Influence of Soil Salinity on Pore Water Phase Composition

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Abstract. In areas of intensive construction on the Arctic coast, river valleys of the Republic of Sakha (Yakutia) non-freezing taliks with a high concentration of pore solution (cryopegs) are found in the strata of permafrost soils. N. P. Anisimova made a great contribution to the study of the cryopegs formation in the cryolithozone [1]. For solutions of any composition, it is established [2] that there is a general dependence of the relative freezing temperature on the relative concentration of the solution. It has also been established that the effect of dissolved salts is additive. The freezing temperature of the solution in the pores of dispersed media is affected, in addition to the concentration and composition of the solution the adsorption capacity of the material in relation to the components of the solution.

1. Introduction

It was shown in [3, 4] that the effect of the hydrophilic surface and the solution on the freezing point of water, and, consequently, on unfrozen water amount, is practically additive.

The phase composition of pore moisture and thermophysical properties for saline sand and clay were studied by our complex method [5]. Previously, we [5-7] investigated the temperature dependence of unfrozen water amount in clay-sand mixtures, including for clean sands and clays moistened with distilled water. For the same samples, Efimov S. S. investigated the dependences of unfrozen water amount on the holding time, on the holding temperature value, i.e. on the freezing rate, and on the number of freeze-thaw cycles. It was found that the main factors affecting the amount of unfrozen water in a particular material are the temperature and the concentration of salt in the pore solution.

2. Results of the pore water phase composition research

The nature of the change in the temperature dependence of unfrozen water amount for sand and clay is identical. During thawing from -40 °C to -30 °C, there is no significant change in the phase composition of the pore solution. For sands, starting from -25 °C, and for clays from -30 °C to the eutectic temperature, a sharp increase in the liquid phase of the pore solution begins. The second stage of changing the phase composition of the pore solution begins with the eutectic temperature. The range of this stage is wider than the previous one, starting from the eutectic temperature and ending at the thawing temperature.

The curves of the temperature dependence of unfrozen water amount are well approximated by the formula [8]:

\[ y = a + bx + cx^2 \]
The experimental values [5, 17] of the temperature dependence of the amount of unfrozen water in clay were found. The values of the empirical coefficients and - from the thawing temperature to the eutectic, and - below the eutectic temperature are also given there. The obtained empirical coefficients are used only for those values of the initial humidity and salt concentration at which they were found. Therefore, there are difficulties, especially when solving problems of heat and mass transfer, when the humidity at each moment and at each point changes over time. Therefore, formulas are needed that give the temperature dependence of the amount of unfrozen water depending on the initial moisture content and salt concentration. To do this, consider the temperature dependence of the salt concentration in sand and clay.

\[
W_{H_6}(T) = W + A \left( \frac{1}{1 + \alpha (T - T_{H_6})} - 1 \right) 
\]  

or by the formula [16]:

\[
W_{H_6}(T) = \frac{a}{(T - T_{H.3})^\omega} 
\]

The freezing temperature of a bulk NaCl solution, depending on the concentration, is given in [9] and is shown by a solid line in Fig. 1.

The same figure shows the temperature dependence of the concentration of a pore solution of sand and clay, the following formulas were used for the calculation:

\[
C = \frac{m_c}{m_n} \cdot 100; C(T) = \frac{m_c}{m_{na}} \cdot 100 
\]  

\[
W = \frac{m_v}{m_{wk}} \cdot 100; W_{na} = \frac{m_{na}}{m_{wk}} \cdot 100 
\]

Where \( C \) is the concentration of salt in thawed sand or clay; \( C(T) \) is the concentration of salt at a negative temperature \( T \); \( m_c \) – the salt mass, kg; \( m_v \) – the mass of dry suspension, kg; \( m_{na} \) – the mass of water, kg; \( m_{wk} \) - the mass of unfrozen water.

Provided that pure ice forms and all unfrozen water dissolve salt, we get:

**Figure 1.** The temperature dependence of the volume and pore solution in sand and clay.
Using the experimental values of the phase composition of the pore solution in the sands at different concentrations in the thawed state, the concentrations of the pore solution \( C(T) \) were calculated depending on the temperature (Fig. 1).

At the same time, the decrease in the freezing temperature of the pore solution in the sand coincides with the curve of the decrease in the freezing temperature of the bulk solution (Fig. 1). The temperature dependence of the concentration of the pore solution in clay calculated both for sand and for the bulk solution, is very different. Some authors explained this difference by the fact that clay has a larger amount of strongly bound water, which does not dissolve salts [10]. Then the remaining solution will have a higher concentration than the originally set one, and therefore there is an apparent shift in the equilibrium temperature of the phase transition of the pore solution. Under this assumption, the formula (6) is written as:

\[
C(T) = \frac{C \cdot W}{W'_{nw}(T)}
\]  

Calculations show that with this method, there is no significant change in the dependence of the salt concentration on the temperature at different initial concentrations for clay.

There are some works about the additivity of unfrozen water amount when mixing various materials [11], as well as about the additivity of unfrozen water amount due to the actions of surface forces and the salinity of the pore solution [11]:

\[
W_{nw}(T) = W_{np}(T) - W''_{nw}(T)
\]

Where \( W''_{nw}(T) \) - unfrozen water amount bound by the surface of mineral particles. Then \( W_{np}(T) \) - unfrozen water amount due to the solution.

When calculating the concentration of the pore solution based on the additivity of unfrozen water amount and assuming that the properties of the pore solution do not differ from the properties of a volumetric one, the formula [12, 13] is used:

\[
C(T) = \frac{C \cdot W}{W'_{nw}(T) - W''_{nw}(T)} = \frac{C \cdot W}{W_{np}(T)}
\]

This calculation is valid under the assumption of the existence of a sharp boundary between the bound water surface and the pore solution, as well as if surface forces do not act on the pore solution.

The amount of unfrozen water bound by the surface forces of mineral particles is determined by unfrozen water amount when the soil is moistened with distilled water.

For clay, the temperature dependences of the concentration are also shown in Fig.1. As the research results show, the temperature dependences of the pore solution concentration calculated for sand according to the formula (7), and for clay according to the formula (9), lie close to the curve for a free solution.

This curve is approximately described by the formula [2]:

\[
t_{зам} = -0.7C
\]

where \( C \) is the salt concentration in \% of the solvent weight; or [14]:

\[
t_{зам} = -0.64C
\]
The straight lines calculated by the formula (10) more correctly approximate this dependence for sand and clay, and the solid line (Fig.1) – for a free solution. Therefore, for numerical calculations, the freezing point for sands and clays is recommended to be determined by the formula (10).

The concentration of salt in the sand at any temperature $T$ is determined by the formula (6), i.e.

$$C(T) = \frac{C_0 \cdot W_0}{W_{ne}(T)}$$

(12)

But, as it was shown above, the same salt concentration determines the temperature of the beginning of freezing:

$$T = -\kappa C(T), \text{ i.e. } C(T) = \frac{T}{\kappa}$$

Then the amount of unfrozen water in the sand is determined by the formula:

$$W_{ne}(T) = -\frac{C_0 W_0 \kappa}{T} = \frac{C_0 W_0 \kappa}{|T|}$$

(13)

Substituting the initial values of humidity $W_0$ and salt concentration $C_0$, we can calculate the temperature dependence of the amount of unfrozen water in the sand for any values of $W_0$ and $C_0$.

The calculation using the formula (13) and the comparison of experimental data at $W_0 = 5\%$ shows a good match. Thus, for sand, the amount of unfrozen water from the temperature obeys a hyperbolic law. For the case of recalculation of the temperature dependence of the amount of unfrozen water in clay soils at any other values of the initial humidity and salt concentration, the formula (15) is used. If $W_0$ - the initial humidity, $C_0$ - the salt concentration in the solution before introduction into the soil. Then

$$C_0 = \frac{m_c}{m_w} = \frac{m_{ck}}{W_0}$$

According to the additivity of unfrozen water amount, the salt concentration at the freezing point

$$C(T_{nz}) = \frac{m_c}{m_w - m_{ne}(T_{nz})} = \frac{m_c}{m_{ck}} \frac{1}{W_0 - W_{ne}^0(T_{nz})}$$

(14)

At any temperature below zero:

$$C(T) = \frac{m_c}{m_{ne}(T) - m_{ne}^0(T)} = \frac{m_{ck}}{W_{ne}(T) - W_{ne}^0(T)}$$

(15)

Where $m_c$ - the mass of salt, $m_w$ - the mass of water, $m_{ck}$ - the mass of skeleton; $m_{ne}(T)$ - the mass of unfrozen water at the temperature $(T)$ of saline soil; $m_{ne}^0(T)$, $m_{ne}(T_{nz})$ is the mass of unfrozen water in the soil moistened with distilled water at temperatures $T$ and $T_{nz}$.

Hence, for a given concentration:

$$\frac{m}{m} = C_0 W_0 = C(T_{nz}) \left[ W_0 - W_{ne}^0(T_{nz}) \right] = C(T) \left[ W_{ne}(T) - W_{ne}^0(T) \right]$$

(16)

Hence:
As stated above, then:

\[ C_0(T) = \frac{C_0 W_0}{W_{\text{int}}(T) - W_{\text{int}}^0(T)} \]  

(17)

As stated above \( T = -\kappa C(T) \), then:

\[ C_0(T) = W_{\text{int}}^0(T) + \frac{C_0 W_0 \kappa}{T} \]  

(18)

Using this formula, we can find the amount of unfrozen water at a temperature \( T \) at any values \( C_0 \) and \( W_0 \). At the same time, the amount of unfrozen water depends on the temperature not according to a hyperbolic law, as in sand, but according to a more complex law, since the amount of unfrozen water in clay moistened with distilled water also depends on the temperature according to a certain law.

Thus, to determine the temperature dependence of unfrozen water amount of saline soils at any values of initial humidity and concentration in the initial solution, formula (13) is used for sand, and formula (18) for clay. The experimental and calculated values of unfrozen water amount in salted clay are given in Table 1.

| Table 1. Experimental and calculated values of unfrozen water amount in salted clay. |
|---------------------------------|-----------------|----------------|
|                                | C=5%            | C=10%          |
| \( -T \) | \( W_{\text{int}} \) | \( W_{\text{int}} \) | \( W_{\text{int}} \) | \( -T \) | \( W_{\text{int}} \) | \( W_{\text{int}} \) |
| 5,6   | 4,19            | 13,5           | 9,9            | 3,18 | 13,5 | 15,7 | 2,03 | 13,1 |
| 7,0   | 3,2             | 10,4           | 9,95           | 12,5 | 2,37 | 10,2 | 9,93 | 17,1 | 1,95 | 11,7 | 10,0 |
| 9,0   | 3,0             | 8,2            | 8,25           | 14,6 | 2,44 | 8,9  | 8,9 | 18,5 | 1,88 | 11,0 | 9,3  |
| 11,0  | 2,6             | 6,9            | 6,9            | 16,2 | 1,99 | 8,2  | 7,82 | 19,9 | 1,8  | 10,5 | 8,7  |
| 14,0  | 2,1             | 5,5            | 5,48           | 19,3 | 1,82 | 7,2  | 6,7  | 22,0 | 1,72 | 10,2 | 7,97 |
| 17,0  | 1,95            | 4,7            | 4,73           | 21,1 | 1,76 | 6,7  | 6,24 |
| 20,0  | 1,8             | 4,0            | 3,45           |      |      |      |      |      |

3. Conclusion
To summarize, we can say that it is impossible to interpret the obtained results unambiguously. The complex nature of the conditions of phase equilibrium of water in zeolites at negative temperatures makes it necessary to conduct complex studies, combining various methods.

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