



Structure formation of composite materials based on technogenic soil modified by additives of high-molecular compounds

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Abstract: The article substantiates the possibility of obtaining organo-inorganic composite materials with improved functional properties based on technogenic soil and high-molecular substances. The specific effective activity of natural radionuclides (^{226}Ra , ^{232}Th , ^{40}K) of technogenic soil was 97 ± 12 Bq/kg, which allows use in the production of building materials without restrictions. Using the methods of atomic emission spectrometry with inductively coupled plasma, infrared spectroscopy, differential scanning calorimetry and thermogravimetry, powder diffraction, scanning electron microscopy, data on the composition, properties and structural features of technogenic soil were obtained, allowing us to assess the possibility of its use as a dispersed filler for the composite. It was revealed that the organo-inorganic composite material is frost-resistant, waterproof, and is characterized by a compressive strength of 6.20 MPa and a thermal conductivity of 0.20 W/(m·K). The mechanism of composite structure formation was established, which consists in the reorganization of hydrate shells and the formation of organomineral complexes during the interaction of the polymer matrix and dispersed filler particles. The effectiveness of cryogenic treatment in transforming the pore space of the composite and improving its functional properties was shown. It was revealed that cryostructuring contributes to an increase in the pore volume of the composite by 1.4 times, which determines its thermophysical properties.

Keywords: technogenic soil, overburden, composite materials, structure formation, cryostructuring, polymer matrix, dispersed filler, pore space, waste disposal

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1. INTRODUCTION

Currently, an urgent task in the field of development of the mineral resource base is the development of methods for the disposal of large-tonnage mining waste, of which more than 50 billion tons have accumulated. Substandard mineral raw materials located in waste heaps are characterized by geochemical activity, altered composition and properties, toxicity, therefore, facts of environmental pollution are revealed. Overburden rocks unsuitable for agricultural use and occupying significant areas contribute to the deterioration of the environmental situation in adjacent territories. As a result of the extraction, transportation and primary processing of mineral raw materials, there is a change in relief, the formation of sinkholes, subsidence of the earth's surface, drying out of the soil and ground cover, dust formation, pollution with chemicals, as well as disruption of the integrity and structure of ecosystems. Alienated lands after mining operations account for approximately 60-90%, and the area of lands removed from agricultural and forest use can reach 0.8 hectares per 1,000 tons of mineral raw materials extracted from the subsoil. At the same time, losses of raw materials and energy resources contained in large-tonnage waste are observed [1-9].

Involvement of these wastes as secondary raw materials in the production of building materials will eliminate waste dumps of mining enterprises and will contribute to the formation of a closed-loop economy [10-17]. Large-tonnage wastes of the mining industry, despite the difference in physical and chemical properties and polydispersity, can act as non-traditional raw materials in the compositions of composite materials with specified properties applicable in the operation of engineering structures of mining enterprises. The introduction of components with different chemical nature into the compositions of composites can contribute to the formation of materials with improved performance characteristics [18-19]. Therefore, the development of methods for targeted changes in the composition and structural features of mineral raw materials, material processing modes that allow imparting a set of target properties to composites seems to be an urgent task.

The objective of this study was to investigate the composition, properties and structural features of technogenic soil to establish the mechanism for forming the structure of organo-inorganic composite materials with specified properties.

The goal was achieved by solving the following problems:

1. Studying the chemical and phase composition, physicochemical and physical properties, structural features of the original technogenic soil to justify the possibility of its utilization as part of a composite material.
2. Synthesis of the polymer matrix of the composite material, study of its properties, structural features and degree of toxicity.
3. Development of the composition of the organo-inorganic composite material, selection of the optimal mode of its cryostructuring.
4. Studying the properties of the composite material and establishing the mechanism for forming its structure.

2. MATERIALS AND METHODS

The composite material is a hybrid system consisting of high-molecular compounds and a dispersed filler – technogenic soil (overburden) of the Balei ore field, Transbaikal Territory, Russian Federation.

The polymer matrix is obtained on the basis of poly(1-carbamoylethylene) with additives of polyelectrolytes, the purity of the reagents is 94%. The synthesis was carried out using an electromagnetic stirrer with synchronous heating IKA C-MAG HS 10. Conditions for the synthesis of the polymer-polymer composition: aqueous medium; $t = 80\text{ }^{\circ}\text{C}$; rotation frequency of the stirring element of the magnetic stirrer – 500 rpm; synthesis time 150 min; mass ratio of high-molecular substances – 3:4; concentration of the active component – 100 g / l. The viscosity of the colloidal solution was determined using a VUB-1R viscometer (water bath temperature 22°C). The optical density of the solution and the average mass radius of supramolecular formations were studied using the turbidity spectrum method (KFK-3 "ZOMZ" photometer, cuvette thickness 3 cm).

The toxicity of the polymer matrix was assessed using biotesting on test objects *Chlorella vulgaris* Beijer ($t = 36.0 \pm 0.5^\circ\text{C}$; pH 7.0-8.5; exposure time 22 hours; photoelectrocolorimetry) and *Daphnia magna* Straus ($t = 21^\circ\text{C}$; pH 7.0-8.5; dissolved oxygen ≥ 6.0 – start; ≥ 2.0 – end; dilution factor 1, 10, 100, 1000, 10000, exposure time 96 hours). The dispersed filler was combined with the composite matrix and the resulting heterophase system was compacted using a vibration platform for 3 minutes (frequency 2900 rpm, amplitude 0.40 mm). The resulting composition was placed in molds and subjected to freezing for 10 hours at a temperature of minus $(20 \pm 2)^\circ\text{C}$. The samples were defrosted at a temperature of $22 \pm 2^\circ\text{C}$ for 4 hours, followed by removal from the molds and drying for 30 days in air (Fig. 1).

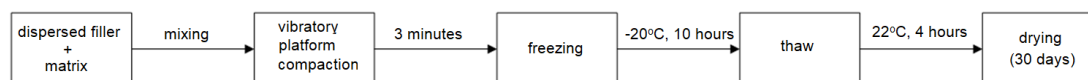


Fig. 1. Scheme for obtaining samples of composite materials.

The physical and mechanical properties of the composites were studied after three cycles of cryogenic treatment on cube samples with a side size of 15 cm, thermal conductivity was determined on cylindrical samples with a diameter of 10 cm.

The chemical composition of the technogenic soil was studied using inductively coupled plasma atomic emission spectrometry on a Perkin Elmer Optima 5300 DV emission spectrometer (167-403 nm).

The phase composition was determined by powder diffraction using a DRON-3.0 X-ray diffractometer ($U = 25$ kV; $I = 20$ mA; Ni filter; $\text{CuK}\alpha$; $2\theta = 5-55^\circ$, scanning step - 0.05°). The mineralogical composition was deciphered using the EVA Diffracplus program, semi-quantitative phase analysis was carried out using the RIR method using corundum numbers of mineral phases from the crystallographic database.

Infrared spectra were recorded on a SHIMADZU FTIR-8400S Fourier spectrometer, the relative intensity of absorption bands was calculated using the baseline method, with the absorption band with a maximum at $1000 - 1100\text{ cm}^{-1}$ used as a unit.

Thermal analysis was performed by differential scanning calorimetry and thermogravimetry using a NETZSCH STA 449F1 synchronous thermal analyzer in the temperature range of $30 - 800^\circ\text{C}$ (heating at a rate of $10^\circ\text{C} / \text{min}$; sample weight 30 mg; dynamic atmosphere – Ar).

The microstructural features of the initial mineral raw materials were studied using a JSM-6510LV-JEOL scanning electron microscope with a microanalysis system – an energy-dispersive X-ray spectrometer model INCA Energy 350, Oxford Instruments. A thin layer of platinum was sprayed onto a non-conductive sample using a JFC-1600 installation. Visual assessment of the pore space of the composite materials was carried out using stereomicroscopy (Saike Digital SK2100HDMI-T2 stereoscopic microscope; optical glass; zoom lens; wide-field eyepieces (WF10x/20); 16 MP digital camera, 1/2.33" CMOS 1080P(4608 x 3456); LED top illumination with brightness control). The microstructure of the composite material was studied using a Tescan Lyra 3 XMH + EDS AZtec X-Max 80 Standart dual-beam scanning electron microscope (deposition – C; coating thickness/density $\sim 10\text{ nm} / 2.25\text{ g/cm}^3$; reflected electron detector – BEI/BSE; secondary electron detector – SEI/SE).

The features of the composite structure formation were studied by the method of computed X-ray microtomography using a Bruker microCT SkyScan 1272 X-ray microtomograph (0.25 mm Al filter; $U = 60$ kV; $I = 180\text{ }\mu\text{A}$; rotation $0-180^\circ$ with a step of 0.2°). The images of the samples were obtained using the Bruker microCT DataViewer 1.5.3.4 (64-bit) and CTvox 3.3.0 r1403 (64-bit) programs. The total porosity of the composites was calculated using the CT Analyser version 1.16.9.0 + (64-bit) program. The specific effective activity of natural radionuclides in technogenic soil was determined using a RADEK MKGB-01 spectrometer-radiometer and a RADEK MKSP-01 spectrometer. The thermal conductivity of the composites was studied using a probe method using a MIT-1 thermal conductivity meter (probe diameter – 6.0 mm), the compressive strength was determined using a SUBRAMAX GIMS-VIII-1000-P-1-4 hydraulic press, and the water resistance index was determined using the air permeability method ("wet spot").

The main peres of the matrix based on high-molecular substances: colloidal solution; $\rho = 1.10 \text{ g/cm}^3$; pH = 7; no stratification; viscosity 58-62 s. The structural features of the matrix were studied on films obtained from a colloidal solution by casting onto a glass slide with subsequent drying (morphological type – inversion). Assignment of absorption bands (Fig. 2) of the main functional groups, cm^{-1} (ν – frequency, stretching vibration; γ – skeletal vibration; δ – deformation vibration): 599 (δCO); 848 (γOH); 916 ($\nu\text{C-C}$); 1095, 1137 ($\nu\text{C-O-C}$); 1235 (γCH); 1327 (δCN , $\delta\text{CH+OH}$); 1416, 1444 (δCH_2); 1560 (δNH); 1622 (δOH); 1660 ($\nu\text{C=O}$); 2909, 2938 ($\nu\text{a+sCH}_2$); 3350 (νNH , OH); 3726 (νOH).

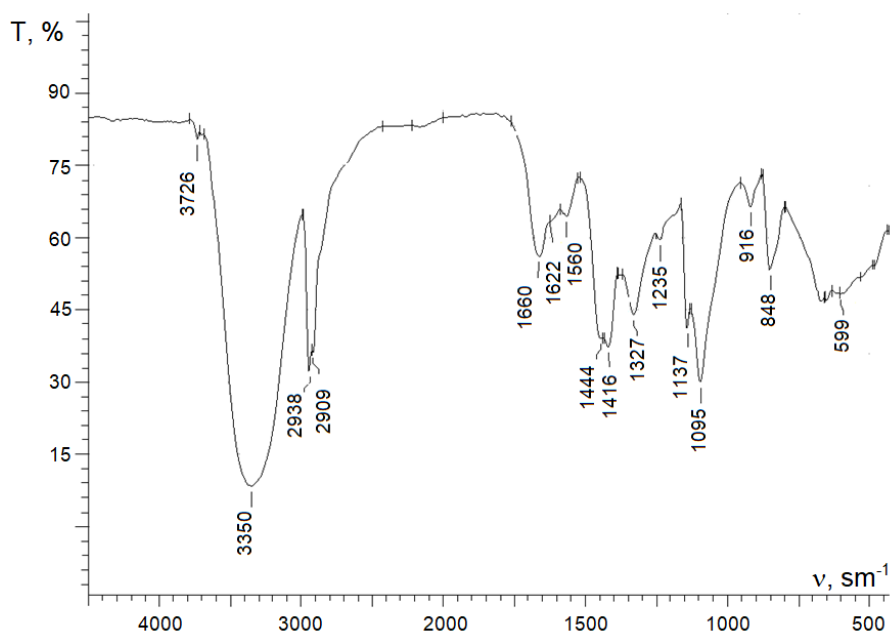


Fig. 2. Infrared spectrum of a matrix based on high-molecular substances.

Using differential scanning calorimetry and thermogravimetry, it was found that endothermic effects (450; 335; 290; 221°C) are accompanied by a mass loss of ~ 52%, caused by thermal destruction of high-molecular compounds and decarbonization. The average mass radius of supramolecular formations was 590 nm, which indicates the presence of a secondary structure in the colloidal system that promotes effective binding of dispersed particles of composites into an organomineral system. It was revealed that the matrix based on high-molecular compounds is safe for human health and the environment. Biotesting data: *Daphnia magna* Straus – mortality in relation to the control 3.3-6.4%; *Chlorella vulgaris* Beijer – deviation in cell count in relation to the control 1.0-17.0%. Sample assessment – does not have an acute toxic effect on test objects.

It was established that the effective specific activity of natural radionuclides in the sample of technogenic soil was $97 \pm 12 \text{ Bq/kg}$, which allows the use of this mineral raw material in the construction industry without restrictions (I class of mineral raw materials, $\leq 740 \text{ Bq/kg}$).

The technogenic soil contains 34.0 wt. % clay minerals; particle density – 2.6 g/cm^3 ; natural moisture content – 0.3 d. units; plasticity index – 0.2 d. units; fluidity index – 0.1 d. units; specific adhesion – 28 kPa; deformation modulus – 25 MPa.

Chemical composition of technogenic soil, ω , %: 67.05 SiO_2 ; 11.05 Al_2O_3 ; 1.56 K_2O ; 0.45 MgO ; 0.10 Na_2O ; 2.50 Fe_2O_3 ; 0.30 CaO ; 0.50 TiO_2 ; 0.10 P_2O_5 ; 0.01 MnO ; 5.80 – trace element impurities; 10.56 – loss on ignition. Numerous absorption bands with maxima in the region of 3392–3693 cm^{-1} in the infrared spectrum of the original mineral raw materials (Fig. 3 a) indicate stretching vibrations of the Si-O-H and H-O-H groups, respectively. The absorption bands in the region of 916–941 cm^{-1} are related to stretching vibrations of the Si-O-Al bonds, 1008–1100 cm^{-1} correspond to stretching vibrations of the Si-O-Si bonds. The absorption band at 794 cm^{-1} indicates the presence of quartz, and the absorption bands with maxima at 472 and 536 cm^{-1} are due to deformation vibrations of the O-Si-O bonds.

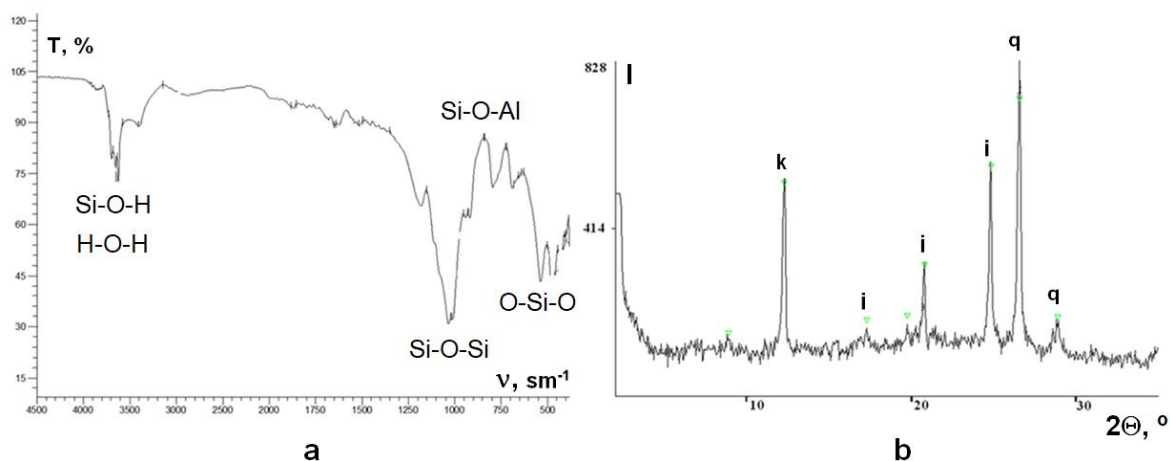


Fig. 3. Infrared spectrum (a) and diffraction pattern (b) of technogenic soil k – kaolinite; i – illite; q – quartz.

The conducted X-ray studies established (Fig. 3 b) that the composition of the technogenic soil includes quartz SiO_2 (3.35; 2.46; 2.12 Å); kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (7.14; 2.56; 2.29 Å); illite $\text{K}_{0.7}\text{Al}_{2.1}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ (4.97; 4.11; 3.20 Å). Data of semi-quantitative analysis of phase composition, ω , wt. %: 73 quartz; 17 kaolinite; 10 illite.

Data of differential scanning calorimetry and thermogravimetry made it possible to reveal that the endothermic minima at 144 and 560°C are associated with the removal of adsorption water and the presence of quartz (Fig. 4 a).

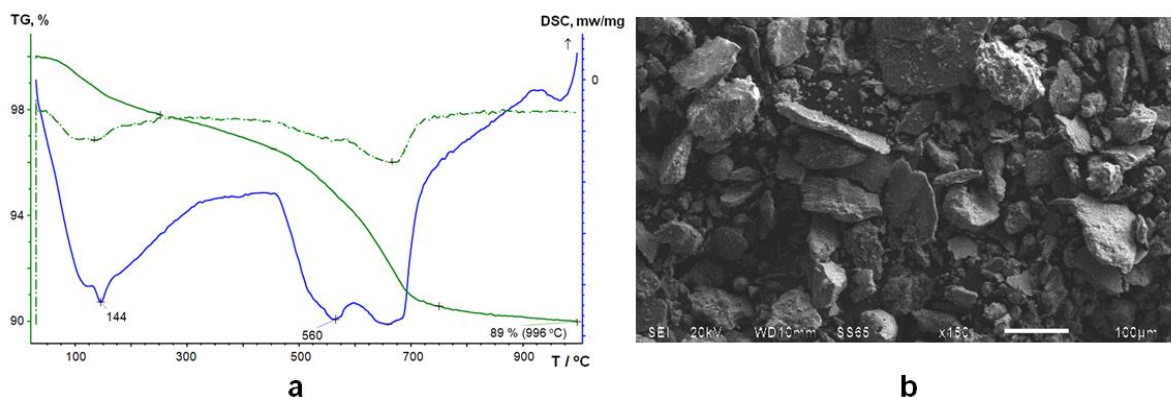


Fig. 4. Thermogram (a) and microphotograph (b) of man-made soil.

Using scanning electron microscopy, it was established that the structure of the man-made soil contains particles with sizes from 100 to 392 μm , belonging to clay and sand fractions (Fig. 4 b).

3. RESULTS AND DISCUSSION

Samples of organo-inorganic composite materials were obtained taking into account the composition and structural features of the technogenic soil, which is a filler of the polymer matrix. It is known [20-23] that successive freezing, keeping in a frozen state and thawing of dispersions of various types of fillers in concentrated solutions of some high-molecular compounds makes it possible to obtain macroporous cryostructured polymer systems. In this regard, the optimal cryostructuring mode was selected experimentally, including 3 cycles of alternating freezing for 10 hours ($t = \text{minus } 20 \pm 2^\circ\text{C}$) and defrosting for 4 hours ($t = 22 \pm 2^\circ\text{C}$). After that, the samples were dried in air for 30 days and their operational characteristics were determined. It was found that the compressive strength of the

obtained organo-inorganic composite materials was 6.20 MPa, thermal conductivity – 0.20 W / (m • K). The water resistance index (ti) was not less than 3600 s.

To establish the mechanism of formation of the structure of composites, studies were carried out using the methods of differential scanning calorimetry and thermogravimetry, infrared spectroscopy, stereomicroscopy, scanning electron microscopy, computed X-ray microtomography. Considering the peculiarity of adsorption of high-molecular substances on solid surfaces, which consists in their interaction with mineral particles only by individual sections of the chain, it is possible to assume additional binding of particles due to adsorbed sections of the polymer chain. Endothermic effects in the region of 600-700 °C, characteristic of clay minerals, are not detected, which indicates swelling of clay particles and disruption of the crystal structure of minerals as a result of interaction with high-molecular compounds (Fig. 5 a).

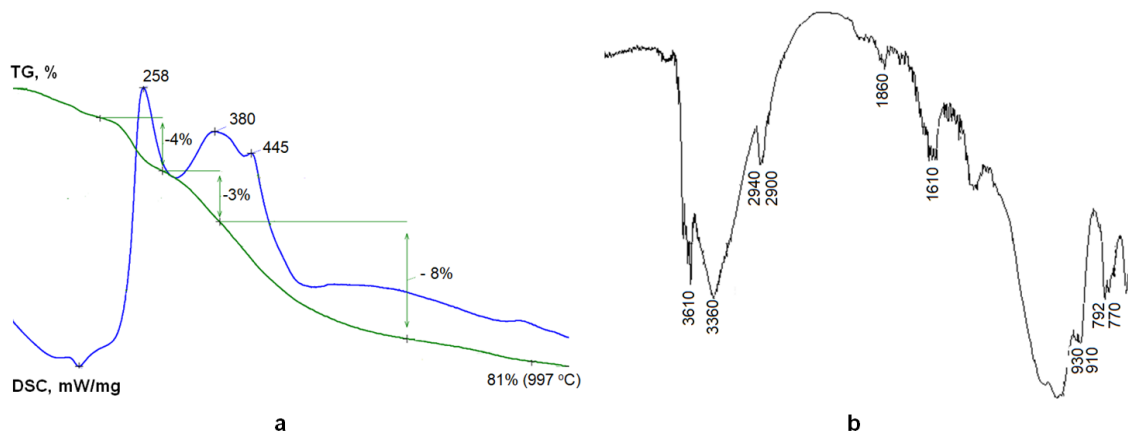


Fig. 5. Thermogram (a) and infrared spectrum (b) of an organic-inorganic composite material.

Exothermic effects (258; 380 and 445°C) are caused by oxidation and decomposition of organomineral complexes, as well as by burnout of high-molecular substances in the composite matrix. Organomineral complexes can appear due to intercalation, stratification and adsorption of high-molecular substances on the surface of mineral particles.

Thus, the binding of filler particles with high-molecular compounds occurs due to the restructuring of hydrate shells and the formation of organomineral complexes with the participation of clay minerals. Regulation of the thickness of hydrate shells can help control the properties of dispersed systems and provide additional "reinforcement" of the composite. To confirm the process of complex formation with the participation of high-molecular compounds and hydroxyl groups of clay minerals, it is advisable to use the IR spectroscopy method. The interaction of the polymer matrix of the composite with highly dispersed mineral particles is confirmed by the appearance of absorption bands in the region of 1400-1450 cm^{-1} (Fig. 5 b), which is caused by deformation vibrations of the C-H bonds in the CH_2 groups and indicates hydrophobization. The absorption band at 3360 cm^{-1} belongs to the OH groups of the polymer matrix, and the bands at 2900 and 2940 cm^{-1} belong to the CH_2 groups of the polymer chain. The absorption bands in the region of 1000-1100 cm^{-1} become wider in comparison with this region in the spectrum of the original soil (Fig. 3 a), which is caused by disordering of the crystalline structure due to swelling of the aluminosilicate oxygen tetrahedrons of clay rocks (34.0 wt.%). Clay is an inorganic polymer material, therefore, an increase in the degree of its dispersion contributes to the enhancement of structure-forming properties in an aqueous medium. The double-let with maxima at 792 and 770 cm^{-1} belongs to quartz, the mass fraction of which, according to the semi-quantitative analysis, is 73%. An increase in the intensity of a wide diffuse band in the region of 3300-3600 cm^{-1} , as well as an intensification and shift of the absorption band at 1600-1650 cm^{-1} were detected, which indicates the participation of OH groups of clay minerals in the formation of bonds with the polymer matrix of the composite. Thus, the recorded changes in the infrared spectra confirm complexation with the participation of functional groups. It was revealed that cryogenic treatment promotes the formation of a macroporous (heterophase) matrix of the composite

(Fig. 6, 7), in which the orientation of microstructural elements depends on the directional growth of ice crystals caused by the crystallization of water and the concentration of high-molecular substances in the unfrozen liquid phase. During the thawing of the material, pores of various sizes are formed in the matrix structure.

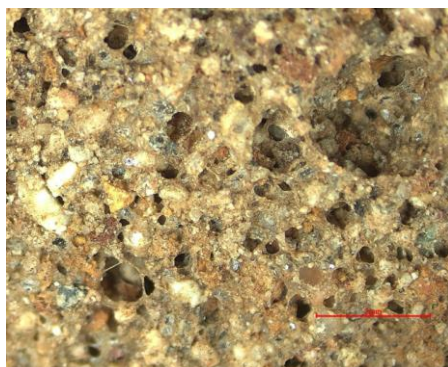


Fig. 6. Stereoscopic image of the pore space of a composite material: scale bar 2 mm.

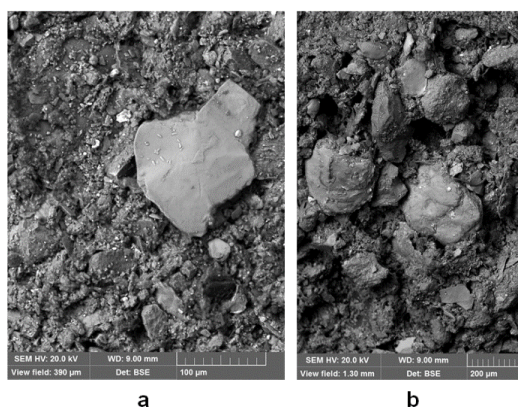


Fig. 7. Micrographs of organic-inorganic composite material after cryogenic treatment: scale bar 100 (a) and 200 (b) μm .

The results of the analysis of microstructural features are consistent with the known literature data [24, 25]. Repeated cryogenic treatment leads to the appearance of solvent polycrystals in the macropores of the formed polymer matrix, which contributes to the transformation of the pore space due to the growth of intermolecular contacts of the polymer component in the walls of the existing pores and, as a consequence, to an increase in the rigidity and strengthening of the composite. It is known that such features of the morphology of the pore space can significantly affect the physical and physicomaterial properties of composites [22, 26-34]. The obtained data are confirmed by the method of computed X-ray microtomography. It was revealed that sequential freezing/thawing of the material contributes to a change in the spatial geometry and volume of the pores (Fig. 8 a-d).

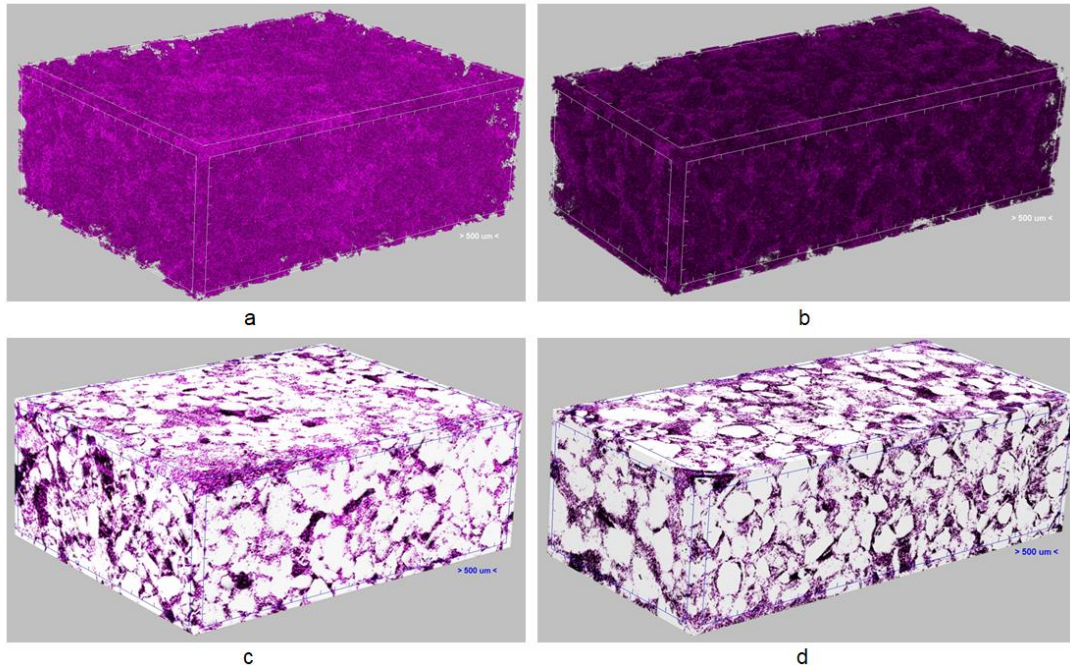


Fig. 8. Microtomographic images of the composite: volumetric image of the sample without cryogenic treatment (a) and after freezing/thawing (b) (pores are shown in black, polymer matrix areas are shown in purple); volumetric image of the distribution of air pores, matrix and filler (black, purple, white, respectively) in a sample without cryogenic treatment (c) and after freezing/thawing (d).

It was found that in the pore space of the composite material subjected to cryogenic treatment and without it, the content of pores with sizes of 0.015-0.045 mm is 53.36 and 53.47%, respectively. At the same time, cryostructuring contributes to an increase in the volume of pores of this size by 1.3 times (Fig. 9). A similar tendency was noted for pores with sizes of 0.045-0.075 mm, the share of which was 40.35 and 37.64%, respectively. The volume of pores with sizes of 0.075-0.105 and 0.105-0.135 mm of the cryostructured sample also increased by 0.70-0.97 times, respectively, in comparison with the composite without cryogenic treatment. The total porosity of the organo-inorganic composite material after cryogenic treatment and without it was 12.04 and 8.37%, respectively.

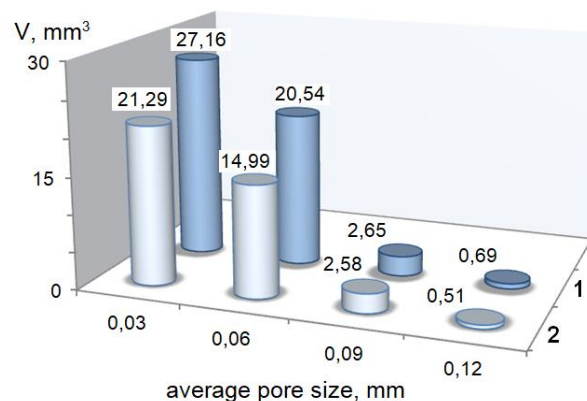


Fig. 9. Characteristics of the pore space of the composite after cryogenic treatment (1) and without it (2).

Thus, cryogenic treatment promotes the formation of a macroporous heterogeneous polymer composition and has a significant effect on the physical properties of the material. Targeted formation of the composite structure will ensure effective management of its performances.

4. CONCLUSIONS

The fundamental possibility of introducing large-tonnage waste of the mining and industrial complex into the compositions of composite materials has been proven. It has been established that the specific effective activity of natural radionuclides of technogenic soil is within the permissible limits ($A_{\text{eff}} = 97 \text{ Bq/kg}$), which allows using this type of waste in the construction industry without restrictions. The chemical and phase composition, physical and physicochemical properties, and structural features of technogenic soil have been studied using methods of atomic emission spectrometry with inductively coupled plasma, infrared spectroscopy, differential scanning calorimetry and thermogravimetry, powder diffraction, scanning electron microscopy, etc., which has made it possible to assess the possibility of its use as a discrete phase in the composite. The mechanism of cryostructuring of the obtained frost-resistant organo-inorganic composite material with a set of specified properties has been established: compressive strength of 6.20 MPa, thermal conductivity of 0.20 W/(m•K), water resistance of at least 3600 s. Differential calorimetry and thermogravimetry methods have shown that the binding of dispersed filler particles with high-molecular compounds in the matrix occurs through the rearrangement of hydrate shells and the formation of organomineral complexes with the participation of clay minerals. Complex formation in the presence of functional groups during the interaction of the polymer matrix of the composite and dispersed filler particles is also confirmed by infrared spectroscopy. Scanning electron microscopy and computed X-ray microtomography methods have revealed the transformation of the pore space, which significantly affects the functional properties of the material. Cryogenic treatment contributes to a change in the spatial geometry and an increase in the pore volume of the composite by an average of 1.4 times, which determines its thermophysical properties.

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