkin Elmer).

3.   Results and discussion

3.1 Thermal effects of vermiculite and lizardite in vermiculite-lizardite product

For the vermiculite-lizardite, thermal effects inherent for both vermiculite and lizardite was observed (Fig. 3). In the temperature range of 120-300°C, the release of interpacket low-temperature water by vermiculite was as follows: at 120-170°C - unbound water and at 170-300°C - associated with magnesium ions water was released.

A dehydroxylation of the lizardite mineral with the formation of the active metastable phase was observed at a temperature above 600°C. It is worth noting the split of the main endothermic effect of the thermolysis of a lizardite mineral compared to vermiculite-lizardite (temperature range 600-700°C). These samples differed in the size of the material. The grain size of the vermiculite-lizardite was 1-2 mm, while sample lizardite was crushed to a particle size of less than 0.08 mm.
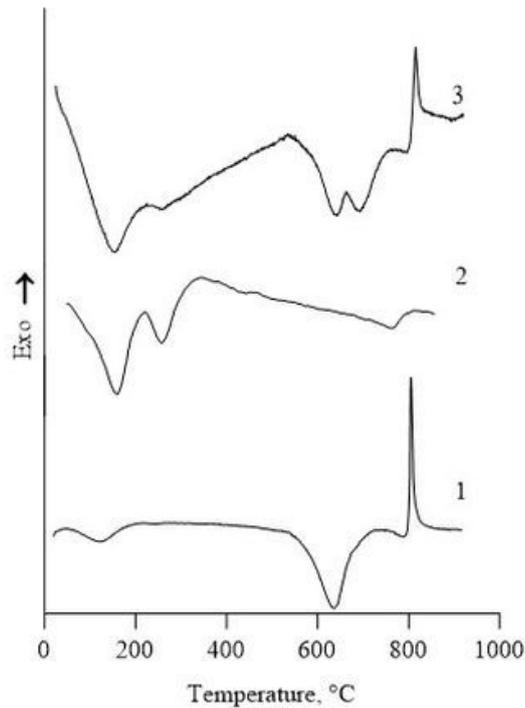
Fig 3. Thermogram of raw lizardite (1), vermiculite (2) and vermiculite-lizardite (3)

The effect of lizardite grinding on the shape of the main endothermic effect was observed in (Kremenetskaya et al., 2012) when studying the effect of mineral dispersion on the thermolysis process.

The formation of equilibrium high-temperature phases in vermiculite and lizardite occurred at temperatures above 750°C. Based on the DTA results, a temperature of 700°C was selected as the upper limit of the temperature range for obtaining an expanded vermiculite-enriched product containing lizardite. The effect of the lizardite presence on the properties of expanded vermiculite-lizardite is greatly shown at 600-700°C, which is the temperature range of the active metastable phase formation. The temperature of 400°C appeared as the lower limit of the temperature range.

3.2. The influence of roasting temperature on the material properties

The difference in the mineral composition of vermiculite-lizardite and vermiculite was reflected in the bulk density, which was significantly higher for vermiculite-lizardite. The bulk density of the original samples was 1.15 and 0.89 g·cm^{-3} for vermiculite-lizardite and vermiculite, respectively. After roasting at 400°C, bulk density decreased, respectively, to 1.07 and 0.50 g·cm^{-3}. With an increase of the roasting temperature from 400 to 700°C, the bulk density of vermiculite decreased to a value of 0.22 g·cm^{-3}, while for vermiculite-lizardite it decreased slightly from 1.07 to 0.99 g·cm^{-3} (Fig. 4).

Vermiculite-lizardite had a higher density due to the high content of heavier impurities (31 % lizardite and 36 % olivine-pyroxenes) compared with vermiculite. Grains of impurity minerals, in contrast to vermiculite, do not have the ability to increase in volume during thermal processing. This property is inherent in vermiculite, that is reflected in a significant decrease in the bulk density of expanded vermiculite.

The closest negative correlation between bulk density and pore volume (correlation coefficient R = -0.71) was observed. The relationship of this indicator with the surface area (R = -0.29) and the mean pore diameter was less (R = -0.47). For water saturation, we found a close positive correlation with the pore volume (R = 0.61) and less significant with the specific surface (R = 0.41) and mean pore diameter (R = 0.31).

Bulk density gradually decreased with the increasing roasting temperature, whereas the maximum value of water saturation was recorded at the temperature of 600°C. The maximum value of the pore volume of expanded vermiculite at a temperature of 600°C was also noted in the work (El Mouzdahir, 2009).

It is well recognized that pH is an important parameter impacting the agronomic properties (Marwa et al., 2009). Figure 5 shows the pH values of the suspensions of the samples in water, obtained in experiments with a reaction time of 1 and 72 hours, as well as in a KCl solution (interaction time 1 hour). pH values denote as pH_1, pH_{72} and pH_{KCl} respectively.
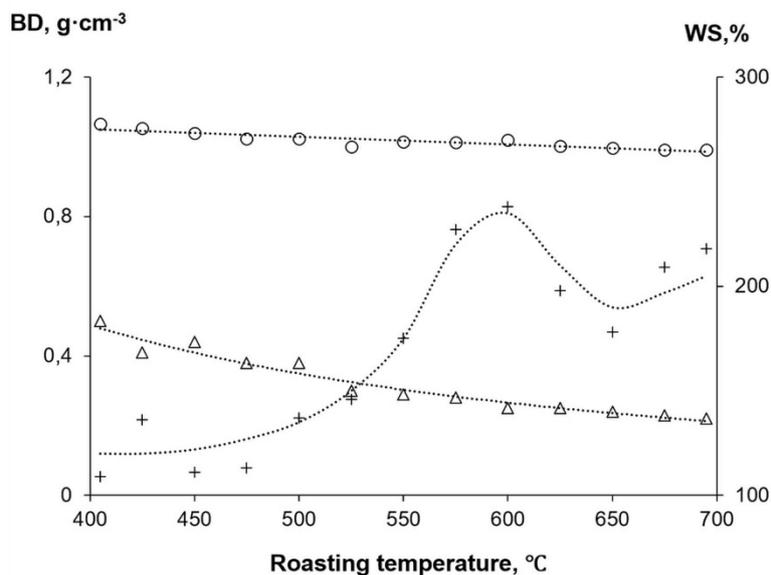

Fig. 4. Relation between roasting temperature and bulk density (BD) for vermiculite (Δ), BD for vermiculite-lizardite (○), and water saturation (WS) for vermiculite (+)
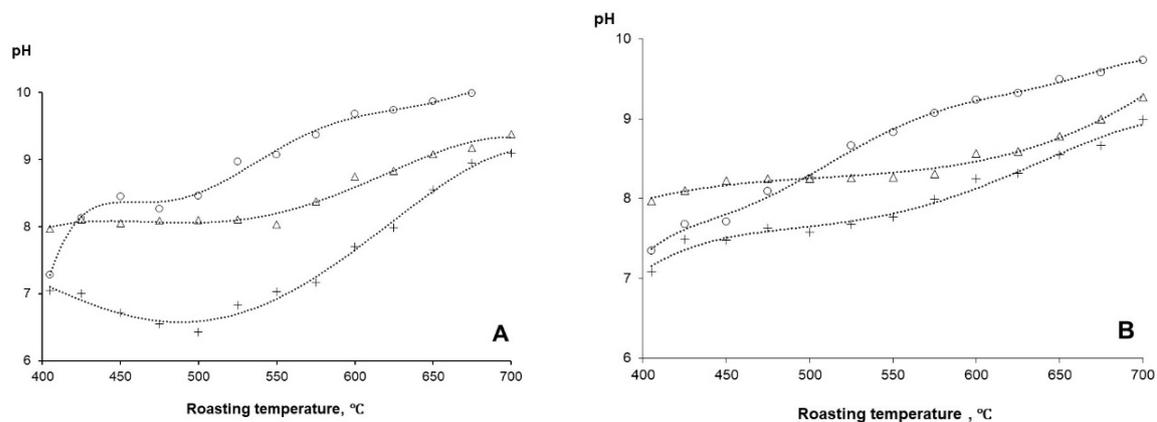

Fig. 5. Effect of roasting temperature vermiculite (a) and vermiculite-lizardite (b) on the pH_1 (○), pH_{72} (Δ) and pH_{KCl} (+)

The most significant differences in the properties of the materials appeared when interacting with the KCl. Value of pH_{KCl} of vermiculite samples, obtained at the temperature 400-500℃, decreased from 7.0 to 6.4, and gradually increased to the value 9.1 with the temperature increase up to 700℃. For the vermiculite-lizardite samples, gradual increase of pH_{KCl} from 7.0 to 9.0 in the range temperature of 400-700℃ was observed.

The decline of pH, i.e. a concentration of H_3O^+ cations increase in a solution, may be related to the K+ ion exchange of a KCl solution (El-Bayaa et al., 2009). It is known that ion exchange on vermiculite packets is due to the presence of ion-exchange and low-stability magnesium in the interpacket layer, as well as the intrinsic potential of the particle surface formed by non-stoichiometric isomorphism in the tetrahedral and octahedral layers (Tarasevich, 1988; Ladonin, 1997). The results of the exchange magnesium determination in vermiculite showed immutability of its availability for ion exchange in the range of 400-500℃ (Fig. 6). Consequently, the process of ion exchange in KCl solution in a given tempe-
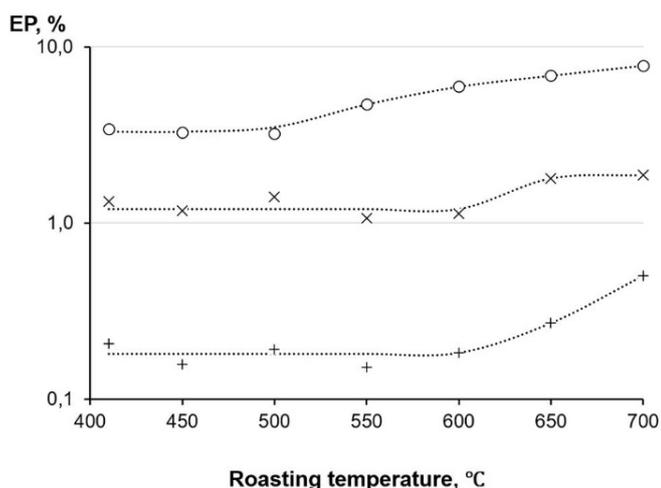
Fig. 6. A portion (EP) of Mg (○), K (×) and Si (+) extracted by ammonium acetate buffer in the expanded vermiculite samples

rature range of heat treatment of vermiculite is influenced by a change in the properties of the surface of vermiculite (Padilla-Ortega et al., 2014), which is caused by the process of its dehydroxylation.

An increase in the uncompensated negative charge of the vermiculite lattice occurred as a result of roasting at a temperature above 400°C. Sorption of H_3O^+ ions on the vermiculite surface in the aqueous suspension and a sharp increase in pH_1 occurred. Ion exchange and H_3O^+ cations transition into the solution of KCl in the presence of an excess of potassium ions was noted in (Vieira dos Santos, Masini, 2007). It also caused a decrease in pH. The presence of a negative charge on the vermiculite surface is considered as the main cause of sorption of metal cations (Gharin Nashtifan et al., 2017).

The content of exchange magnesium (at temperatures above 500°C), as well as the content of potassium and silicon (at temperatures above 600°C), increased with the roasting temperature rise. The increase in the portion of exchangeable potassium and silicon in the expanded vermiculite indicates the destruction of the tetrahedral layers under thermal exposure. This process is undesirable when using thermo-vermiculite as an agronomical substrate.

Data for the vermiculite-lizardite indicated that the interaction of the dehydroxylated surface of vermiculite with the components of the solutions in the presence of lizardite occurred differently. Vermiculite-lizardite differed from vermiculite by the presence of the magnesia-silicate mineral lizardite, partial leaching of which creates an increased background for magnesium and changes the state of the magnesium exchange vermiculite complex (Tarasevich et al., 2013). Sorption of magnesium on a dehydroxylated surface is reflected in the pH dependence on the vermiculite-lizardite roasting temperature. The effects described for vermiculite as a result of the sorption of magnesium cations on the surface of vermiculite particles are absent for the pH_1 and pH_{KCl} relations.

Values pH_{72} for vermiculite and vermiculite-lizardite samples, obtained in the temperature range 400-550°C, do not differ much. The pH_{72} values for samples obtained at temperatures of 400-550°C (vermiculite) and 400-600°C (vermiculite-lizardite) are stable and make up the values of 8.0-8.1 (vermiculite) and 8.0-8.25 (vermiculite-lizardite). The results of pH_{72} determination occurred both an increase and a decrease in pH of the water suspensions of vermiculite and vermiculite-lizardite with an increase in the duration of the contact of the sample particles surface with an aqueous solution. These processes probably reflect the presence of magnesium in the system, which is capable of partially passing into the solution. The increase in pH may be associated with the process of dissolution, and a decrease with dissolution and subsequent sorption of magnesium cations on the dehydroxylated surface of vermiculite. For vermiculite, an increase in pH_{72} is observed at temperatures above 550°C, and for vermiculite-lizardite - above 600°C, while the pH_{72} value difference between samples did not exceed 0.2 units.

The redox potential of samples was also slightly different and decreased with increasing roasting temperature in the range of Eh 240-140 (vermiculite) and 200-140 mV (vermiculite-lizardite).

Accumulation of dissolved organic matter in soils with these Eh values (Pansu, Gautheyrou, 2006) is favorable for the use of these materials as agronomic substrates.

Hydrogen potential rH is commonly used to obtain approximate estimates of the redox conditions in media with different pH values (Pansu, Gautheyrou, 2006). The rH change interval is 23–25 for vermiculite and 21–24 for vermiculite-lizardite, showing slightly more reducing medium in a substandard vermiculite-lizardite substrate than in vermiculite (Fig. 7).
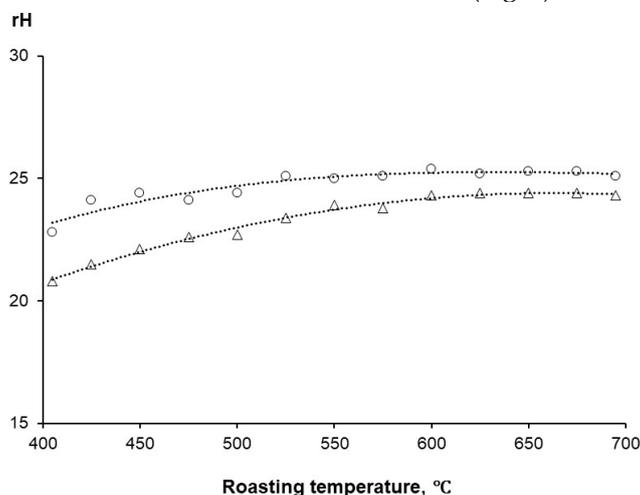

Fig. 7. The relation between roasting temperature and rH for vermiculite (○) and lizardite (Δ)

4. Conclusions

Expanded vermiculite obtained after the beneficiation of vermiculite-lizardite mining waste can be successfully used to improve soil fertility and agronomic soil properties in the Arctic region. The scheme of gravitational beneficiation of a vermiculite-lizardite waste from phlogopite mining at the Kovdorslyuda enterprise (Murmansk region, Russia) included a technological chain of a hydro separator, a spiral separator, and gravity tables. We were able to develop the optimal operation mode of the circuit, obtain beneficiation products, and proposed variants of their application.

The presence of lizardite (serpentine mineral) influenced the properties of thermally activated products. The effect of temperature in the range of 400-700℃ with a step of 25℃ on the properties of calcined products was investigated. It has been shown that the hydrophysical characteristics of vermiculite are determined by structural parameters; the most important indicator is the volume of pores that are formed in vermiculite under the influence of temperature. The bulk density of vermiculite-lizardite granular material was naturally higher compared with pure vermiculite due to the presence of lizardite and impurities of olivine-pyroxene composition in an amount of more than 30 %.

Restrictions on the use of heating products for agrotechnical purposes may be associated with high pH value. The results of the studies have shown that the alkalinity of vermiculite-lizardite and vermiculite samples did not differ. It has been shown that in the temperature range studied, the structure of vermiculite was partially destroyed, which led to an increase in the pH of suspensions of both pure vermiculite and vermiculite-lizardite samples. Thus, the chemical properties of vermiculite-lizardite product correspond to vermiculite concentrate in considering its application for agricultural technology.

The results obtained in this work allowed proposing a method for utilization of phlogopite waste from the vermiculite-lizardite composition. Waste disposal will help return the territory alienated for storage of waste into national economic circulation and restore the damaged natural landscape. Waste beneficiation products can be used to create artificial soil or improve degraded soils properties.

Acknowledgments

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