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CORRELATION BETWEEN THE SUPERCOOLING PARAMETERS OF A FREEZING MOIST MATERIAL AND THE TEMPERATURES OF TRANSITIONS TO THE PLASTIC- AND SOLID-FROZEN STATE AND ITS LONGEVITY

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The dependence of supercooling parameters of a freezing moist material on its properties and cooling temperature is discussed (using soil as the example). It has been shown that there is an approximate correlation between the supercooling temperature and the temperature at the interface between the solid-frozen and the plastic state, and between the supercooling period and the longevity in the frozen state. A formula for calculating the longevity by the supercooling parameters has been obtained.

Keywords: *frozen soil, supercooling temperature, supercooling period, longevity, long-term strength.*

Introduction. As is known, freezing of a soil is preceeded by its cooling to a temperature (t_{sc}) lower than the temperature of subsequent crystallization of the soil moisture (t_c). Such supercooling of the liquid phase is observed in all substances. The nature of this phenomenon and its relations with external forces and physical properties of the substance are still not clearly understood. The supercooling parameters — its temperature and duration — do not enter into the fundamental equations defining the state, the heat conduction, and the evolution of the substance and are in no way taken into account in thermal or mechanical (force) calculations. Researchers do not often attach much importance to this phenomenon, which is rather ephemeral, not always manifest, and whose significance is unknown; they treat it as a hindrance to experiments. For example, in the aid to methods [1], it is recommended not to allow supercooling at all, for which it is necessary to shake the test sample periodically.

The aim of the present work is to show the significance of the supercooling parameters of a freezing soil and their important role in the formation of its rheological properties — long-term strength and longevity — and give a quantitative estimate of this role.

The ideas and notions advanced in the paper are based on the investigations carried out by N. A. Tsytovich [2], P. I. Andrianov [3], A. P. Bozhenova [4], E. D. Ershov [1], S. E. Grechishchev [5], L. T. Roman [6], G. P. Brovka [7], etc. who have made their contribution to the theory of phase transformations of the soil moisture. The proposed ideas and notions develop the above investigations in terms of the strength properties of soils and ice.

"Embryonic" Stage of Freezing. Figures 1 [1] and 2 [2] give typical examples of the temperature curve of a moist unsalted soil at atmospheric pressure in the freezing-melting cycle illustrating the features of these processes. Supercooling is observed in the freezing half-cycle when the temperature t falls below the t_c value to the value of t_{sc} and then increases stepwise again to t_c. Let us call the peak (cyclic) portion between two passages of the temperature through t_c of length (period of the cycle) τ_{sc}, on which the crystal lattice of ice is formed imperceptibly for the observer and then the first ice crystals "come to light," the latent or embryonic stage of freezing.

Structurization of ice begins when the water temperature decreases to below $+4^{o}$C when the density of water begins to decrease slowly, at a rate of the order of hundredths fractions of a percent per degree. When the temperature reaches some negative value of $t_{sc} < t_c$, a sharp practically stepwise decrease in the density to values corresponding to the density of ice with a simultaneous increase in the temperature to t_c takes place and ice crystals come to light.

The formation of ice crystals is also accompanied by an increase in the internal pressure due to the increase in the volume from V_w and V_{ice} and, accordingly, by a relative deformation $j_c = (V_{ice} - V_w)/V_w \approx 0.09$. Moreover, at

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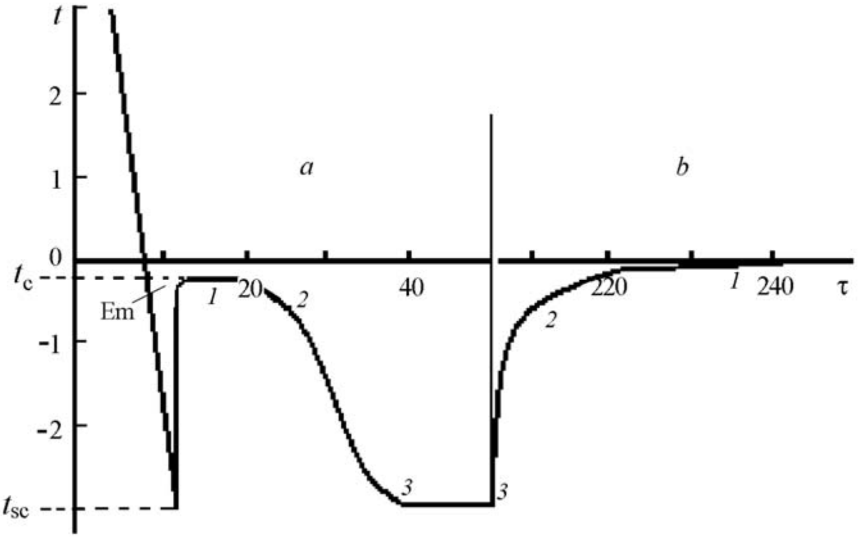


Fig. 1. Freezing (region a) and melting (region b) curves of polymineral clay at W_t = 40% and a cooling temperature of −10°C: 1, 2, 3) numbers of the characteristic portions of the apparent freezing stage (explanations in the text); Em, embryonal freezing stage (supercooling). t, °C; τ, min.

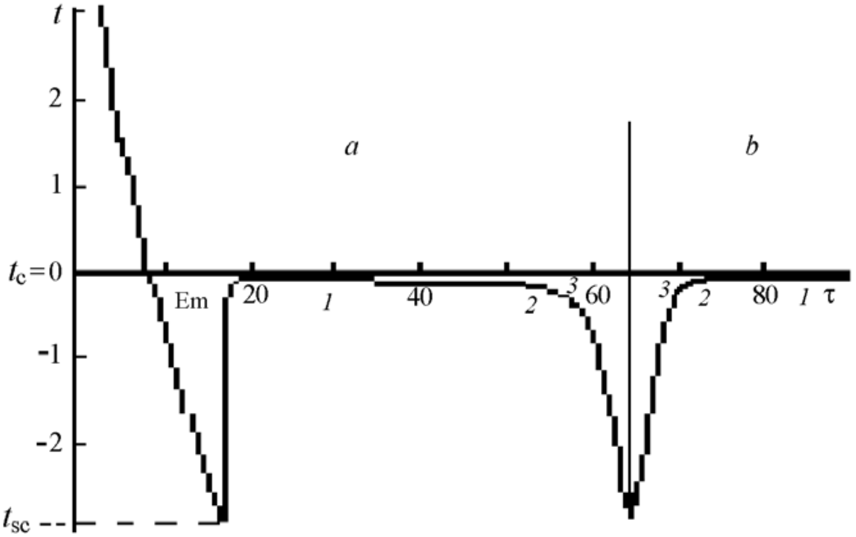


Fig. 2. Freezing and thawing curves of sand at W_t = 19.6% and a cooling temperature of −10°C. Designations 1–3, Em same as in Fig. 1.

this moment the initial portion of latent heat ΔQ_{ph} is released, which is evidenced by the stepwise increase in the temperature from t_{sc} and t_c.

Thus, as to the character of the processes, the supercooling period consists of two sharply asymmetric portions, conventionally, "half-periods." In the first "half-period" of duration τ_{sc} heat is absorbed (ΔQ_{ph}) and nuclei of crystals are formed, and in the second one of duration of one moment (*instant*) heat is released and simultaneously nuclei "come to light." In the theory of strength, by an instant (elementary time) is meant the period of temperature oscillations of atoms — the time of their settled life, $\tau_a \approx 10^{-13}$ sec.

The aggregate of nucleation points of the first crystals forms a crystallization front — a solid-liquid interface representing a moving microinterlayer of thickness of the order of the ice crystal nucleus diameter with a constant temperature t_c. Supercooling creates a temperature potential ($t_c - t_{sc}$) needed for its formation. It can be decreased or even nullified, for example, by shaking the sample. The period of supercooling and its value can also be decreased by increasing the external pressure or with the aid of crystallization seeds, for which any mechanical additives or substances close in structure to ice can be used. Natural seeds are salts dissolved in groundwater whose ions increase the number of active surfaces serving as crystallization centers [1, 2, 6].

The crystallization temperature t_c of a moist soil largely depends (decreases) on its salinity and pressure [1, 2, 6]. At atmospheric pressure and zero salinity it differs slightly from zero (Figs. 1, 2).

At the same time the cooled soil temperature depends on the ambient temperature (coolant) t_{cool} and in the limit tends to it at a rate depending on the heat capacity and thermal diffusivity of the soil. But with the onset of soil moisture crystallization this dependence is overlapped to a great extent by the influence of the internal heat source, which is the crystallization front, and the heat capacity (and the thermal diffusivity) becomes an effective quantity: [1]

$$C_{ef} = C_{sp}\rho_{sk} + (dW_{un}/dt)\, Q_{ph}\rho_{sk}\,. \tag{1}$$

The total value of the latent heat of phase transitions Q_{ph} is the difference between the energy contents of water and ice determined by their specific heat capacities, respectively, $C_w = 4.2$ kJ/(kg·deg) and $C_{ice} = 2.1$ kJ/(kg·deg) and the temperature distribution in the range from absolute zero (–273°C) to t_c, which can be characterized by the temperature averaging coefficients in this range — k_{av}, i.e.,

$$Q_{ph} = k_{av}\,(C_w - C_{ice})\,[(t_c - (-\,273)]\,. \tag{2}$$

Substituting into (2) the known values of C_w and and C_{ice}, as well as as $t_c = 0^{o}$C and the value of $Q_{ph} = 334$ kJ/kg (6 kJ/mole) corresponding to this temperature, we find the k_{av} value for $t_c = 0^{o}$C which for ice turns out to be equal to 0.58. Calculations have shown that in the most probable range of change in the crystallization temperature of water from 0 to -3–4^{o}C this value changes to tenths of a percent, i.e., we can assume $k_{av} \approx 0.58 = \text{const}$.

With decreasing temperature the Q_{ph} value markedly decreases. At a finite temperature of existence of ordinary water (i.e., water whose crystallization temperature decreases with increasing temperature), -22^{o}C, it is already equal to 235 kJ/kg [8, 9], or 4.2 kJ/mole, which practically coincides with the energy quantum value (4 kJ/mole). Neither does the value of $Q_{ph} = 5$ kJ/mole average in the 0 to -22^{o}C temperature range differ from it significantly. To take into account the supercooling at which the temperature decreases to below t_c, it is necessary to add ΔQ_{ph} to Q_{ph}:

$$\Delta Q_{\text{ô}} = 0.58\,(C_{\text{â}} - C_{\text{ë}})\,(t_{\text{ê}} - t_{\text{ïåð}})\,. \tag{3}$$

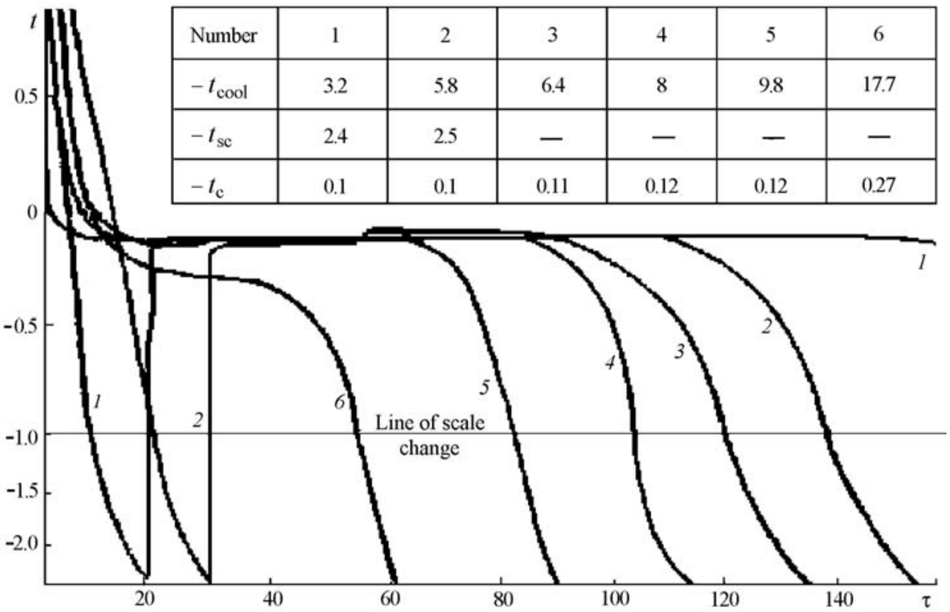
The value of ΔQ_{ph} is an order of magnitude smaller than that of Q_{ph}. For example, at typical values of $t_{sc} = -3^{o}$C and $t_c = -0.3$, $\Delta Q_{ph} = 1.22\cdot 2.7 = 3.3$ kJ/kg. In salted soils, the difference between t_c and t_{sc}, according to the observations of L. T. Roman [6], is 0.1–0.4°. In this case, the value of ΔQ_{ph} is only 0.1–0.5 kJ/mole. The extreme values of ΔQ_{ph} throughout the range of $|t_{sc} - t_c|$ from 0 to -22^{o}C calculated by formula (3) are 0 and approximately 27 kJ/kg, i.e., the value of $\Delta Q_{ph}/Q_{ph}$ varies from 0 to 27/334 = 0.081 almost as the relative melting deformation of ice $j_m = (V_{ice} - V)/V_{ice}$ varying from 0 at $V = V_{ice}$ at the start of the process to 0.083 at its end at $V = V_w$. Deformation of crystallization develops as V changes from V_w to V_{ice} according to the formula $j_m = (V - V_w)/V_w$ from 0 to 0.09. In the first approximation, $j_m = j_c$ can be assumed. The limits of variation of $\Delta Q_{ph}/Q_{ph}$ can also be found directly from the ratio between formulas (3) and (2):

$$\Delta Q_{ph}/Q_{ph} = (t_c - t_{sc})/[(t_c - (-\,273)]\,. \tag{4}$$

The temperature of chemically "pure" water at atmospheric pressure is close to 0°C, and the supercooling temperature can vary theoretically from 0°C to –22°C [9, 10]. Then the limits of variation of $\Delta Q_{ph}/Q_{ph}$ are equal to 0 and 0.083 as in the melting deformation.

Thus, the values of $\Delta Q_{ph}/Q_{ph}$ practically coincide with the relative deformation of the water–ice phase transformations:

$$\Delta Q_{ph}/Q_{ph} = j_m \approx j_c\,. \tag{5}$$



Number	1	2	3	4	5	6
$-t_{\text{cool}}$	3.2	5.8	6.4	8	9.8	17.7
$-t_{\text{sc}}$	2.4	2.5	—	—	—	—
$-t_{\text{c}}$	0.1	0.1	0.11	0.12	0.12	0.27

Fig. 3. Thermograms of the freezing soil at various temperatures ($^{\text{o}}$C) of: cooling (t_{cool}), freezing (t_{c}), and supercooling (t_{sc}); 1–6) numbers of experiments. t, $^{\text{o}}$C; τ, min.

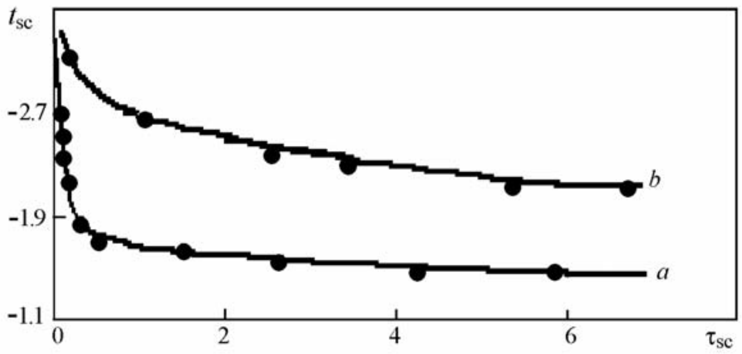


Fig. 4. Relation between the temperature ($^{\text{o}}$C) and the duration of supercooling (10^5 sec or 20.6 h).

The second term in (1) at atmospheres close to zero is hundreds of times larger than the true heat capacity C_{sp}. Under such conditions the crystallization front becomes a shield ("zero screen") protecting the freezing soil from external cooling. The lower the coolant temperature (t_{cool}), the shorter the duration of the crystallization front formation, or, which is the same, the shorter the supercooling period τ_{sc}. At sufficiently low values of t_{cool} the τ_{sc} value becomes smaller than the resolution of measuring instruments and the entire supercooling portion goes from the material region into a virtual (not apparent) region. For illustration, Fig. 3 presents the results of our experiments, performed jointly with L. T. Roman, on determining the dependence of t_{c} on τ_{sc} of peated clay soils (the degree of peatedness was 0.4, the relative moisture was 0.56) at various values of t_{cool}. From Fig. 3 it is seen that as the cooling temperature (t_{cool}) decreases, the supercooling region decreases, and at t_{sc} of about –6 to 8$^{\text{o}}$C it disappears from view.

As soon as the water reaches the temperature τ_{sc}, the crystallization front is formed instantaneously. As the absolute value of t_{sc} decreases, the supercooling time τ_{sc} increases (due to the first half-period, the second one, equal to an instant, remains practically unaltered). If the coolant temperature is close to t_{c}, then the τ_{sc} value tends to infinity.

The dependence of the supercooling temperature on its duration has been investigated in detail by S. E. Grechishchev et al. [5]. Some of the results of their experiments are given in Fig. 4: a) for a clayey soil with a moisture of 26.2% and a freezing temperature $-t_c$ = 0.4–0.5°C; b) for a clayey soil with a moisture of 20.5% and $-t_c$ = 0.26–0.34°C. Dots on the graph show the experimental data; the curves have been constructed by the formula approximating this graph:

$$t_{sc} = t_{min} (\tau_{min}/\tau_{sc})^g \, . \tag{6}$$

The minimum supercooling temperature t_{min} corresponding to the minimum supercooling period τ_{min} (as observed in the experiment) is reckoned, as t_{sc}, from t_c.

The initial data of the approximation in variants are: a) g = 102, τ_{min} = 30 sec, t_{min} = –3.3°C, t_c = –0.4°C; b) g = 105, τ_{min} = 8.1 h, t_{min} = –3°C, t_c = –0.3°C.

Formula (6) satisfies the boundary conditions: at $\tau_{sc} \to \infty$ t_{sc} = 0; at $\tau_{sc} = \tau_{min}$ $t_{sc} = t_{min}$. Note that the exponent g is close in value to the relative deformation of crystallization $g \approx j_c \approx$ 0.09–0.1, and the maximum possible supercooling (instantaneous, at $\tau_{sc} \approx \tau_a \approx 10^{-13}$ sec) in both variants turns out to be equal to –22–25°C. This is close to the minimum temperature at which ordinary water can still exist (not freeze) before turning to ice-1 (at a pressure of 220 MPa [9, 10]), i.e., the highest and lowest possible values of t_{sc} (approximately 0 and –22°C) are equal to the highest and lowest possible values of t_c.

From (6) follows

$$t_{sc} (\tau_{sc})^g = t_{min} (\tau_{min})^g = \text{const} = \mathcal{L} \, . \tag{7}$$

The constant can be estimated approximately by substituting into (7) $g \approx 0.1$, t_{min} = –22°C, and $\tau_{sc} \approx \tau_a \approx 10^{-13}$ sec. We obtain $\mathcal{L} \approx -1.1^{\circ}\text{C}\cdot\text{sec}^{0.1}$.

Apparent Stage of Crystallization. At this stage the liquid crystallizes spontaneously, without the participation of external forces, at the cost of the portion of energy ΔQ_{ph} released stepwise by the formation of the crystallization front at the end of the latent stage — formula (3). At the first time step (at the first instant of time) of the apparent stage this energy is expended in increasing the frozen zone by Δh_1 with release of a portion of energy $\Delta Q_{ph.1}$, which in turn at the second time step (at the second instant of time) is expended in increasing the frozen zone by Δh_2 with release of a portion of energy $\Delta Q_{ph.2}$, and so on until the whole of the thermoactive moisture is frozen. Thus, the crystallization process can be represented as a sequence, a stepwise chain of interconversions of the heat ΔQ_{ph} initially released at the latent stage into work and back, and the latent stage itself and its duration τ_{sc} can be given as an elementary link of this chain. In all, during the crystallization time ΔQ_{ph} turns over ($Q_{ph}/\Delta Q_{ph}$) times, approximately from 12 to infinity (see the above calculation of $\Delta Q_{ph}/Q_{ph}$).

The apparent stage of crystallization includes three portions (Figs. 1, 2). On portion 1 characterized by constancy of the temperature t_c, free water freezes. On the thermograms, this portion has the form of a horizontal straight line. Then in the temperature range from t_c to t_{sf}, the temperature corresponding to the onset of the solid-frozen state (portion 2), loosely bound water crystallizes. On these two portions, practically the whole of the thermally active ground water freezes. Freezing is followed by an increase in the volume in the limit by about the value of the difference between the volumes of water and ice, as well as by an increase in the pressure on the unfrozen water and a decrease in the temperature in the limit (in a closed, rigid system) to values of $t \approx -22^{\circ}$C and $P \approx 220$ MPa, respectively [9, 10].

The strongly bound water (in a negligibly small quantity) continues to freeze on portion 3 at lower temperatures when the intensity of phase transitions sharply decreases, and the leading roles in the formation of the soil temperature begin to be played again by the cooling temperature and the heat capacity.

Despite the different character of the thermograms at the latent and apparent stages of crystallization, their similarity can easily be seen: both stages begin from t_c, in either of them ice is formed, but at the latent stage this process proceeds at the microlevel and, because of its smallness, is unavailable (or hardly available) for observations. The limits of variation of the temperatures, t_{sc} responsible for the nucleation of ice crystals and t_c responsible for the further crystallization, from 0 to –22°C, are also the same, i.e, the role (assignment) of t_{sc} at the latent stage is the same as that of t_c at the apparent stage — conversion of water into ice. To each supercooling temperature the freezing and thawing temperature are equal in value.

The observed value of t_{sc} in a certain (optimal) range of cooling temperatures from −6 to -10^oC approximately coincides in value with the temperature of the end of freezing of the thermally active (free and loosely bound) water and the beginning of the solid-frozen state of the soil: $t_{sc} \approx t_{sf}$ (Figs. 1, 2). At higher values of t_{cool} the τ_{sc} value tends to infinity (and it is only in this case that it is recommended to shake the sample in order to continue the experiment); at lower values the supercooling step is not observed (it goes out of "sight"). More precisely, the optimum value of t_{cool} is determined from a set of experiments with samples — twins.

Melting proceeds in the reverse order (region b in Figs. 1, 2): first the ice of strongly bound water melts (portion 3), then the ice of the loosely bound water frozen at low temperatures close to t_{sf} (portion 2) melts, and then, as the temperature increases, the ice of free water melts (portion 3). Melting-out of free water occurs sometimes in a small temperature range whose average temperature is somewhat higher than the crystallization temperature. Additional expenditures of energy for creating the interface, "melting front," are not required, since practically at any negative temperature in the frozen soil a certain quantity of unfrozen water exists, i.e., the interface in the frozen soil is always present as opposed to the melted soil.

As is seen from Figs. 1 and 2, to the crystallization temperatures there correspond also certain melting temperatures, in particular, to the maximum supercooling the temperature of onset of melting of loosely bound water corresponds. The crystallization front has transformed to a melting front moving in the opposite direction.

Phase Equilibrium Equation. Changes in the volume, pressure, and temperature in the process of phase transitions occur simultaneously, in accordance with the Clapeyron–Clausius phase equilibrium equation [11, 12]. Here we restrict ourselves to its classical, limiting variant (when the specific volumes of ice upon freezing and of water upon melting have reached their limiting values) in the form of the relationship between the melting temperature and pressure:

$$t_m = Pj_m T_0 / L_m = Pb \quad \text{or} \quad P = t_m / b \,. \tag{8}$$

In the analogous formula for the crystallization temperature t_c, the volume values of the relative deformation and the latent heat change by an equal number of times, but the phase transition temperature remains unaltered: $t_c = t_m$, i.e., the Clapeyron–Clausius equation does not take into account the details of the freezing and melting processes. It also ignores the temperature dependences of Q_{ph}.

The temperature of the phase transitions is reckoned (as t_{sc}) from the initial value (at atmospheric pressure and zero salinity) depending on the composition, moisture, and other factors that are difficult to take into account. The decrease in the freezing (melting) temperature due to these factors is, in general, small. In sandy soils it is close to zero, in clayey soils it is in the range of $0.1–0.4^o$ [1].

Multiplying Q_{ph} by the density of ice ρ_{ice}, we find the value of the volume melting heat L_m, whose dimension (kJ/m^3) is easily reduced to the pressure dimension (MPa), and then the L_m value can be interpreted as the highest possible pressure at which ice-1 still exist, or as the "instantaneous" strength (melting or breaking strength) at a threshold temperature of -22^oC. At other, higher temperatures the instantaneous strength is smaller. The ratio T_0/L_m in measuring L_m in MPa is approximately equal to 1, then the b value in (8) without account for the dimension is approximately equal to j_m, i.e., $b \approx j_m \cdot 1^oC/MPa$; from one experiment two constants can be determined.

By analogy with solutions, let us call the temperature and pressure at the upper boundary of existence of ice-1 the eutectic ones and denote them as $t_{eu} = -22^oC$ and $P_{eu} = L_m = 235 \cdot 0.917 = 215$ MPa (according to [9, 10], this pressure is somewhat higher, 220 MPa). With account for the temperature dependence of Q_{ph} the equation for water–ice-1 phase equilibrium can be written as follows [13, 14]:

$$\frac{t}{t_{eu}} = \left(\frac{P}{P_{eu}} \right)^{1.2} . \tag{9}$$

Another basic factor causing a decrease in the freezing temperature is salinity, and, notably, it has been established [14] that the dependence of the relative freezing temperature of the soil moisture on the relative concentration of dissolved salts has a form identical to (9):

$$\frac{t}{t_{\text{eu}}} = \left(\frac{K}{K_{\text{eu}}}\right)^{1.2}. \tag{10}$$

This makes it possible to express the soil salinity in terms of the equivalent pressure

$$P_{\text{eq}} = \left(\frac{K}{K_{\text{eu}}}\right) P_{\text{eu}}, \tag{11}$$

which, for taking into account the simultaneous influence of the pressure and salinity on the freezing temperature, is added to the pressure value in formula (9):

$$\frac{t}{t_{\text{eu}}} = \left[\left(P + \left(\frac{K}{K_{\text{eu}}}\right) P_{\text{eu}}\right) \Big/ P_{\text{eu}}\right]^{1.2} = \left[\frac{P}{P_{\text{eu}}} + \left(\frac{K}{K_{\text{eu}}}\right)\right]^{1.2}. \tag{12}$$

If the solution contains several salts, then the sum of the ratios K/K_{eu} of each salt is substituted into formulas (10)–(12). Formula (12) is valid provided that the sum of the relative pressures and concentrations is smaller than 1. For real soils for which the threshold moisture represents low-concentration solutions, this condition is always fulfilled.

The phase equilibrium equation practically stops working by the beginning of the third portion of the apparent stage; by this time almost the whole of the thermally active water has frozen and the soil has gone to the solid-frozen state. The temperature t_{sf} here is approximately equal to t_{sc} (Fig. 1).

Plastic- and Solid-Frozen States of the Soil. N. A. Tsytovich [2] distinguished three regions of phase transitions of the soil moisture depending on the change in the content of unfrozen water W_{un} per degree of temperature decrease, i.e., on the value of the moisture derivative with respect to the temperature at the cost of unfrozen water $dW_{\text{un}}/dt = \xi$:

1) the region of significant phase transitions in which $\xi \geq 1\%$;

2) the transition region in which ξ varies from 1 to 0.1%;

3) the region of a practically frozen state in which $\xi < 0.1\%$.

These three regions approximately coincide with the freezing portions of free, loosely bound, and strongly bound water that appear at the apparent stage of phase transitions (Figs. 1, 2). The first two regions form a zone of plasticity of frozen soils within which the volume (plastic deformation) of the freezing soil moisture increases to the volume of ice. In melting, vice versa, the volume of this region decreases to the volume of water; under mechanical loading in this state, progressive creep develops. In the third region, frozen soils are in the solid-frozen state. Knowing the temperature dependence of the content of unfrozen water, we can approximately estimate the boundary temperature t_{sf} from which the solid-frozen state begins and with which the peak supercooling temperature t_{sc} coincides approximately. The formula of this dependence has the form [14]

$$W_{\text{un}} = \Pi\ |t|^{-n}, \tag{13}$$

where $\Pi = W_{\text{t}} |t_{\text{c}}|^n$ and n are empirical coefficients, and $|t_{\text{c}}|$ is the freezing temperature of the soil with the initial total moisture W_{t} (fractions of unity).

The n value weakly depends on the kind of soil and is largely determined by its consistency, solid ($n \approx 0.25$) and liquid ($n \approx 0.125$); in "pure" water $n \approx 0.125$ also. The most probable values of Π for the basic categories of soil are: 0–0.01 for sands, 0.01–0.03 for sand loams, 0.03–0.08 for loams, and 0.08–0.15 for clays.

Taking from (13) the derivative ($dW_{\text{un}}/dt = \xi$), we obtain

$$\xi = -n\Pi\ |t|^{-(1+n)}, \tag{14}$$

whence, taking into account that the minus sign before the right side of (14) points only to a decrease in ξ with increasing $|t|$ and is omitted in the calculations, we get

TABLE 1. Approximate Values of Π, $|t|_{\mathrm{lb}}$, and $|t|_{\mathrm{sf}}$ for the Basic Kinds of Soil

Indices	Soil						
	sand	sand loam and loams			clay		
Π	0.01	0.03	0.05	0.07	0.09	0.1	0.15
$\lvert t\rvert_{\mathrm{lb.1}}$	0.33	0.8	1.2	1.6	1.9	2.1	2.9
$\lvert t\rvert_{\mathrm{lb.2}}$	0.16	0.42	0.65	0.9	1.1	1.2	1.7
$\lvert t\rvert_{\mathrm{sf.1}}$	1.2	2.9	4.3	5.7	6.9	7.5	10.4
$\lvert t\rvert_{\mathrm{sf.2}}$	0.7	1.7	2.8	3.7	4.6	5.1	7.3

$$|t| = (n\Pi/\xi)^{1/(1+n)}\,. \tag{15}$$

Evidently, it is more expedient to draw the boundary between the solid-frozen and the plastic-frozen states in the scheme of N. A. Tsytovich not by $\xi = 0.001$ (0.1%) but by $\xi = 0.002$ since this relative deformation has been adopted in the solid mechanics, including the frozen soil mechanics [15], as a conventional flow boundary. Substituting into (15) $\xi = 0.01$ and $\xi = 0.002$, we can approximately estimate the temperature at the boundary between the free and loosely bound states (t_{lb}) as well as between the loosely bound and strongly bound states (t_{sb}) of water in the freezing soil. The t_{lb} and t_{sf} values calculated by formula (15) for $n = 0.25$ ($|t|_{\mathrm{lb.1}}$ and $|t|_{\mathrm{sf.1}}$) and $n = 0.125$ ($|t|_{\mathrm{lb.2}}$ and $|t|_{\mathrm{sf.2}}$) are given in the Table 1.

The parameter t_{sf} can also be considered as the temperature characterizing the plastic-frozen–solid-frozen transition of the soil, which practically coincides with the lowest possible value of $|t_{\mathrm{sc}}|$, at least with that observed and in the experiments. If the cooling temperature $t_{\mathrm{cool}} < t_{\mathrm{sf}}$, then supercooling is not observed, and the apparent crystallization stage begins immediately.

Supercooling, Longevity, and Long-Term Strength. Let us write the expression for the longevity of the frozen soil [12, 13] in the relative form

$$\left(\frac{\tau_{\mathrm{lt}}}{\tau_{\mathrm{a}}}\right)^{j_{\lim}} = \frac{P_{\max}}{P}\,. \tag{16}$$

The maximum $P_{\max}$ (at a maximum duration of the action of load τ_{a}) and the current pressures P in the inverse problem for determining the long-term strength by the given longevity have the sense of the maximum (instantaneous) and current long-term strength.

The value of $j_{\lim}$ in (16), judging from the experimental data of [12–15], is close to the change in the volume of ice due to melting (about 0.08–0.12), i.e., $j_{\lim} \approx t_{\mathrm{m}}$, and $P_{\max}$ is determined from Eq. (8), into which the current temperature of the frozen soil is substituted instead of the melting temperature.

The temperature directly influences only the maximum (instantaneous) strength. According to (16), the long-term strength depends on the instantaneous strength (and already by means of it on the temperature) and longevity. At instantaneous application of the load ($\tau_{\mathrm{lt}} = \tau_{\mathrm{a}}$) formula (16) transforms to the Clapeyron–Clausius equation (8).

Substituting (8) into (16) and taking into account that $j_{\lim} \approx j_{\mathrm{m}}$, let us express the longevity in terms of the temperature

$$\left(\frac{\tau_{\mathrm{lt}}}{\tau_{\mathrm{a}}}\right)^{j_{\mathrm{m}}} = \frac{P_{\max}}{P} = \frac{t}{bP} = \frac{t}{t_{\mathrm{m}}}\,. \tag{17}$$

Formula (17) is essentially the Clapeyron–Clausius equation expanded in time.

From a comparison of formulas (6) and (17) describing the formation and fracture of an iced body it is seen that they have the opposite character of the time-temperature relation: the lower the temperature, the shorter the embryonal phase of the icy structure but the longer the period of its existence, and vice versa. The relation between the supercooling temperature and the crystallization and melting temperatures permits using this parameter (t_{sc}) in tentative calculations of the longevity by formula (17) upon substituting into it t_{sc} instead of t:

$$\left(\frac{\tau_{lt}}{\tau_a}\right)^{j_m} = \frac{t_{sc}}{t_m} .$$

Conclusions. The supercooling temperature and time depend on the physical parameters of the soil and the temperature of the coolant t_{cool}. Judging from the experimental results, t_{sc} is close in value to the temperature on the lower boundary of the solid-frozen state t_{sf} as it goes from the solid-frozen to the plastic-frozen state at which loss of stability begins. However, this shows up only at $t_{sf} > t_{cool}$. But if $t_{cool} > t_{sf}$ (and, therefore, $t_{cool} > t_{sc}$), then the supercooling sufficient for the formation of ice crystals is not attained. In this case, supercooling lasts for an indefinitely long time.

There is a correlation between the supercooling temperatures and the temperature at the boundary of transition of the solid-frozen state to the plastic one in which progressive creep begins, and the "half-period" of the practically stepwise transition from t_{sc} to t_c (Figs. 1, 2) corresponds to the initial (elementary) longevity equal approximately to τ_a. This permits using the supercooling parameters in estimating calculations of the longevity and strength of a frozen (iced) body.

NOTATION

b, pressure-melting (crystallization) temperature proportionality coefficient, ^{o}C/MPa; C_{ef}, effective heat capacity of the freezing (thawing) soil, kJ/(m^3·deg); C_{sp}, specific heat capacity of the freezing (thawing) soil, kJ/(kg·deg); C_{ice}, C_w, specific heat capacities of ice and water, kJ/(kg·deg); g, empirical coefficient (exponent); Δh_1, Δh_2, ..., first, second, and subsequent increments of the crystallization front, cm; j_m, j_c, changes in the volume of the body (volume relative deformation) under melting and crystallization, fractions of unity; j_{lim}, limiting (breaking) deformation, fractions of unity; k_{av}, coefficient of temperature averaging, fractions of unity; K, K_{eu}, current and eutectic concentrations of the solution, fractions of unity; L_c, L_m, volume crystallization and melting heat, kJ/m^3; P, current pressure, MPa; P_{max}, maximum pressure, MPa; P_{eu}, eutectic pressure, MPa; P_{eq}, equivalent pressure, MPa; Q_{ph}, latent crystallization (melting) heat, kJ/kg; ΔQ_{ph}, initial portion of latent crystallization heat, kJ/kg; $\Delta Q_{ph.1}$, $\Delta Q_{ph.2}$, ..., first, second, and subsequent portions of latent crystallization heat, kJ/kg; t, temperature, ^{o}C; T_0, melting temperature of "pure" ice at atmospheric pressure ("initial" melting temperature), K; t_{eu}, eutectic temperature, ^{o}C; t_{cool}, coolant temperature, ^{o}C; t_c, crystallization temperature, ^{o}C; t_{sc}, supercooling temperature, ^{o}C; t_{min}, minimal (in absolute value — maximum) supercooling temperature (from the experimentally observed ones); t_{sf}, temperature of the transition to the solid-frozen phase, ^{o}C; t_{lb}, temperature of the transition to the loosely bound state, ^{o}C; V, current specific volume, m^3/kg; V_{ice}, V_w, specific volumes of ice and water, m^3/kg; W_t, total moisture, fractions of unity; W_{un}, moisture due to unfrozen water; $\mathcal{L}$, constant in formula (7); ρ_{sk}, ρ_{ice}, density of the soil skeleton and ice, kg/cm^3; τ, time, min; τ_{min}, minimum duration of supercooling (from the experimentally observed values); $\tau_a \approx 10^{-13}$ sec, period of temperature oscillations of atoms (minimum longevity); τ_{sc}, supercooling time; τ_{lt}, longevity. Subscripts: a, atom; w, water; lt, long-term; c, crystallization; ice, ice; av, averaging; cool, cooling; m, melting; lim, limiting, sc, supercooling; lb, loosely bound; t, total; sk, skeleton; sf, solid-frozen; ph, phase; eu, eutectic; eq, equivalent; min, minimum; 0, initial.

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