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THE "WATER CRYSTALLIZATION-ONSET" METHOD FOR DETERMINING THE FREEZING POINT OF SOILS

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A new method is proposed for measuring the temperature of water freezing in soils, which is termed the "water crystallization-onset" method. The implemented experiments with kaolin clay at different moisture content allowed to compare the proposed method with the known "supercooling" method. The experiments have revealed that the "water crystallization-onset" method gives higher values of freezing point, as compared to the "supercooling" method. Ice inception in soils at this temperature can cause soil skeleton deformation. The range of soil moisture liable for such processes has been determined.

Water–ice, open-ended pores, phase change, dispersed medium

INTRODUCTION

Design and construction of infrastructure facilities in the zone of permafrost distribution is based on the knowledge of physical and mechanical properties of frozen soils strongly affected by their transitions from frozen to thawed state (and reversibly) [*Tsytovich, 1973*]. The most significant changes in water-saturated fine-grained soils occur under alternating freeze-thaw conditions.

When water-saturated soils transit from the unfrozen to frozen state, their structure can change significantly [*Cheverev, 2004; Rogov, 2009*]. From the perspective of thermodynamics this can be explained by the fact that in porous media, pressures differ in the solid and liquid phases of water [*Gorelik and Kolunin, 2002*]. The application of generalized Clapeyron-Clausius equation pertaining to the relationship between the pressure and temperature for conditions of equilibrium between the two pahses showed that the pressure at which ice and water are at equilibrium decreases when the temperature increases (e.g. a 0.1 °C decrease in temperature translates to an increase of about 1.2 atm, which is difference between phase pressures).

Results of numerous experimental studies have demonstrated that redistribution of soil components occurs most intensely at the frozen–unfrozen soil interface, i.e. in the zone subjected to freezing [*Shumsky, 1955; Popov, 1967; Ershov et al., 1979; Solomatin, 1986*]. This zone is delimited by a temperature at which the mass transfer rate in frozen ground decreases sharply [*Horiguchi and Miller, 1980*], as well as by the onset of freezing, i.e. some temperature below the freezing point at which the water freezes spontaneously and quite suddenly. This temperature range is fairly negligible and is largely dictated by the composition of soil; even in the case of fine-dispersed soils, it does not exceed tenths of a degree. Computing these temperatures is therefore an important practical objective.

EXISTING KNOWLEDGE REVIEW

At present, there is no generally accepted experimental method for determination of temperature at which liquid water and ice phases are in equilibrium (i.e. the freezing point for water) in dispersed and porous media with low ice content. Given that no state standard for determining the freezing point had thus far been adopted, there is some temperature value used in the calculation tables to illustrate normative documents for engineering design and construction in permafrost regions, and in thermotechnical calculations [*Building Code, 2012*]. The most widespread method is referred to as "supercooling", suggesting that the analyzed unfrozen sample is cooled to a certain subfreezing temperature, at which water crystallization begins [*Ershov, 1985*]. Ice formation in the system causes the sample temperature to rise rapidly to a certain ultimate value, which is taken as the freezing onset temperature. Results of different investigations have demonstrated that the freezing point of a sample depends on the degree of supercooling [*Chistotinov, 1973*], while the measurement error can be greater than 0.5 °C, which is out of compliance.

As suggested by some authors, such a high measurement error can be lowered by means of the degree of supercooling reduced by admixing ice grains, or "seeds" (nucleators) to the sample. Given that the freezing point is not known before the experiment, it is recommended to set the supercooling temperature at around −1 °C [*Richards et al., 1950*], while true freezing point temperature is measured in the absence of supercooling. Characteristically, the measurement method however involves supercooling, without which it would be impossible to capture the moment of ice inception in the system.

There can be distinguished two major identifiable sources of errors: (1) a sudden (stepwise) change in the amount of unfrozen water in soil while it passes from unfrozen to frozen state at the initial time (inception) of crystallization [*Starostin, 2008*]; (2) dependence of the temperature at the phase boundary between fluid water (liquid) and solid water (ice) on crystallization rate [*Grechishchev et al., 1980*].

Given that soil moisture content (SMC) is low, the first factor yields a significant error in determination of the freezing point. The second (kinetic) factor which is associated with the non-equilibrium state of the system, is primarily governed by the rate of heat exchange between ground and atmosphere. Even at a low rate of ice aggradation (1 μm/s), the temperature at the ice-water interface is approximately equal to −0.1 °C.

The complexity of maintaining the quasi-equilibrium state of the system is largely responsible for the error of the "supercooling" method when measuring the freezing point temperature. This however can be implemented through the "water crystallization-onset" method [*Kolunin and Ishkova, 2015; Ishkova and Kolunin, 2017*], which served as a basis for a number of experiments on various samples of ceramics and membranes showing good reproducibility of results.

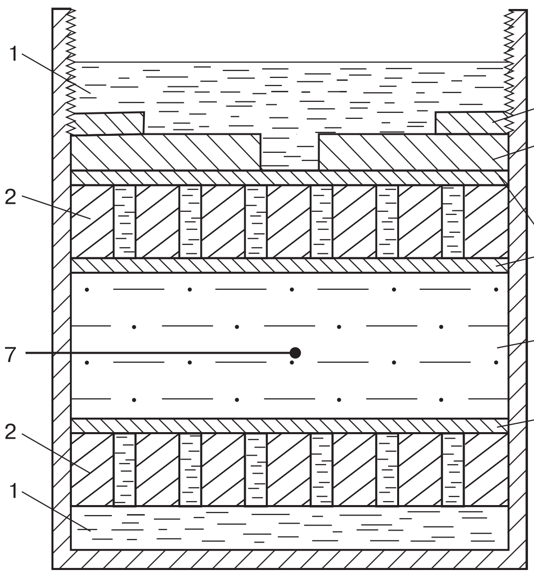

Fig. 1. Schematic drawing of the test cell:

1 – water; 2 – plexiglass sheets; 3 – filter paper; 4 – sample; 5 – retaining ring; 6 –punch; 7 – thermocouple sensor.

If the surface of unfrozen soil sample comes in contact with ice in macroscopic volume at 0 °C, then quasi-equilibrium cooling will yield a certain temperature in the system causing water crystallization in larger soil pores at the water-ice interface, thereby promoting further ice penetration into the porous medium. In other words, the water contained in soil will start freezing without appreciable supercooling. In the physical sense, this is the temperature at which water begins to freeze (i.e. changes phase from a liquid to frozen state) in a porous medium. Determination of temperature at which ice penetrates through a porous medium constitutes the basics of the "crystallization onset" method.

EXPERIMENT METHODOLOGY

The necessary preparations before the experiment involve filling in the experimental block with soil-kaolin clay with moisture content in the range from 0.57 to 0.60 g/g (Fig. 1). Cylindrical soil samples ~4–6 mm thick and ~30 mm in diameter completely infill the middle part of the experimental block, while containers located at the periphery and filled with distilled water are hydraulically connected to soil. Then, the sample is exposed to compression compaction in a stepwise manner, until specified loading p_c is attained, at which the volume is fixed with a locking nut. This is followed by the test cell relocation from the compression unit, and then by soil flushing with distilled water, in order to sweep gas bubbles (degassing) and other impurities out of samples, and saturate them with water. After that, the test cell is placed in a thermostat at atmospheric pressure and ambient temperature, to determine the freezing point.

Below, we describe the sequence in which the experiment was run. First, the thermostat temperature is set slightly below the temperature of equilibrium of the water and ice bulk phases which approximates ca. −0.08 °C. After stabilization of the temperature, ice grains are introduced into the upper container, causing thereby the entire volume of liquid to freeze. The container on the other side of the porous sample holds supercooled water. Then the thermostat temperature is lowered sequentially with a 0.05 °C step over a 4–8 hour (and more) time interval. Prior to lowering the thermostat temperature, the reading on the thermocouple installed in the sample should not change during a time longer than 1 hour. Stabilization of the cooling process is shown on the diagram as a temperature curve that has reached a constant value (straight line).

At a certain below-freezing temperature, which actually is the temperature of the onset of soil freezing, crystallization of water taking place in the pores helps the ice move through the sample into the container with supercooled water, triggering thereby the process of its freezing. This moment is reported as a dramatic increase in the temperature readings on the thermocouple sensors placed in this container. Upon the experiment, weight moisture content of the sample is determined to an accuracy of 0.01 g/g. The time required for conducting a single experiment is one to two weeks. In order to compare results of the above discussed methods, some samples were chosen afterwards for experimental measuring the freezing point using the "supercooling" method [*Ershov, 1985*].

The methodology of experimental works whose results are presented in this paper, involved membrane filters and porous ceramics as major constituents [*Kolunin and Ishkova, 2015; Ishkova and Kolunin, 2017*] and included a compression seal, a new element for soil compaction prior to the experimental measurements. This was the reason why the design of the experimental block had to be modified.

EXPERIMENT RESULTS AND ANALYSIS

The plots constructed for the studied parameters based on the experiments results show the relationship between: (i) moisture content of kaolin clay and compression pressure (Fig. 2); (ii) freezing point and soil moisture content (Fig. 3).

The experimental data revealed that the "water crystallization-onset" method yields higher values of the temperature of freezing point, as compared to the method of "supercooling" (Fig. 3). The difference is particularly conspicuous if the sample moisture content is <0.34 g/g. The obtained temperature range indicates that the freezing point of rocks increases with an increase in moisture content due to soil thawing: from −1.2...−0.8 °C (SMC: 0.3 g/g), to −0.2...−0.1 °C (SMC: 0.40–0.45 g/g).

At low moisture content of soil samples the crystallization onset values spread over a wider temperature values, whereas they show a significantly decreasing trend as SMC increases. This type of relationship was probably a result of the nonlinear dependence of temperature of phase equilibrium between water and ice on the capillary radius. The freezing point of water in the capillary tends to be lower, as its radius decreases [*Gorelik and Kolunin, 2002*]. In this experiment, the water freezes first in larger capillaries. Conversely, the maximum radius of open-ended channel in soil decreases with reducing SMC. In itself, this dependence is statistical, inasmuch as the longest open-ended channel will differ in size for a series of samples of this type of soil with uniform SMC. The nonlinear relationship between the freezing point of water in the capillary and its radius will cause the freezing point to diverge from the mean value proportionally to a decrease in the average capillary radius, even if there is fixed relative divergence in the capillary radius from the mean.

The presented experimental data provide an insight as to whether the ice penetration through the soil induces deformation of its skeleton. As it was noted above, when soil temperature is measured at the freezing point by the "crystallization-onset" method, the system is found to be in a state close to equilibrium. Inasmuch as the unfrozen water is at atmospheric pressure, the relationship between the pressure and temperature for conditions of equilibrium between two phases (i.e. the liquid and the ice pressures and temperature of the medium) is expressed by the generalized form of the Clapeyron–Clausius equation:

$$p_i - p_w = -\frac{\kappa\left(T - T_0\right)}{V_i T_0}, \tag{1}$$

where p_i, p_w are pressures of the solid and liquid phases of water, Pa; $p_w = 10^5$ Pa; T is temperature of the medium, K; κ is molar heat of fusion (ice-to-water phase change), J/mol; V_i is molar volume of ice, m^3/mol; $T_0 = 273.15$ K.

Based on the results of measurement (Fig. 2, 3) and equation (1), the dependence of the excess pressure in the ice ($\Delta p_i = p_i - p_w$) transmitted to soil skeleton at the temperature of its penetration through porous medium was plotted versus the compression pressure (p_c) resulting from compacting load (Fig. 4).

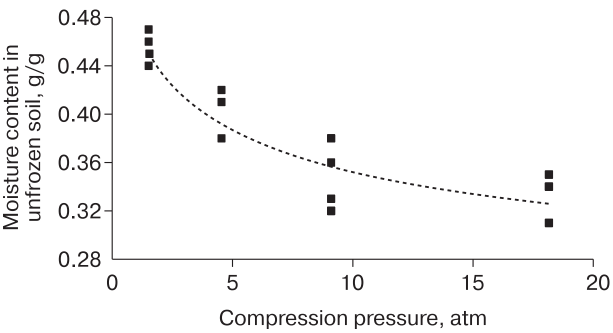

Fig. 2. A relationship between moisture content in kaolin clay and compression pressure.

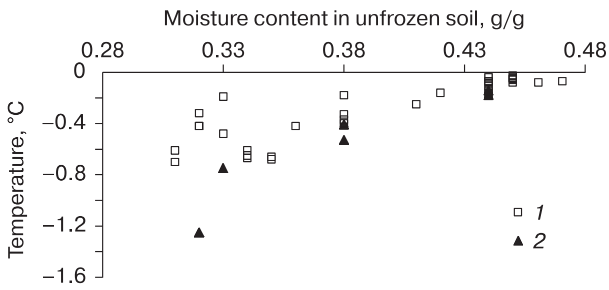

Fig. 3. A relationship between the freezing point of kaolin clay measured using the "water crystallization-onset" (*1*) and "supercooling" (*2*) methods, and moisture content.

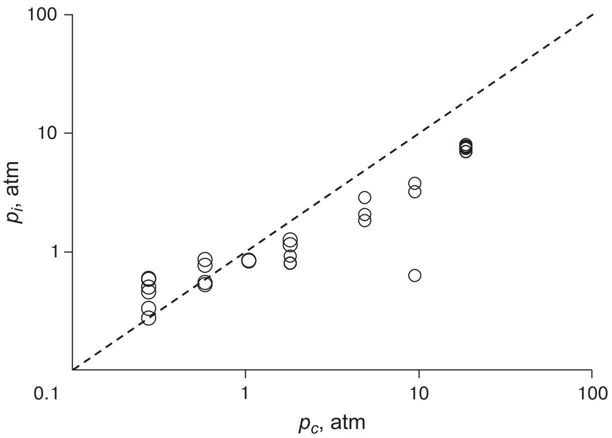

Fig. 4. A relationship between pressure in the ice p_i at the freezing point and the compression pressure p_c.
The dashed line represents equal values of p_i and p_c.

Under significant loading, the excess pressure in ice is usually lower than pore pressure developed in the soil skeleton, so the consolidation of soil particles does occur in the ice and therefore the pore space structure remains unchanged. But the reverse is true for soils compacted under low loading. When compression pressures of less than 0.7 atm (corresponding to soil moisture $W = 0.44$ g/g) is applied, the excess pressure in the ice Δp_i can exceed the compression pressure p_c, thereby creating conditions for the soil skeleton deformation and formation of macro-inclusions in the ice. Figure 4 shows the line of equal values for excess pressure in the ice and compression pressure.

CONCLUSIONS

The considered "water crystallization-onset" method yields higher values of freezing point of water in kaolin clay, as compared to the "supercooling" method. The discrepancy in determining the freezing point by these methods decreases with the increase of moisture content in kaolin clay.

The presence of ice in kaolin clay at the freezing point can cause deformation of soil skeleton when moisture content is in excess of 0.44 g/g.

The proposed method for determining the freezing point in kaolin clay is more accurate in relation to the well-known "supercooling" method.

Since the experiments used specimens with homogenous structure, the "water crystallization-onset" method can be applied only to this type soil samples.

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