Electrophysical parameters and NMR-characteristics of cryogel

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Abstract. There has recently been great interest in the cryogels based on polyvinyl alcohol. Cryogel usage allows improving existing materials and creating new ones. Cryogel is completely safe, both for humans and for the soil. It protects the soil from drying out and erosion and enhances plant growth, making them more adaptive to the environment. Under the conditions of the Far North, cryogels might be used to strengthen building structures in order to prevent destruction. There is a question of monitoring cryogel distribution in the treated environment. To do this, one needs to know the physical properties of cryogel and composites with ground on its basis. This work aims to study the electrical properties and pore space structure of the composites made from ground and cryogel at various temperatures and various amounts of freezing cycles.

1. Introduction.
Cryogel is a colorless aqueous solution based on a water-soluble polymer, which changes from viscous-elastic polymer to the state characterized by a substantial reversible deformation after passing through the freezing and defrosting cycles. A significant challenge in building in the conditions of the Far North is the construction of foundations and roadways. Because of a large amount of sediments in such areas the foundation of building structures is eroded, with water flows carrying away building material. Measures are needed to strengthen the soil and to create thermal insulation of permafrost to avoid subsidence. For these purposes, it is advisable to apply the new technologies of construction, one of which is the usage of cryogel [1-3] in the Far North in order to prevent the destruction of structures. As a result, there is a question of monitoring cryogel distribution in the treated environment. To map the distribution of cryogel in the soil it is necessary to study the physical properties of cryogel and ground composites. There is also a question of describing the structural features of such ground composites. In this paper, we study the dependence of the electrical resistivity of the ground composites with different amount of cryogel on temperature, with different numbers of freezing/defrosting cycles. One can study the structure of the ground composites with a variety of physical methods, such as NMR-relaxometry, which recommended itself for studying the structure of the pore space of porous media [4-6].

Thus, in this paper we present the results of a study of the physical properties of ground composites with different contents of three types of cryogel, namely, electrical resistivity and NMR-characteristics depending on the number of freezing/defrosting cycles in the temperature range from + 20°C to -17°C. There have been a lot of works aimed at studying physical and chemical properties of cryogels. At the same time, the dependence of electrical resistivity and NMR-characteristics on the temperature in the published literature does not occur.

2. Subject of research.
We study the sand that is used in the construction of the Yamal-Nenets Autonomous District (YaNAO) and cryogel of different chemical composition (Table 1). The soil used to create composites has a density of 1.657 g/cm$^3$, mineral density 2.65 g/cm$^3$ and porosity of 37.47%. Preparation process consisted of two phases: weighing and mixing. The sand and cryogel were blended in the right proportions until being smooth. The maximum proportion of the cryogel was 35%. It is necessary to completely fill the pore space of the ground used. In addition, composites with 25% and 15% content of cryogel were prepared. The prepared samples were stored at room temperature in a closed container.

| Cryogel number | Description                                                |
|---------------|------------------------------------------------------------|
| 1             | 10% polyvinyl alcohol solution (density 1.022 g/cm$^3$)    |
| 2             | 10% polyvinyl alcohol solution with boric acid (density 1.083 g/cm$^3$) |
| 3             | 10% polyvinyl alcohol solution and borax (density 1.064 g/cm$^3$) |

3. Measurement of the electrical properties.

Resistivity measurements were performed using LCR Meter E7-8. It is known that this device is highly reliable and suites for harsh operating conditions. The main disadvantage is that the measurements are carried out only on one frequency of 1000 Hz. E7-8 meter measures the parameters of capacitors, inductors, and resistors. The measuring principle is based on the method of bridge balancing with balancing phase change detectors. First class accuracy electronic scales were used for weighing samples. The error of the analytical balance is ± 0.5e during the initial calibration and ± 1.0e during operation. Three textolite 2-electrode cells with different inner diameters $d_1 = 1.96$ cm, $d_2 = 1.86$ cm, $d_3 = 1.96$ cm and a height of 2.96 cm were made. The cells contained a built-in electronic temperature sensor (DS18B20). It enables to determine the temperature in the range from -55°C to +125°C. The measurement accuracy is ± 0.5°C. The samples of ground composites were placed in the measurement cell and in the freezer where measurements were conducted. After reaching the minimum temperature, the cells were taken out and the resistivities of the samples during the natural thawing were measured. The electrical resistivity was calculated using a standard formula:

$$\rho = \frac{R \cdot L}{S}$$

where $\rho$ - electrical resistivity; $R$ - resistivity; $S$ - cross sectional area; $L$ - length of the sample [7].

It follows from the measurements that ground composites based on cryogels №3 have the highest resistivity. During freezing the electrical resistivity of the sample reaches a maximum in the temperature range from -7 to -10 °C. After reaching a maximum with temperature drop, resistivity drops 2-3 times when reaching the minimum temperature of the freezer (- 17°C). During thawing, the maximum electrical resistivity of ground composites is observed in the temperature range from -2°C to 0°C, after this electrical resistivity decreases to initial values, which were obtained at room temperature. The results of the measurements of pure cryogel №1 are presented in Figure 1.

When pure cryogel is freezed/defrosted, a hysteresis is observed in the dependence of electric resistivity from temperature. With an increase in the number of freezing cycles the form of the curve is saved, and the values of electrical resistivity change only in a small range.
Figure 1. Dependence of the electrical resistivity of cryogel №1 from temperature during freezing, defrosting. The first cycle is on the left, the second cycle is on the right.

Figure 2. Dependence of the electrical resistivity of the soil composite containing 35% of cryogel №1 from temperature. The second cycle is on the left, the fifth cycle is on the right.

The samples with 15%-content of cryogel №3 have the highest electrical resistivity; the dependence of resistivity on temperature remains despite the number of cycles. Such results seem not to have been published before, and the dependence of the resistivity of the ground composites from temperature differs from a similar dependence in case of pure cryogel (see. Figures 1, 2 and 3). The measurement results show that at temperatures below -15°C the values of electrical resistivity differ by several times from those at room temperature. At the same time, the values obtained are different from the electrical resistivity of frozen sand at low temperatures (over 15000 ohmm [4]), allowing one to regard it as an identifying feature. Figures 2 and 3 show that when the samples experience one freezing/defrosting cycle, the subsequent freezing cycles do not seriously affect the observed electrical resistivity values.
4. Study of NMR characteristics.
NMR measurements were made using the relaxometer «MST-05» at a frequency range of 2.2-2.3 MHz. The NMR method is known as a reliable method for studying the pore structure of a porous medium. This method does not have a mechanical impact on a sample [8, 9].

The laboratory NMR measurements of three cryogels and four ground composites based on cryogel show that the cryogel №3 has shorter transverse relaxation time ($T_2$) than the cryogels №1 and №2 (Fig. 4). All three cryogels have a high hydrogen content – more than 65%.

![Figure 3](image)

**Figure 3.** Dependence of the electrical resistivity of the soil composite containing 25% of cryogel №2 from temperature. The forth cycle is on the left, the fifth cycle is on the right.

![Figure 4](image)

**Figure 4.** Spectra of the transverse relaxation times of three cryogels (a) and of their mixture with sand (b).

The Spectra show that the cryogel №3 has the lowest transverse relaxation times, i.e. it is the most viscous. All the NMR spectra are narrow, it confirms the uniformity of the samples’ composition. The reverse situation is observed for the sample consisting of 35% of cryogel and 65% of sand: a mixture of sand with the cryogel №3 has the highest transverse relaxation times and the highest value of porosity index ($\phi$), a mixture of cryogel №1 with sand has the lowest transverse relaxation times. Probable, this is due to different interaction of the cryogels with sand. The cryogel №1, as the least viscous, mixes well with sand and forms a porous sample with good reservoir properties. The cryogel
№3 does not provide a homogeneous mixture with sand, partially remaining in its original form, which leads to an increase in transverse relaxation times as opposed to the cryogel №1.

In addition, we carried out the measurements of NMR spectra of cryogels and ground compositions, depending on temperature. The measurements were performed in the following way. A sample was placed in a recipient with 20 ml volume, and then in a foam container with a build-in temperature sensor (DS18B20), which was placed in the freezer with a minimum temperature -8°C. Then NMR measurements were carried out with a measurement interval of 3°C. Then the container was removed from the freezer and the NMR measurements were carried out during natural defrosting of the ground composite sample with the same interval of 3°C.

During frosting we observe a decrease in transverse relaxation times at the temperature of -2°C for ground composite and at the temperature of +5°C for cryogel. The relaxation times remain constant at these temperatures, which indicates the invariability of pore structure and state of cryogel, which is a part of a porous medium. During defrosting both samples are characterized by a constant increase in transverse relaxation times. A hysteresis is observed in both cases. (Fig. 5).

![Figure 5. Temperature dependence of transverse relaxation time for the cryogel (a) and ground composite with 35% cryogel (b).](image)

As noted previously, during frosting we observe a typical decrease in transverse relaxation times for any cryogel content in the sand. While frosting, the porosity index decreases at temperatures below 0°C, which indicates a decrease in the mobile fluid portion. The porosity index at positive temperatures slightly changes with decreasing temperature. During defrosting the porosity index gradually increases, which indicates an increase in the mobile fluid portion contained in ground composite (Fig. 6). The 3rd and 4th frosting cycles are characterized by the smallest changes of both $T_2$ and $\phi$. During defrosting, each cycle is described by an increase in typical transverse relaxation times and porosity index for all the samples. All the cycles except the first are characterized by the approaching of a constant value $\phi$ and $T_2$ at temperatures above 0°C.
Figure 6. Temperature dependence of the porosity index for the ground composite with the 35% cryogel №3 (a) and cryogel №3 (b).

It should be pointed out that the NMR spectra of the study samples change slightly during frosting/defrosting at all the observed changes of NMR parameters ($\varphi$ and $T_2$) except for pure cryogel. When frosting, the transverse relaxation time spectra of ground composites based on cryogel begin to move towards low $T_2$ values at sub-zero temperatures. At the same time, the NMR spectra of ground composites move towards high relaxation times only to temperatures about +4°C, after which the change hardly occurs. The pure cryogel spectra shift towards high relaxation times when the temperature rises. The cryogel №1 has the highest transverse relaxation times ($\approx$1000 ms), whereas the cryogel №3 has the lowest ones ($\approx$750 ms). During frosting, the cryogels №1, 2 also have similar relaxation times, and the cryogel №3 is characterized by high transverse relaxation times. Probably it is related to the change of its internal structure caused by temperature (Fig. 7).

Figure 7. Temperature dependence of the transverse relaxation times corresponding to the maximum spectra amplitude when frosting (a) and defrosting (b) the cryogels.

The transverse relaxation times of all three cryogels gradually decrease with decreasing temperature (Fig. 7a). The cryogel №3 is characterized by the highest value of $T_2$ at both the maximum and minimum temperature. During defrosting a significant increase in transverse relaxation times is observed only at temperatures above +5°C. The cryogel №3 has highest $T_2$ value. Such
considerable relaxation time changes are not observed in case of ground composites. The $T_2$ values change significantly only at temperatures below -2°C during frosting, until reaching the temperature of 0°C during defrosting.

5. Summary.
We made the temperature-dependent measurements of the electrical properties and NMR-characteristics of ground composites. The measurement results show that at temperatures below -15°C the values of electrical resistivity differ by several times from its electrical resistivity values at room temperature. After the second cycle of freezing/defrosting, the type of resistivity-temperature curve does not change, and the values vary slightly despite an increase in the number of freezing/defrosting cycles. After the 3 cycles NMR-characteristics vary slightly with an increase in the number of freezing/defrosting cycles. At the same time the values of electrical resistivity obtained are different from the electrical resistivity of frozen sand at low temperatures (over 15000 ohmm [10]), allowing one to regard it as an identifying feature. Temperature effect on the transverse relaxation times and porosity index of cryogels and ground composites based on cryogel was studied. It is found that both the relaxation time and porosity index decrease during frosting and increase during defrosting. It allows detecting a change in the mobile fluid portion contained in ground composite. NMR spectra during frosting/defrosting show alteration of a pore structure formed by cryogel and sand under the influence of temperature.

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