Temperature Dependence of Unfrozen Water Quantity in Clay Soil with Different Moisture Content

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Abstract. We have investigated the relationship between the unfrozen quantity and total moisture content in clay soils in hygroscopic humidity region. To determine the unfrozen water quantity the method of continuous heat supply has been used (calorimetric method). Because crystallization heat of hygroscopic water in soil and that of volume water and different, the crystallization heat of soil water has been determined first during the experiment as a function of moisture and temperature, then it has been used to calculate the quantity of unfrozen water. It has been found that the dependence of unfrozen water quantity on total moisture content is more pronounced at low ice content and is not evident at all when it increases. In this case the dependence of unfrozen water quantity on total moisture content is of more complex pattern than that of the kind at high humidity. Besides the dependence is moistly evident at low ice content and becomes extinct at ice content increasing.

1. Introduction
Notwithstanding establishment of the point that quantity of unfrozen water increases with increase in total moisture content the overall pattern is still not clear. In some instances it has been proposed that the mentioned relationship is characteristic of swelling rocks only, otherwise monolithic structure of material skeleton is considered to be the reason leading to this phenomenon. A number of authors speculate that kaolinitic clays are referred to the rocks not confirming the dependence of unfrozen water quantity on total moisture content, or, vice versa, some researchers state that this relationship in kaolinitic clays is pronounced enough.

The research works dealing with quantitative assessment of dependence of unfrozen water quantity on total moisture content almost have not been performed but for a few examples.

As yet no systematic investigations are available dealing with the reveal and assessment of the factors responsible for the dependence of unfrozen water quantity on total moisture content. An overview of the investigation on this problem shows that it is possible to indicate the factors which according to some authors’ opinion may be the reason of dependence mentioned:
- occurrence of quasi-liquid film on the ice surface [1];
- structural transformations caused by interaction of water with mineral skeleton of dispersion medium [2, 3, 4, 5];
- development of the excessive pressure under water freezing in monolithic dispersion materials [6, 7];
- the effect of a mineral skeleton of a dispersion medium on the chemical potential of ice, i.e. the occurrence of the bound ice in the dispersion medium [5, 8, 9].

Although the presence of quasi-liquid film on the ice surface has been verified with certainty [1, 10] the majority of the researchers hold to the idea that the contribution of the film to the unfrozen water quantity is unessential [10, 11, 12]. However it should be noted that the contribution increases in the area of temperature near 00C. This fact is of great interest as it is often observed in practice in full-scale conditions.

Whereas there are some reports on the first factor mentioned above and the critical assessment of its role in detail, the same cannot be said of the former three factors.

The effect of structural transformations on the unfrozen water quantity under transaction of water with mineral skeleton is quite possible but it is not likely to be the only cause of the dependence mentioned.

It may be indicated by the fact that the dependence is well pronounced in such dispersion materials as brick, concrete where swelling with increasing moisture is not observed contrary to clays [8]. It is widely believed that ice in dispersion media shares the properties identical to those for volume ice, and the chemical potentials of ice are equal [13, 14].

Hence the conclusion follows that the quantity of ice is subject to increase with no effect on the unfrozen water content. It is used for example on describing the phase state of water at subzero temperatures on the basis of sorption and desorption isotherms [12, 15].

However the reported results [5] of the experiment show that the concept is not justified enough and call for further investigation. If the reported results on the occurrence of bound ice dispersion media are confirmed during further investigation, this factor may be considered as the governing out from ones mentioned.

It is a matter of general experience that the change in porosity of dispersion media, for example the occurrence of mesoporous structure on pressing, affects the sorption isotherm [8, 16]. One can assume that the change in porosity under ice formation affects the sorption isotherm as well. Alternatively, the sorption isotherm characterizes the phase state of water at given temperature. Thus the factor responsible for the dependence of unfrozen water quantity on ice content, and hence on total moisture content, might be the change in porosity of dispersion medium during the formation of ice.

Most likely the dependence of the unfrozen water quantity on total moisture content is caused by all the factors taken together. At present there is no way to estimate the contribution of the individual factor and describe it quantitatively as a functional dependence.

### 2. Experiments

The determination of the unfrozen water quantity has been performed with the method of continuous heat supply as a variation of calorimetric method [17]. The unfrozen water quantity in this case is calculated on evidence of temperature diagrams obtained in the process of thawing the sample pre-frozen through to certain temperature. The mathematical formula of the method are the equations of heat balance and contain the values of water crystallization heat depending on temperature.

Formerly [18, 19] on determining the unfrozen water quantity by this method to describe the crystallization heat there has been used the Kirchhoff’s equation in the form as:

\[ h_w - h_i = L^0_w + (c_w - c_i)(t_f - t_B) \]  
(1)

Where \( h_w \) and \( h_i \) - enthalpy of water and ice, respectively, at temperature \( c_w, c_i \) -heat capacity of water and ice, respectively; \( t_f \) - water freezing temperature; \( L^0_w \) - crystallization heat of bound water at \( t_B = 0^0 C \).

As the formula (1) describes the state of the volume water, the present report gives the above mentioned equation for bound water crystallization heat as the following one:

\[ L_{bw} = h^0_{bw} - h_i^0 + (c_{bw} - c_i)(t_f - t_B) \]  
(2)
Where $h_{bw}^0, h_i^0$ - enthalpy of bound water and ice, respectively, at temperature $t_B$; $c_{bw}, c_i$ – heat capacity of bound water and ice, respectively; $t_f$ - freezing temperature of bound water.

In the course of the experiment the water crystallization heat has been determined first in samples in the form of expression (2) as a function of moisture and temperature. While calculating the unfrozen water quantity this function has been used.

The setup for conducting experiment consist of cylindrical measuring cell containing a sample and is heated by a constant – power source. Three concentric heaters maintain the adiabatic heating conditions. Measuring and recording the temperature dynamics of a sample with time and maintaining the adiabatic conditions in the measuring cell during the experiment are performed by computer-oriented systems. Quantity of unfrozen water has been investigated in samples of polymineral clay. The samples in air – dry state have been sieved using the 0.2 - mm cell sifter. Moistening the samples was accounted for by sorption inside the exsiccator with distilled water during two months until moisture reached about 10%.

The experiments first were conducted at this moisture. Thereafter the moisture of samples was decreased on drying by about 2%, and the experiments were carried out at moisture obtained as well. The procedure was performed as long as the moisture became equal 2%. At this moisture value all moisture content in samples within the temperature range tested has remained in the liquid state. For every moisture value there were conducted three experiments.

3. Results and discussion
On thawing temperature diagrams there have been obtained a lot of unfrozen water quantity curves for every sample depending on the temperature at different values of total moisture content.

Figure 1 shows a lot of curves mentioned for one sample.

![Figure 1](image_url)  
**Figure 1.** Dependence of unfrozen water amount on temperature in a clay sample at different moisture.

The temperature effect on the dependence of unfrozen water quantity on total moisture content can be illustrated as follows. Let us select the points in the curve (figure 1) corresponding to the certain temperature and make a plot with values for total moisture content (figure 2) or ice content (figure 3) along the x – coordinate.
Figure 2. Dependence of unfrozen water amount on total moisture content at different temperature t.

The analyses of the data makes it possible to assume that the dependence is evident at low ice content. Although the unambiguous conclusion should not still result from the above consideration [5], the very phenomenon might be a plausible explanation for a given fact.

As one may point out, the dependence of unfrozen water quantity on total moisture content comes into particular prominence with temperature increasing (going toward 0°C). As the temperature goes down to -25°C within the tested region of total moisture content the mentioned dependence decreases and becomes insignificant within the limits of experimental error.

The problems on quantitative assessment of the dependence of unfrozen water quantity on total moisture content have been as yet adequately investigated [4, 20]. This fact makes it difficult to compare the data obtained with various investigation results.

Besides the mentioned reports deal with the investigation of the dependence of unfrozen water quantity on total moisture content at high moisture values, i.e. above maximal hygroscopic moisture.

Figure 3. Dependence of unfrozen water amount on ice content at different temperature.

The NMR-method has been used in paper [20] to determine the unfrozen water quantity within the wide range of temperature and moisture. The dependence of unfrozen water quantity on ice content at the certain temperature is approximated by a linear function.
This means that there is a linear relationship between unfrozen water quantity and total moisture content as well, because ice content is determined as difference between total moisture content and unfrozen water quantity.

Similar results for clays soils have been reported in paper [5] and in earlier one [4] for peat. Contrast to it one can see from figure 2 and figure 3 that within the range of hygroscopic moisture the dependence of unfrozen water quantity on total moisture content is of more complex pattern, and being mostly evident at low ice content it becomes extinct as ice content increases.

Estimations on data from paper [20] show that the dependence of unfrozen water quantity on total moisture content becomes extinct at temperature decreasing. The very phenomenon is observed in mentioned above investigation but within the range of hygroscopic moisture.

4. Conclusion
As follows from mentioned scientific paper within the range of moisture exceeding maximal hygroscopic one in dispersion systems the dependence of unfrozen water quantity on total moisture content can be approximated by a linear relationship.

The calorimetric investigation has determined taken into account the change in crystallization heat of bound water within the range of hygroscopic moisture that the dependence of unfrozen water quantity on total moisture content in clay samples is of more complex pattern comparing with that at high moisture. Besides the dependence is mostly evident at low ice content and becomes extinct at ice content increasing.

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