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PHASE EQUILIBRIUM AND KINETICS OF SALINE SOIL WATER FREEZING

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Abstract

A thermodynamic model of phase equilibrium and kinetics of saline soil water freezing and thawing was developed and verified. X-ray studies of pore ice formation in water-saturated clays were carried out. The ice phase existence in freezing soils was studied. The experiments showed that after soil thawing the ice phase in pores exists up to +1 to +3 °C. In freezing soils, the ice phase appears at temperatures from -2 to -4 °C. During soil thawing the ice content decreased in a step-shaped manner. An electrometery technique for simultaneous measurement of local electrical conductivity and phase front temperature depression was developed. The dependence of the phase front temperature versus its velocity was obtained for fresh and saline water-saturated soils (clay, loam, sand). It was shown that the phase front temperature depression under equal freezing velocities is larger if the soil particle size is smaller and the salinity is greater.

Theoretical model

In previous publications (Grechishchev et al., 1980; 1984), a kinetic theory of heat - mass-transfer in freezing - thawing water-saturated non-saline fine-grained soils was developed. In Grechishchev et al., (1984), it was also noted that in thermodynamic processes with phase transitions in soils, it is necessary to take into account the concentration of substances dissolved in water. An analysis of the literature shows that experimental study of frozen saline soils has resulted in the accumulation of significant information about them. However, theoretical and experimental research on phase transition kinetics in saline soils remains poorly developed.

Consider the thermodynamic (physico-chemical) conditions in freezing water-saturated soil where the pore-water contains dissolved substances, making it a solution. The freezing front can be considered as a system of the following interacting phases: (1) ice, (2) water solution in small (not freezing at given temperature) pores, (3) water solution in large (i.e. freezing at given temperature) pores. A thermodynamic condition for all phases can be characterized by Gibb's equations (Grechishchev et al., 1984).

$$S_j \bullet dT + V_j \bullet dp_j + kT \bullet dC_j + d\mu_j = 0 \quad [1]$$

where j - phase number (1 - ice, 2- solution in small pores, 3 - solution in large pores), k - Boltzman's constant, C_j - concentration of dissolved substances in j phase, S - specific entropy, V_j - specific volume, p - pressure, T - temperature, μ - chemical potential.

Consider an interaction of a solution in small pores with an ice phase, and write a Gibb's equation for each of these two phases:

$$S_1 \bullet dT + V_1 \bullet d\sigma_n + kT \bullet dC_1 + d\mu_1 = 0$$
$$S_2 \bullet dT + V_2 \bullet dp_2 + kT \bullet dC_2 + d\mu_2 = 0 \quad \text{[2] and [3]}$$

where σ_n - a full pressure (pressure on the ice lens), the indexes 2 and 1 refer to film solution (solution in small pores) and to ice, respectively.

Let's assume as usual that the differences of chemical potentials and pressure in neighboring phases are proportional to phase interaction velocity, i.e.:

$$\mu_i - \mu_j = a'_{ij} \bullet q'_{ij}$$
$$p_i - p_j = a'_{ij} \bullet q'_{ij} \quad \text{[4] and [5]}$$

where α_{ij} - empirical factors of proportionality, q_{ij}- phase interaction velocity. Subtracting these equations from Gibb's equations for film solution and ice and assuming that

$$S_2 - S_1 = -L / T \quad [6]$$

where L - latent heat of fusion, and also assuming Terzaghi's equation

$$\sigma_n = \sigma_n^e + p, V_2 \cong V_3 \quad [7]$$

where σ^e_n- effective pressure (in soil skeleton), p - pressure in solution in large pores; V_3 - specific volume of water, we derive:

$$-L \bullet dT/T + V_1 \bullet d\sigma^e_n + (V_1 - V_3) \bullet dp + k \bullet T \bullet d(C_1 - C_2) = -V_3 \bullet a_{32} \bullet dq_{32} + a_{12} \bullet dq_{12} \quad [8]$$

where q_{32}- flow velocity of a solution from a large pore to a film solution (i. e. it is the flow of pore solution to the freezing front), q_{12} - velocity of freezing of a solution in small pores, C_1 - residual concentration of dissolved substance in ice, C_2 - concentration of the same substance in small pores on the ice-water boundary.

In the specific case when segregated ice lenses are growing, the water flow velocity at the freezing front q_{32} should be equal to the freezing velocity water q_{12}. The residual concentration of dissolved substances in ice should be proportional to a flow of this substance from film to ice, i. e.

$$C_1 \cong \beta \bullet q^{(c)}_{21} \quad [9]$$

where $\sigma^{(e)}_{21}$- dissolved substance flow from film to ice, β - empirical factor of proportionality.

Substituting the last expression into the previous one, we derive an equation for the kinetics of phase transitions in small pores:

$$a_1 \bullet dq_{32} + a_2 \bullet dq_{21} + a_3 \bullet dq^{(c)}_{21} = L \bullet dT/T - V_1 \bullet d\sigma^e_n - (V_1 - V_3) \bullet dp - kT \bullet dC_2 \quad [10]$$

where σ_1, σ_2, σ_3- new symbols for former empirical factors of proportionality.

After integrating both equations in linear approximation we derive the following kinetic equations:

$$a_1 \bullet dq_{32} + a_2 \bullet dq_{21} + a_3 \bullet dq^{(c)}_{21} = L \bullet (T_0 - T)/T_0 - V_1\sigma^e_n - (V_1 - V_3)(p - p_0) - k \bullet T \bullet C_2$$

$$a_4 \bullet dq_{32} + a_5 \bullet dq_{21} + a_6 \bullet dq^{(c)}_{21} = L \bullet (T_0 - T)/T_0 - (V_1 - V_3)(p - p_0) - k \bullet T \bullet C_3 \quad [11] \text{ and } [12]$$

where P_0- atmospheric pressure, T = 273 K.

These equations characterize the kinetics of phase transitions in small and large pores accordingly and include dissolved substances, which a former model did not include (Grechishchev et al., 1980). From the last two equations it follows that the mechanical pressures σ_n and p act in this model in the same way as in our previous model (Grechishchev et al., 1980). The first expression shows that the phase transition which is developed in the right-hand part of the equation is not equal to zero, and therefore can result in flows of water and of substances dissolved in it. If the right-hand part of the equation equals zero, the equation describes conditions of phase equilibrium of a solution with ice in porous media i. e.:

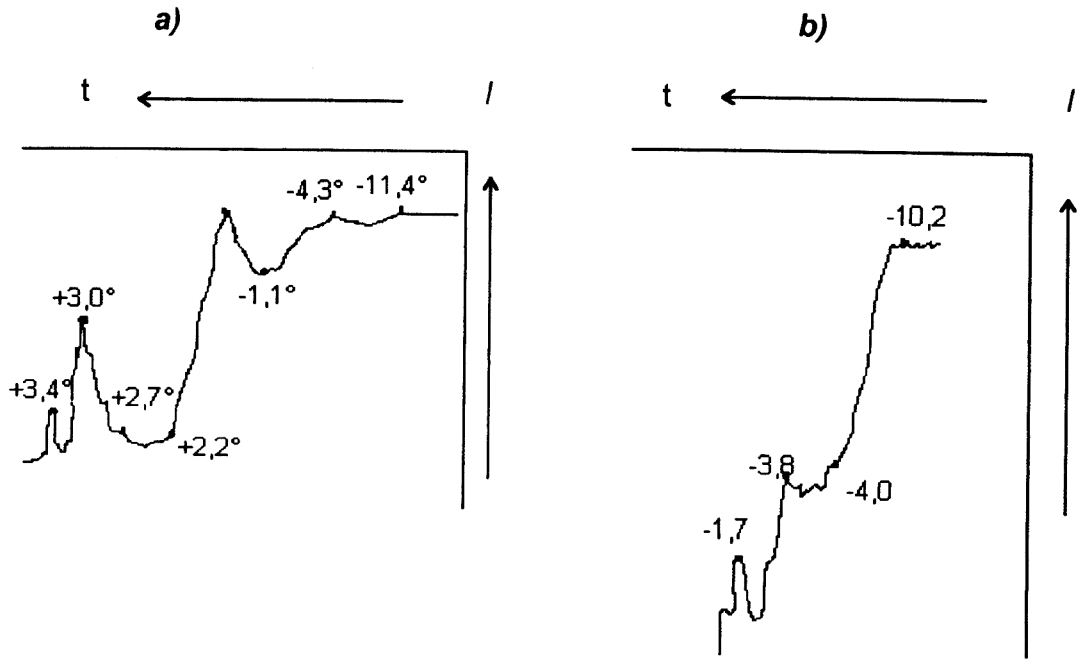


Figure 1. Ice phase x-ray intensity (I) versus time (t) at frozen pastes thawing: (a) bentonite w = 270%, (b) Yamal loam w = 33% (w - water content, numbers - temperature).

Table 1. The main x-ray investigation results

#	Soil type and water content (%)	Temperature depression before freezing, °C	Temperature of ice phase origin at freezing, °C	Change of distance bentonite, temperature changes	interlayer d_{001} of nm, at the	Temperature of ice phase disappearance at thawing, °C
				to - 10 °C	from -10°C to +15 °C	
1.	Kaolinite, 35-50 %	-4.7 -1.0	-2 -3.0	-	-	+1.0
2.	Bentonite, 60%	-	-3.6 -4.6	1.86-1.54	1.54-1.80	+1.0
3.	Bentonite, 100%	-5.0 -2.2	-2.4 -3.1	1.92-1.70	1.70-1.90	+1.0
4.	Bentonite, 270%	-4.5 -0.1	-2.9	1.94-1.76	1.76-1.90	+4.0
5.	Bentonite compressed (load 0.075 Mp•), 86%	-4.7 -0.1	-2.3 -3.2	1.86-1.82	1.82-1.86	+2.4
6.	Yamal loam, 38%	-4.1 0	-2.7	-	-	+1.0
7.	Yamal loam fraction >0.05 mm, 37%	-3.5 -0.1	-1.0 ÷-1.3	-	-	+2.0
8.	Yamal loam fraction 0.01-0.05 mm, 37%	-4.0 -0.1	-2.4	-	-	+1.0
9.	Yamal loam fraction < 0.001-0.01 mm, 35%	-2.0 -0.1	-4.0	2.2-1.88	1.88-2.0	+3.0
10.	Yamal loam fraction < 0.001 mm, 34%	-4.4 -1.8	-5.0	2.1 -1.9	1.96-2.1	+4.0
11.	Yamal loam compressed (load 0.1 Mpa), 25.3%	-5.2 -2.1	-2.8	-	-	+1.0

$$L \bullet (T_0 - T) / T_0 - V_1 \bullet \sigma_n^e - (V_1 - V_3) \bullet (p - p_0) - k \bullet T \bullet C = 0 \quad [13]$$

It is easy to see that the derived expression is general by examining the following well-known conditions of partial phase equilibrium: (a) in closed system without dissolved substances, i.e. at $\sigma_n^e = C = 0$

$$L \bullet (T_0 - T) / T_0 = (V_1 - V_3) \bullet (p - p_0) \quad [14]$$

(b) in open system without dissolved substances, i.e. at $p = p_0$, C = 0

$$L \bullet (T_0 - T) / T = V_1 \bullet \sigma_n^e \quad [15]$$

(c) in closed system under atmospheric pressure and with dissolved substances, i.e. at $\sigma_n^e = 0, p = p_0$

$$L \bullet (T_0 - T) / T_0 = k \bullet T \bullet C \quad [16]$$

The first expression is the Clausius-Clapeyron equation, the second one is Haimov-Malkov's equation, and the third one is Van't Hoffs Law connecting the temperature of phase equilibrium to the concentration of a solution.

The two kinetic equations given above, combined with equations for heat and water conductivity and diffusion of dissolved substances, form a kinetic physico-chemical model of phase transitions (freezing - thawing) in porous and fine-grained media, saturated with solutions. The empirical factors included in these equations to describe phase transition kinetics can be found from experiments that have been done using x-ray and electrometer techniques, which are reported below.

One of the main problems deserving further study in this area is the local concentration of dissolved sub-

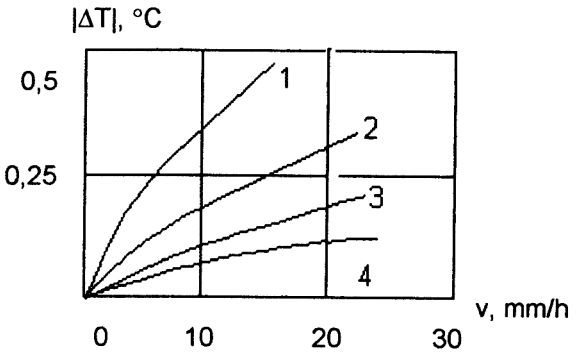


Figure 2. Phase front temperature depression modulus |DT| versus freezing or thawing velocity for non-saline soils (1 - Kudinovskay clay, 2 - Sakhalin loam, 3 - Yamal loam) and for fresh water (4).

stances in small and large pores. The local exclusion of the salts from large to small pores and the origin of "saline pockets" after passage of the freezing front could be important for phase transition kinetics.

X-ray investigations

The X-ray difractometery technique gives valuable information about freezing of soil moisture in pore space (Anderson and Hoekstra, 1965a; 1965b; Norrish and Raussel-Colom, 1962; Filatov, 1981; Grechishchev et al., 1992; Grechishchev and Pavlov, 1994). It is applied to research on ice structure formed in pores of different sizes, and changes of the crystal lattice of clayey minerals in freezing soils. This problem is important for the correct application of thermodynamics to freezing soils, as soil properties are closely connected to the properties of pore ice.

In earlier work (Grechishchev et al., 1992; Grechishchev and Pavlov, 1994) where x-ray and electrometeric methods were used, it was established that (a) during thawing, at the phase transition of ice to water, with disappearance of ice, reflections had a wavy form on difractograms at temperatures from -1 to -2°C; in Na-askangel-clay with a water content of 384%, this process was recorded at + 1°C ; (b) the dependence of temperature depression on crystallization front versus freezing velocity in water-saturated sandy-clayey soils, is symmetrical in relation to freezing and thawing as in water. The latter means, that for numerically equal freezing and thawing velocities, the values of phase transition front temperature deviations from 0°C are equal to each other.

Recently we extended the low temperature range of x-ray investigations of freezing kinetics in clayey soils. An improved low temperature attachable x-ray device to the difractometer, using thermoelectrical elements and a new system of temperature regulation, with thermocouples that measure temperature directly in samples, was developed for the study of phase transitions. This research was carried out on pastes of kaolinite and bentonite of various water content and density, and on Yamal loam and its grain-size fractions.

The aims of the investigations were to estimate: (a) the influence of grain- mineralogical composition upon the mechanics of ice and unfrozen moisture formation; (b) the mechanics of ice formation in pores of various diameters, down to micropores and microcapillaries, and the unfrozen moisture migration in pore space between the crystal lattice of minerals and the pore space of soil.

The main techniques of the studies were described in Grechishchev et al. (1992). The main results of the investigations are shown in Table 1. We first measured experimental curves of changes in ice phase intensity in time. These curves register precisely the moment of occurrence of the ice crystal phase, connect it in time to a temperature jump, which is registered by the thermocouple in a sample, estimate growth of the ice phase in time, quantify the magnitude of this phase, and estimate change in ice particle orientation.

In experiments, a difference in the character of ice phase intensity versus time (termed here "curve IPIT") at freezing and at thawing was observed. A freezing curve IPIT has a monotonous character (except for the initial jump at the moment of occurrence of the ice phase), and at thawing is step-shaped with jumps (see for example Figure 1). This is evidence that in frozen

Table 2. Soil properties before one-dimensional freezing water content

Soil type	Water content, W, %	Dry density ρ_d, kg/m^3	Water - saturation, G	Bulk density, ρ, kg/m^3
Yamal loam	30.55	1430	0.93	1830
Kudinovsky clay (particles size <0.063mm)	39.8	1220	0.86	1610
Sakhalin loam	36.5	1350	0.97	1880

Table 3. Distributions of water W, dry density ρd and water saturation G with depth h of freezing Sakhalin loam sample (freezing from below with velocity 6 mm per hour)

•	Depth, h, mm	Sample state	Water content W, %	Dry density ρ_d, kg/m^3	Water saturation, G	Ice saturation G_i for ice density ρ_i	
						910 kg/m^3	700 kg/m^3
1	0 - 5		35.5	1350	0.94	-	-
2	5 - 10		35.6	1350	0.94	-	-
3	10 - 15		34.8	1370	0.95	-	-
4	15 - 20	**unfrozen**	35.8	1380	0.97	-	-
5	20 - 25 at freezing front		30.4	1490	0.99	-	-
6	25 - 30		35.4	1380	0.98	1.08	1.40
7	30 - 35		39.3	1320	1.0	1.10	1.43
8	35 - 40 in the bottom	**frozen**	44.8	1230	1.0	1.10	1.43

soil during ice crystal growth, a discrete spectrum of temperatures of phase equilibrium is formed. As the displacement of thermodynamic equilibrium occurs under the influence of adsorption forces in the soil skeleton, the step-like behavior of temperatures of phase equilibrium evidently reflects a step-like behavior of pore size distribution.

Fluctuations of curves IPIT are of interest also during thawing of a soil (see Figure 1). They show that during a general thaw of ice, short-term local freezing of thawed or previously unfrozen water in pores is possible. We noted previously (Grechishchev et al., 1992) that during freezing from large pores through small-sized and ultra small-sized pores and capillaries, water outflow occurs from interlayer spaces of a crystal lattice. This is shown by a x-ray difractometery of the size of the interlayer distance of a crystal lattice of montmorillonite minerals (bentonite). As research has shown (see Table 1), at freezing of water-montmorillonite pastes, interlayer water, except 2 to 3 monomolecular layers, moves into pore space forming ordinary ice. The remaining interlayer water is "unfrozen" water. The unfrozen interlayer water quantity basically depends on temperature and on the nature of the exchange cations.

The disappearance of the ice phase in bentonite pastes with water contents of 270%, 100% and 60% occurred at temperatures from + 4 to + 1°C. The existence of "warm" ice is probably connected to special thermodynamic conditions in specific pore space of clays. Thus there is the active reorganization of ice and bentonite particles, together with their aggregates and

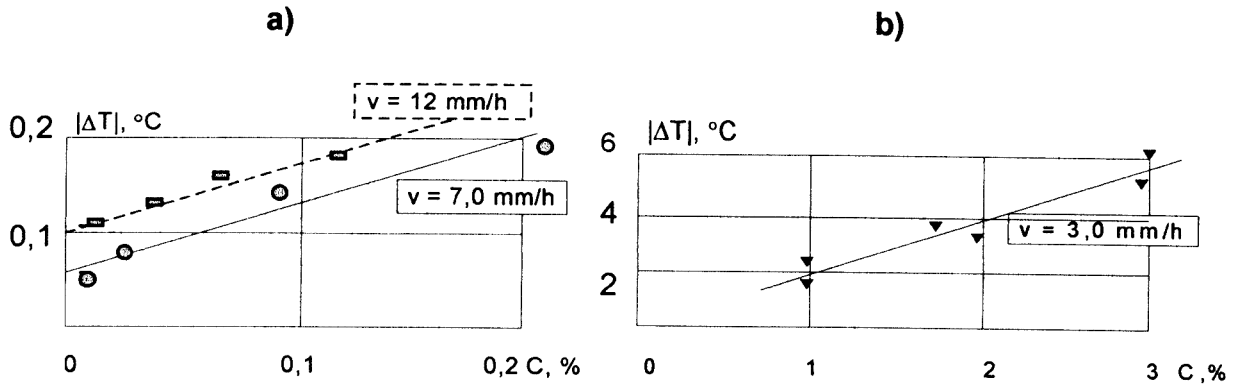


Figure 3. Phase front temperature depression modulus |DT| versus concentration C and freezing velocity v for (a) water solution of NaCl and (b) Yamal loam saturated with water solution of NaCl; experimental data

Table 4. Temperature (T) of the crystallization front of NaCl solutions versus concentration (C) and freezing velocity (v). (T_{eq} - phase equilibrium temperature, T_{pw} - temperature of fresh water freezing)

C, %	v = 7 mm/hour		v = 12 mm/hour		T_{eq}, °C
	T, °C,	$T - T_{pw}$, °C	T, °C	$T - T_{pw}$, °C	
0.02	-0.083	-0.013	-0.110	-0.013	-0.013
0.05	-0.110	-0.040	-0.138	-0.041	-0.036
0.1	-0.138	-0.040	-0.167	-0.070	-0.061
0.2	-0.194	-0.068	-0.222	-0.125	-0.122
0	-0.07	--	-0.097	--	0

blocks, that is marked by brightly expressed fluctuations of ice and bentonite phase reflection intensity.

After bentonite pastes thaw, the water from large pores through small-sized ones comes back to the crystal lattice, which increases but not quite up to the initial d_{001}.

Electrometery investigations

The purpose of our electrometery studies was to assess the temperature dependence of phase transition fronts (water freezing or ice thawing) on phase transition velocity (freezing or thawing) in fine-grained water-saturated non-saline and saline soils. This dependence characterizes phase transition kinetics in fine-grained (sandy-clayey) soils, which in turn, defines the process of ice segregation at freezing.

The electrometery study technique was published previously (Grechishchev et al., 1994). This technique involves the simultaneous measurements of (a) local freezing (or thawing) velocity and (b) temperature of freezing (or thawing) front with help of a device developed by the authors - the electrothermometer "spider". The latter consists of three electrodes, located on corners of a right-angled triangle with each leg being 3 mm long. The electrodes are placed such that one of the legs is placed horizontally and other one vertically. With the help of these electrodes, electrical conductivity is measured continuously at a "point" in a soil in vertical and horizontal directions under freezing or thawing. The freezing velocity is counted during an interval of time between beginnings of the recession of electrical conductivity in vertical and horizontal directions.

A thermocouple indicated the moment of crystallization front passage, which was taken as the phase front temperature. The freezing of samples 4 cm in height and 3 cm in diameter was made in a system that was open from below. The electrothermometer "spider" is placed 15 mm from the bottom of a glass. The electrometric studies of pore moisture freezing kinetics were carried out using one-dimensional crystallization. Materials investigated were non-saline Kudinovsky clay and Sakhalin loam, non-saline and saline Yamal loam, fresh water, and NaCl solutions.

In Figure 2, the results are shown for the average dependence of the module of phase front temperature depression on phase front velocity (i.e. on freezing or thawing velocity). The results displayed are for non-saline soils and fresh water. The variability of experimental measurement was up to 20% of $|\Delta T|$. The soil properties are given in Table 2. During fractioning of Kudinovsky clay and Sakhalin loam, it was observed that the clay content of these soils increased from Yamal loam to Sakhalin loam to Kudinovsky clay, i.e. in the same order as the module of phase front temperature depression.

In Table 3, for example, data describing the distribution of the water content of a mineral skeleton density and ice saturation of freezing samples are shown for a Sakhalin loam. The freezing velocity was 6 - 7 mm/h. The frozen thickness was 25 mm in both cases. The ice saturation was calculated for two measurements of ice density: 910 and 700 kg/m^3. An anomalously low density for segregated ice (700 kg/m^3) was found in earlier experiments on heaving properties of Sakhalin loam (Grechishchev and Shankov, 1993) and is used in Table 3 for comparison. The ice saturation of the frozen part of the Sakhalin loam at ice densities of 910 to 700 kg/m^3 is considerably larger than 1. It shows an extra ice segregation, arising in this case during unidirectional freezing from below.

The results of experiments with NaCl solutions and samples of Yamal loam saturated with NaCl solutions are given in Table 4 and on Figure 3. These data allow us to establish an important empirical expression for water solutions

$$|T(v,C)| = |T_{eq}(C)| + |T_{pw}(v)| \qquad [17]$$

where v and C - freezing velocity and solution concentration, respectively; $T(v,C)$ - the freezing front temperature at given v and C, °C: T_{eq} (C); - temperature of phase equilibrium at given C and at v =0, °C; T_{pw} (v) - temperature of freezing front for fresh water at given v, °C. These experimental data allowed us to estimate the empirical constants that are included in our kinetic model.

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