

Influence of Temperature and Total Water Content on the Unfrozen Water Content Below 0° in Three Model Soils

Tomasz Kozłowski

Chair of Geotechnics, Kielce University of Technology, 25-314 Kielce, Al. 1000-lecia Państwa
Polskiego 7, Poland

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Abstract

A version of the calorimetric method of estimating the unfrozen water content in frozen soils, has been formulated. The method takes into account a more strict description of the parameters of the balance equation, particularly the specific heat of dry soil as a function of temperature. Measurements of the specific heat of soils dried at 110°C and 220°C have been taken. In three soils investigated (bentonite from Chmielnik BCh, bentonite MAD BM and kaolin Sedlec KS), the specific heat decreases linearly with decreasing temperature.

In three model soils investigated the unfrozen water content u at fixed total water content is a non-decreasing function of temperature. Instead, the unfrozen water content at a fixed temperature is a decreasing function of the total water content. A concept of limiting unfrozen water content u_L has been introduced. The value of u_L is, at given temperature, the maximum total water content at which ice crystals are absent in the system.

1. Introduction

The existence of a significant quantity of unfrozen water below the so-called "freezing point" in a soil-water system has been reported by many authors (Pietrzyk 1968, Skarżyńska 1969, Tsytoich 1973, Jumikis 1977, Anderson and Andersland 1978, Frivik 1982, Farouki 1968). The amount of the liquid phase has an important effect on the thermal and mechanical properties of frozen soil. Determining the effect of frost on soil used as a foundation material for roads, air fields, pipelines, and buildings is of critical importance in cold regions. Calculations of the depth of frost or thaw rely on reasonable estimates of the unfrozen water content at temperatures below freezing point.

In the case of normal water in bulk, the initiation of freezing does not usually occur at 0° and some supercooling is necessary. Similarly, soil samples chilled in laboratory conditions usually show evidence of supercooling (Bozhenova 1953, Anderson 1968, Kozłowski 1989). Then, the amount of liquid phase equals the

total water content. At a temperature of T_{SN} , the temperature of spontaneous nucleation, embryo nuclei form and grow to critical sizes. As a consequence of the release of the latent heat, the temperature of the system rises to the value T_o (usually $T_o < 0^\circ\text{C}$), the temperature of equilibrium freezing. Further dissipation of heat lowers the temperature, but the amount of unfrozen water is now a function of temperature, pressure and various properties of the system, and under conditions of thermodynamics equilibrium remains constant.

The unfrozen water content of soil is defined analogically to the total water content:

$$u = \frac{m_u}{m_s} 100\% \quad (1)$$

where m_u is the mass of unfrozen water and m_s is the mass of dry soil.

It has been established that at a given temperature and pressure, the principal factors governing the unfrozen water content are the total water content, the specific surface area of the soil, the number and kind of exchangeable cations, and the species and concentrations of soluble substances present.

Most studies of the unfrozen water content of porous materials did not quantitatively address the effects of the total water content. Investigations of Jung (1932) and Nersesova (1953) showed that the unfrozen water content u decreased with increasing total water content w , but the effect is not significant. Therefore, many investigators (Kolaian and Low 1963, Anderson 1967, Tsytoich 1973, Pietrzyk 1979) accepted the thesis that the unfrozen water content is independent of the total water content to a good approximation. Next, Ananyan (1978) published results that showed that an increase of water content near 0° caused an increase in the unfrozen water content, and the opposite effect at lower temperatures. Tice et al. (1982) reported that u increased with increasing w in wide temperature ranges. At last, in the paper of Xiaozu et al. (1985) extensive data were presented showing evidence of decreasing unfrozen water content with increasing total water content in Morin clay.

This author conducted his own research the goal being to formulate an empirical function $u = u(T, w)$ for three model soils.

2. Materials

For this study, three virtually mono mineral clays were used: bentonite from Chmielnik (BCh), bentonite MAD (BM) and kaolin from Sedlec (KS). Soil properties are shown in Table 1.

Pastes consisting of dry soil material and distilled water were used. The total water content varied between $w = w_p$ and $w = 1.2w_L$. The pastes were stored in closed vessels for about three weeks before the experiment.

Table 1. Soil properties

Property	Bentonite Chmielnik	Bentonite MAD	Kaolin Sedlec
W_p , %	74	27	34
W_L , %	96	291	70
Specific surface, m^2/g	838	226	46
Fraction $< 2\mu^{1>}$, %	1.0	73.7	53.8
Fraction $< 2\mu^{2>}$, %	66.4	75.5	54.7
Main mineral	mont.	mont.	kaol.
Main exchangeable cation	Ca^{2+}	Na^+	Ca^{2+}
CEC, meq/g	1.13	0.81	0.06

^{1>2>} with or without a dispersing agent

3. Method

3.1. A Review of Methods of Determining the Phase Composition of Frozen Soil

The existing research methods may be divided into four basic groups.

A) Dilatometer method (Bouyoucos 1917, Jung 1932, Push 1978). The soil sample is placed in the dilatometer under an immiscible liquid that does not freeze in a wide temperature range. After the crystallization of soil water, the volume of expansion during freezing is calculated. Taking the normal value associated with freezing water to ice, the expansion observed is converted into an equivalent quantity of water and compared to the total amount of water present in the sample (Anderson and Tice 1973).

One of the critical assumptions involved in this method involves the extent to which the immiscible liquid remains completely inert when it covers the sample and fills all the interstices. If the interface so formed is large enough, and if partial solubilization or some other interaction occurs with an associated volume change, then a potentially large error can result. The other critical assumption is that soil water expands when frozen in the same manner as pure water in bulk (Anderson and Tice 1973).

B) Adiabatic calorimetry (Nersesova 1953, Kolaian and Low 1963, Pietrzyk 1979). A sample of frozen soil is brought to thermal equilibrium at a desired temperature below freezing and then quickly transferred to an adiabatic calorimeter filled with a liquid at a positive temperature. Heat exchange occurs between the sample and the liquid until the sample is thawed and raised to a new temperature somewhat below the original temperature of the liquid. The energy yielded by the

liquid is equal to the energy gained by the sample constituents. After calculating the energy expended in melting ice present in the frozen sample, in the next step, it is possible to calculate the mass of ice.

Aside from the sources of possible error characteristic of adiabatic calorimetry, the accuracy of the determination of ice content rests entirely on the following assumptions (Anderson and Tice 1973):

(a) the values of the heat capacities of all of the sample components and their temperature coefficients are known;

(b) during thawing, no process involving heat effects takes place other than the adsorption of the latent heat of melting ice in the sample;

(c) the latent heat of ice melting in the frozen soil is 333.62 J/g.

C) Nuclear Magnetic Resonance. Estimates of the phase composition of frozen soils may be obtained from nuclear magnetic resonance spectra. Ananyan (1978) proposed a method, based on measurements of both the relaxation time of nuclear spins in magnetic fields and the spin echo amplitude which is proportional to the amount of liquid phase in a soil sample. Results obtained by the NMR method were presented by Kuyala (1989).

The critical assumption inherent in this method is that the amount of unfrozen water at a given temperature is independent of the amount of ice. In addition, calibrated samples and several spectra taken at different instrumental settings are required. Akimov (1978) revealed a problem connected with the effect of the hydroxyl groups in clay minerals on results of measurements.

D) Other methods are used rather incidentally. Isothermal calorimetry (Anderson and Tice 1973) should be mentioned here, as well as a "contact" method (Akimov 1978), a method of sublimation (Ershov et al. 1976), a TDR method based on the measurement of dielectric constant (Patterson 1980) and finally the DSC method (Yong et al. 1978, Horiguchi 1985). The last method uses the differential scanning calorimetry technique. In spite of its special limitations (e.g. very small-size samples), this method has great potential. Results of investigations with the use of DSC will soon be published by this author.

There is no perfect method of determining phase composition of frozen soil. Each of them has its own advantages and disadvantages. The purpose of investigation should determine which experimental technique is used. If the results are to be applied to thermal computations, then the calorimetric methods have proved to be the most useful. Therefore, in this paper, the results of experiments using the developed adiabatic calorimetry method are presented.

3.2. The Adiabatic Calorimetry Method

3.2.1. Experimental Procedure

In comparison with previously reported investigations, improvements in both precision and accuracy were possible with the use of a differential calorimeter. There

is no need to consider the influence of the environmental conditions on measurements, when the KRM differential micro calorimeter is used (Budziosz 1980). Changes connected with thermal effects are determined by the measurement of electromotive force on terminals of thermopile connecting two identical vessels placed in a common isothermal jacket. The investigated process takes place in the right vessel. This makes it possible to measure the difference in temperatures with an accuracy of about 0.001 K.

Soil samples containing about 25 g of the paste were put in aluminium containers, 4.8 cm high, 2.8 cm in diameter, and closed with tight-fitting polypropylene lids. The containers with soil pastes were stored for 24 hours at 20°C, then weighed again with an accuracy of 0.01 g and placed in a TBV 2000 thermopressure chamber.

To avoid complications connected with the supercooling effects, the test samples were first frozen at -35°C and the temperature in the chamber was raised to the value T_1 , which was maintained during at least 24 hours with a variation of about 0.1 K. The tested samples was transferred to the calorimeter in the Dewar flask previously cooled to the same temperature T_1 . While thawing the sample in the right vessel, another soil sample of a similar mass and water content was present in the left one. After the experiment, each sample was dried at 110°C and its own total content was determined.

3.2.2. Basic Balance Equation

Experimenters using adiabatic calorimetry in the investigation of the frozen soil phase composition (Nersesova 1953, Kolaian and Low 1963, Pietrzyk 1979) based on the heat balance equation, written for greater clarity in the following form:

$$Q_k = A + B + C \quad (2)$$

where Q_k is the heat yielded by the calorimeter liquid (water) during the process consisting in warming the soil sample from the initial temperature T_1 to the final temperature T_2 (the value of Q_k was calculated taking into account corrections for the heat exchange between the calorimeter and the environment), A is the heat gained by liquid water and ice in the sample (together with heats of possible phase transitions), B is the heat gained by the soil mineral substance, C is the heat gained by additional sample constituents (e.g. container). One can show that the mass of the unfrozen water m_u is the only one unknown quantity in Eq. (2).

Calculating the values of components A , B , C , the previously cited authors become inaccurate which as a consequence of the accepted assumptions. In particular, the assumption was made that the specific heats of dry soil, ice and water were irrespective of temperature. 0°C was assumed to be the melting temperature of ice in a soil-water system. Due to their inherent margins of error, these assumptions should be restricted. In this investigation, an attempt was made to

define parameters A , B , C of the balance equation (2) precisely and when possible, required values in a set of self-dependent experiments were previously estimated.

3.2.3. The Parameters of the Balance Equation (2)

A – heat gained by water in a soil sample

The value of A can be explained in terms of the thermodynamic definition of the specific heat and change of enthalpy in the system;

$$A = m_u \int_{T_1}^{T_0} c_u dT + m_i \int_{T_1}^{T_0} c_i dT + Lm_i + m_w \int_{T_0}^{T_2} c_w dT \quad (3)$$

where:

- c_u, c_i, c_w – respectively specific heats of unfrozen water, ice and all water in the sample after thawing, J/g · K;
- m_u, m_i, m_w – the masses, g;
- T_1 – the initial temperature of the sample, K;
- T_2 – the final temperature of the sample, K;
- L – the latent heat of fusion of ice (333.62 J/g).

The mass of ice is substituted as follows:

$$m_i = m_w - m_u. \quad (4)$$

The reference data on specific heat of the bound water differ from each other. In particular, the relation of this value to the specific heat of water in bulk (4.19 J/g · K in 15°C) is not known. Andryanov (vide Zlochevska 1968) and Kurilyenko (1957) reported that the specific heat of the bound water is less than that of water in bulk. Skuratov (1951) and Nersesova (1953) maintained that these two values are very similar and finally, Berezin et al. (1960) and Oster and Low (1960) published data indicating that specific heat of the bound water increased with decreasing total water content.

It can be expected that in general, specific heat is a function of distance from mineral surface, therefore the values c_u and c_w in Eq. (3) are distinguished from each other. However, if no data were available, the author assumed that $c_u = c_w$ and that the dependence of specific heat of the bound water versus temperature can be approximated by means of the empirical equation of Roberts (Dorsey 1940), describing the specific heat of water in bulk:

$$c_w = 4.2048 - 1.768 \cdot 10^{-3} T + 2.645 \cdot 10^{-5} T^2. \quad (5)$$

The specific heat of ice is described by the following formula of Dickinson and Osborne (Dorsey 1940):

$$c_i = 2.1173 + 7.8 \cdot 10^{-3} \cdot T_o \quad (6)$$

The temperature of melting, T_o , is a very important parameter in Eq. (3). A previous investigation (Kozłowski 1990) enabled one to find an empirical relationship, describing the freezing point depression, θ_o , as a function of water content:

$$\theta_o = a w^b \quad (7)$$

In general, the values of a and b are functions of the consistency limits, mineral composition and specific surface area (Kozłowski 1995). Assuming that both freezing and melting points are equal, one obtains:

$$T_o = -\theta_o \quad (8)$$

B – heat gained by solid particles

Analogically to Eq. (3), the formula

$$B = m_s \int_{T_1}^{T_2} c_s dT \quad (9)$$

can be written, where c_s is the specific heat of soil dry substance, $J/g \cdot K$, and m_s is the mass, g.

Most often, the constant value $0.84 J/g \cdot K$ is accepted in the references (Grabowska-Olszewska and Siergiejew 1977; Andersland and Anderson 1978). Kay and Goit (1975) determined the specific heat of three investigated soils (Na-bentonite, silt and sand) as a linear function of temperature:

$$c_s = a_s + b_s \cdot T \quad (10)$$

Assuming that in general, Eq. (10) is a good approximation, the present writer achieved his own measurements of the specific heat c_s in temperature range between $-40^\circ C$ and $+25^\circ C$.

The unfrozen water content is estimated in relation to the mass of soil dried at $110^\circ C$. But in such a soil, a quantity of bound water exist. Stepkowska (1977) reported that not earlier than at $220^\circ C$ all interlamellar water absorbed on the external surface evaporated. Therefore, the present investigation was executed with samples dried at both $110^\circ C$ and $220^\circ C$.

Air-dried soil samples were powdered and put into aluminium containers 6.8 cm high and 2.5 cm in diameter. Next, the samples were dried at $110^\circ C$ or $220^\circ C$. After cooling in a desiccator, the containers were closed using weighed polypropylene lids and accurately weighed to within 0.01 g. The samples were cooled to a chosen temperature T'_1 in the TBV 2000 chamber and after 24 hours were carried

over to the calorimeter in the Dewar flask, were the endothermic effect connected with warming the sample to a final temperature T'_2 was measured. After taking into account heat gained by the aluminium container and the lid, the heat Q_{1-2} gained by dry soil from T'_1 to T'_2 was determined. Because Q_{1-2} can be expressed by Eq. (9), after combining Eqs. (9) and (10), integration, and rearranging, one obtains

$$\frac{Q_{1-2}}{m_s(T'_2 - T'_1)} = a_s + b_s \frac{T'_1 + T'_2}{2} \quad (11)$$

The right side of Eq. (11) expresses the value of the specific heat at temperature T'_3 being the arithmetic mean of T'_1 and T'_2 , the left one is a function of the measured parameters. Carrying a series of self-dependent measurements, pairs of values $(T'_{3,i}, c_{s,i})$ were obtained, where $c_{s,i}$ is equal to the left side of Eq. (11). The results are shown in Figs. 1-3. Approximating the values obtained by means of the least squares method, the values of the coefficients a_s, b_s in Eq. (10) shown in Table 2 were produced.

Table 2. Parameters of the empirical equation (10)

Temperature of drying	Parameter	Bentonite BCh	Bentonite BM	Kaolin KS
110°C	$a_s, \text{J/g} \cdot \text{K}$	0.7986	0.7503	0.8631
	$b_s, \text{J/g} \cdot \text{K}^2$	$2.59 \cdot 10^{-3}$	$1.94 \cdot 10^{-3}$	$5.06 \cdot 10^{-3}$
	number of samples	16	18	16
	correlation coefficient	0.7856	0.8985	0.9657
220°C	$a_s, \text{J/g} \cdot \text{K}$	0.7581	0.7287	0.8540
	$b_s, \text{J/g} \cdot \text{K}^2$	$2.30 \cdot 10^{-3}$	$1.77 \cdot 10^{-3}$	$5.02 \cdot 10^{-3}$
	number of samples	12	15	15
	correlation coefficient	0.9162	0.7805	0.9795

C - heat gained by additional components of the sample

The heat gained by additional components can be expressed by the following formula:

$$C = m_a \int_{T_1}^{T_2} c_a dT + m_p \int_{T_1}^{T_2} c_p dT \quad (12)$$

where c_a, c_p are respectively specific heats of aluminium and polypropylene, $\text{J/g} \cdot \text{K}$; m_a, m_p are the masses, g. In Table 3, the coefficients of the linear equation (13)

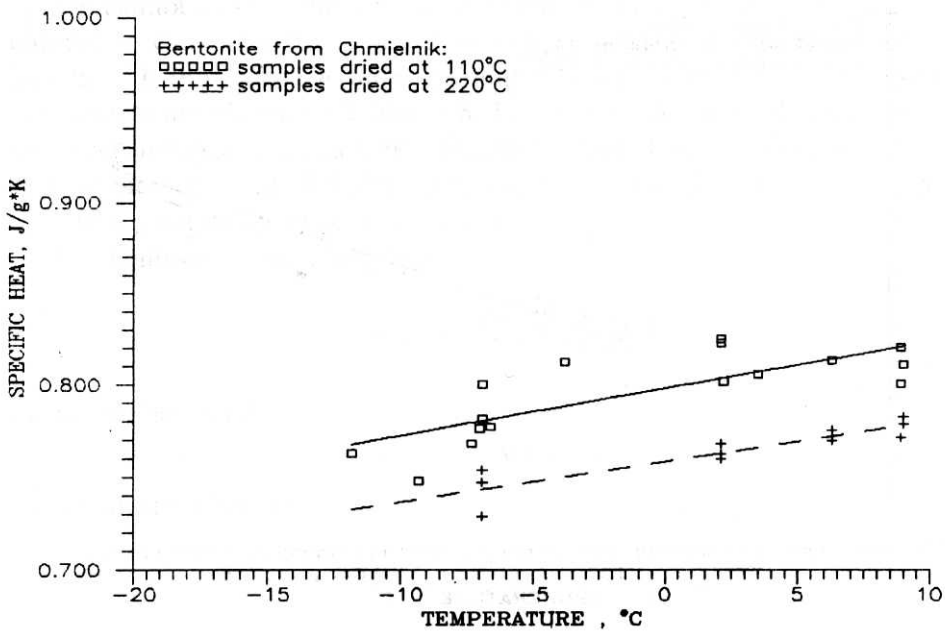


Fig. 1. The specific heat of dry soil vs. temperature - bentonite from Chmielnik

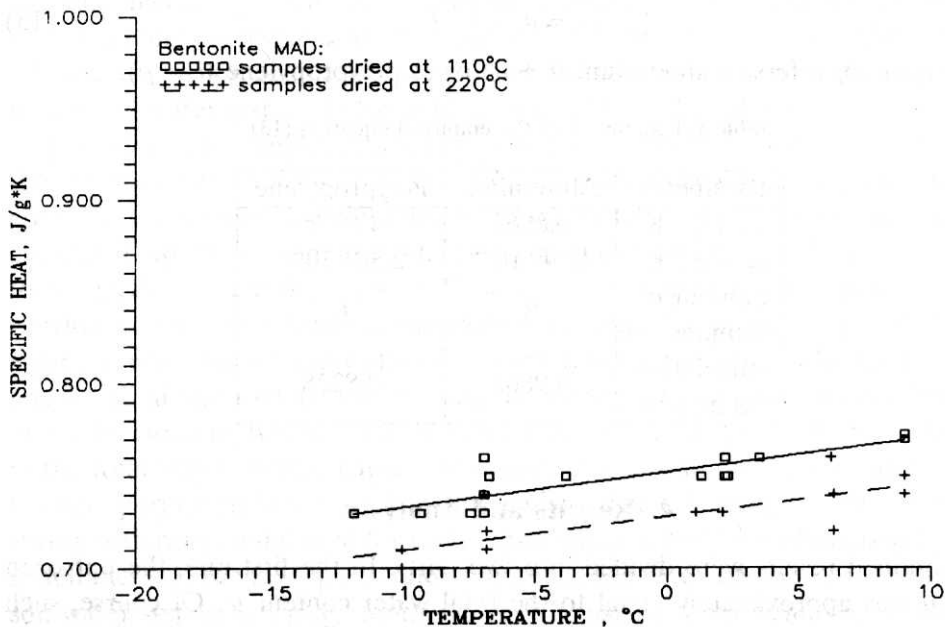


Fig. 2. The specific heat of dry soil vs. temperature - bentonite MAD

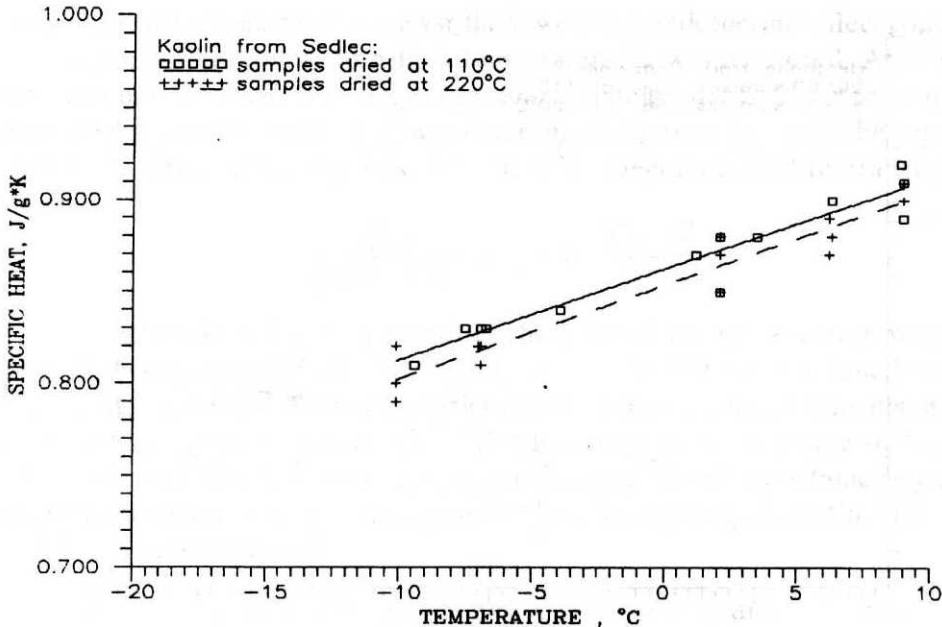


Fig. 3. The specific heat of dry soil vs. temperature – kaolin Sedlec

are shown, which were found in a series of experiments similar to those described above:

$$c_i = a_i + b_i T \quad (13)$$

where c_i , a_i , b_i refers to aluminium ($i = a$) or to polypropylene ($i = p$).

Table 3. Parameters of the empirical equation (13)

Parameter	Aluminium	Polypropylene
a_i , J/g · K	0.8963	1.9376
b_i , J/g · K ²	$4.79 \cdot 10^{-4}$	$2.30 \cdot 10^{-3}$
number of samples	8	6
correlation coefficient	0.9863	0.8328

4. Results and Analysis

The obtained results were divided into two parts. In the first one, the unfrozen water u was approximately equal to the total water content w . Of course, such result meant that freezing did not occur in the samples. The freezing (and melting) point T_0 is a function of the total water content w (Kozłowski 1994). Generally, the lower water content w the lower freezing point T_0 . At given minus temperature,

T_f , ice cannot exist in the soil-water system in the case, when the current water content w_1 causes freezing point $T_o = f(w_1)$ less than T_f . The other part contains results with the unfrozen water content u less than the total water content w . The results are shown in Tables 4–6. In order to attain a full representation of the relationship $u = u(T, w)$, 30 different functional models were tested using the least squares method. Reliable approximations were obtained at the expense of the often postulated “simplicity” of model.

For bentonite from Chmielnik

$$u = \exp \left(aw^b + \frac{aw^d}{\sqrt{\theta}} \right) \quad (14)$$

for bentonite MAD

$$u = aw^b \exp(cw^d \ln \theta), \quad (15)$$

for kaolin from Sedlec

$$u = \exp \left(a + b \ln w + \frac{c + d w}{\sqrt{\theta}} \right), \quad (16)$$

where u is unfrozen water content, %; w the total water content, %; θ temperature depression in relation to °C, a, b, c, d are constant coefficients gathered in Table 7, r is the correlation coefficient and n is the number of samples.

The functions given by Eqs. 14–16 are decreasing both vs. temperature depression θ at constant water content w and vs. w at constant θ . Because the situation, when $u > w$ is impossible, the domain of the functions refers only to the partly frozen soil water system. If a pair (θ, w) one obtains the value $u > w$, it is evident that the system is completely unfrozen and $u = w$. For the three investigated soils, the relationships are shown in Figs. 4–6. At constant total water content w , a decrease in the temperature depression θ leads to an increase in the unfrozen water content u up to the moment when $\theta = \theta_o$ (the temperature depression equals to the freezing point depression). Now, $u = w$ and the system is quite unfrozen. Further raising of the temperature does not change the phase composition. Then again, if in the frozen soil-water system the temperature should be kept constant and the total water content decreased, the unfrozen water content would increase up to the moment, when $u = w$. Now ice is absent in the system. Further decrease in the total water content causes, of course, decrease in the frozen water content because permanently $u = w$. It is self-evident that a limiting content of the unfrozen water, u_L , must exist for each temperature below the melting point. This is simultaneously the maximum water content at which ice crystals are absent in the soil-water system at a given temperature. The experimental values of u_L could be obtained from the following system of equations:

$$u = f(w, \theta), \quad (17a)$$

Table 4. The unfrozen water content u in samples of bentonite from Chmielnik for different freezing temperatures T_f and total water contents w

Number	T_f , °C	w , %	u , %	Number	T_f , °C	w , %	u , %
1	-0.3	80.03	79.95	50	-5.0	95.73	35.69
2	-0.3	81.28	80.59	51	-5.0	99.93	37.31
3	-0.3	81.41	81.15	52	-5.0	100.58	35.64
4	-0.3	82.22	82.20	53	-5.0	102.88	36.75
5	-0.3	82.57	82.27	54	-5.0	103.66	37.06
6	-0.3	86.32	86.27	55	-5.0	105.14	37.03
7	-0.3	116.07	87.22	56	-5.0	117.49	36.41
8	-0.3	116.14	83.95	57	-5.0	118.54	38.67
9	-0.3	117.08	92.03	58	-7.0	73.10	31.63
10	-0.3	117.11	84.18	59	-7.0	73.72	29.51
11	-0.3	117.55	86.98	60	-7.0	74.11	31.49
12	-0.3	118.78	89.58	61	-7.0	74.95	33.26
13	-0.5	77.82	77.70	62	-7.0	84.22	31.84
14	-0.5	77.94	77.86	63	-7.0	85.39	30.32
15	-0.5	78.85	79.02	64	-7.0	114.74	31.18
16	-0.5	79.11	79.11	65	-7.0	114.76	31.39
17	-0.9	96.78	45.68	66	-7.0	115.72	28.98
18	-0.9	99.62	45.08	67	-7.0	117.55	31.75
19	-0.9	101.72	46.88	68	-7.0	117.84	30.68
20	-0.9	105.11	44.85	69	-7.0	118.19	29.39
21	-0.9	117.98	47.63	70	-9.9	77.13	32.42
22	-1.0	76.97	46.38	71	-9.9	78.82	30.16
23	-1.0	76.98	45.09	72	-9.9	115.84	29.12
24	-1.0	77.46	45.23	73	-9.9	119.40	30.95
25	-1.0	77.76	44.30	74	-19.5	75.87	28.76
26	-1.0	80.39	46.68	75	-19.5	76.57	30.98
27	-1.0	114.93	43.74	76	-19.5	77.19	28.91
28	-1.0	115.39	46.90	77	-19.5	77.53	28.75
29	-1.0	115.66	44.48	78	-19.5	79.42	28.30
30	-1.0	117.23	45.60	79	-19.5	113.85	31.12
31	-1.0	117.40	48.14	80	-19.5	116.51	30.24
32	-1.6	71.89	41.39	81	-19.5	116.59	23.98
33	-1.6	73.18	41.96	82	-19.5	117.26	29.04
34	-1.6	73.22	44.22	83	-19.5	117.34	29.54
35	-1.6	73.60	44.53	84	-19.6	81.02	31.43
36	-1.6	81.73	44.08	85	-19.6	83.28	28.11
37	-1.6	82.45	42.60	86	-19.6	84.88	32.33
38	-1.6	83.50	42.87	87	-19.6	97.37	28.29
39	-1.6	84.23	43.82	88	-19.6	97.46	32.35
40	-1.6	85.00	43.30	89	-19.6	98.19	31.39
41	-1.6	86.81	44.09	90	-19.6	98.44	31.53
42	-1.6	116.16	40.39	91	-19.6	99.45	27.19
43	-1.6	117.98	39.99	92	-19.6	100.59	28.88
44	-3.5	76.81	39.89	93	-19.6	101.07	31.79
45	-3.5	78.90	40.03	94	-19.6	102.10	31.76
46	-3.5	115.23	37.89	95	-19.6	115.97	30.71
47	-3.5	118.23	37.55	96	-19.6	117.99	32.39
48	-5.0	78.17	37.08	97	-19.6	118.55	31.37
49	-5.0	80.17	36.31				

Table 5. The unfrozen water content u in samples of bentonite MAD for different freezing temperatures T_f and total water contents w

Number	$T_f, ^\circ\text{C}$	$w, \%$	$u, \%$	Number	$T_f, ^\circ\text{C}$	$w, \%$	$u, \%$
1	-0.2	154.12	154.16	51	-5.0	107.93	19.17
2	-0.2	157.11	157.07	52	-5.4	146.47	18.51
3	-0.2	160.80	160.62	53	-5.4	152.74	18.60
4	-0.2	162.12	162.08	54	-5.4	157.01	14.77
5	-0.5	358.91	115.63	55	-5.4	168.98	16.98
6	-0.5	361.27	112.24	56	-5.4	170.24	16.80
7	-0.5	363.12	113.58	57	-5.4	173.32	17.59
8	-0.5	367.80	113.14	58	-5.8	344.63	11.92
9	-0.9	151.35	63.12	59	-5.8	353.77	11.94
10	-0.9	157.34	63.06	60	-5.8	354.38	15.21
11	-0.9	162.57	67.21	61	-5.8	366.57	16.71
12	-0.9	163.31	63.93	62	-9.9	63.84	18.24
13	-1.0	344.78	66.76	63	-9.9	73.45	16.37
14	-1.0	354.13	67.98	64	-9.9	76.39	16.27
15	-1.0	355.00	67.58	65	-9.9	80.09	18.69
16	-1.0	355.79	70.99	66	-9.9	85.27	20.61
17	-1.0	357.76	66.89	67	-9.9	99.63	15.34
18	-1.0	358.98	74.64	68	-10.2	339.52	7.62
19	-1.0	360.39	71.67	69	-10.2	344.29	4.56
20	-1.0	361.58	66.06	70	-10.2	350.61	5.45
21	-1.0	361.59	66.31	71	-10.2	358.29	6.78
22	-1.0	361.93	70.79	72	-10.2	359.87	4.22
23	-1.0	363.65	69.07	73	-10.2	362.09	5.75
24	-1.0	363.67	66.94	74	-10.2	366.04	6.65
25	-1.0	364.33	70.62	75	-10.2	367.06	4.84
26	-1.0	364.87	71.16	76	-19.5	61.43	13.34
27	-1.0	368.89	70.67	77	-19.5	63.53	12.19
28	-1.2	64.18	64.02	78	-19.5	67.60	14.06
29	-1.2	66.17	65.97	79	-19.5	67.85	12.90
30	-1.2	69.12	69.77	80	-19.5	72.78	13.37
31	-1.2	70.02	70.28	81	-19.5	73.18	13.80
32	-3.0	356.67	26.52	82	-19.5	73.52	13.21
33	-3.0	357.87	24.42	83	-19.5	75.65	14.16
34	-3.0	363.59	26.36	84	-19.6	147.08	11.97
35	-3.0	365.88	28.59	85	-19.6	147.97	13.66
36	-3.4	82.12	26.66	86	-19.6	148.58	10.97
37	-3.4	84.86	27.91	87	-19.6	149.57	11.61
38	-3.4	86.01	27.16	88	-19.6	156.59	10.50
39	-3.4	88.39	27.80	89	-19.6	157.41	11.79
40	-3.5	62.14	25.95	90	-19.6	160.12	10.62
41	-3.5	63.32	26.95	91	-19.6	166.49	11.77
42	-3.5	76.32	26.94	92	-19.7	340.91	3.71
43	-3.5	89.28	25.92	93	-19.7	347.75	2.70
44	-5.0	60.72	20.08	94	-19.7	351.32	5.08
45	-5.0	61.19	19.20	95	-19.7	351.74	6.18
46	-5.0	71.40	17.80	96	-19.7	359.78	1.69
47	-5.0	73.45	19.39	97	-19.7	361.11	2.46
48	-5.0	77.41	20.80	98	-19.7	361.48	1.92
49	-5.0	79.39	18.29	99	-19.7	363.53	1.70
50	-5.0	81.52	17.40	100	-19.7	364.82	2.93

Table 6. The unfrozen water content u in samples of kaolin from Sedlec for different freezing temperatures T_f and total water contents w

Number	$T_f, ^\circ\text{C}$	$w, \%$	$u, \%$	Number	$T_f, ^\circ\text{C}$	$w, \%$	$u, \%$
1	-0.5	64.11	33.81	44	-5.8	66.55	2.29
2	-0.5	65.37	35.30	45	-5.8	67.07	1.81
3	-0.5	66.02	32.48	46	-5.8	67.28	2.97
4	-0.5	66.73	34.97	47	-5.8	68.09	2.13
5	-0.5	67.72	33.29	48	-5.8	68.24	2.33
6	-0.5	68.48	35.24	49	-5.8	68.44	3.24
7	-0.5	68.89	33.05	50	-5.8	68.55	2.23
8	-0.5	70.82	32.87	51	-5.8	69.88	2.61
9	-0.6	32.18	32.18	52	-9.0	33.75	5.33
10	-0.6	33.25	33.09	53	-9.0	35.60	3.32
11	-0.6	34.18	34.07	54	-9.0	36.47	4.04
12	-0.6	35.80	35.82	55	-9.0	37.92	4.18
13	-1.0	33.14	20.98	56	-9.0	81.06	1.07
14	-1.0	33.14	21.31	57	-9.0	81.51	1.29
15	-1.0	33.84	21.51	58	-9.0	83.91	1.45
16	-1.0	34.26	22.12	59	-9.6	67.11	1.90
17	-2.5	33.51	6.75	60	-9.6	67.79	1.32
18	-2.5	33.63	5.99	61	-9.6	68.23	1.39
19	-2.5	36.83	6.85	62	-9.6	68.91	2.02
20	-2.5	78.88	3.97	63	-9.6	69.46	1.07
21	-2.5	83.36	7.04	64	-9.6	69.98	1.84
22	-2.5	85.89	6.87	65	-9.6	70.65	1.29
23	-2.5	87.15	3.29	66	-9.6	70.93	1.30
24	-2.6	64.08	5.41	67	-19.2	33.42	2.02
25	-2.6	67.75	5.61	68	-19.2	33.76	3.29
26	-2.6	68.55	6.57	69	-19.2	35.47	2.13
27	-2.6	69.62	6.08	70	-19.2	36.21	3.85
28	-1.6	33.61	13.03	71	-19.2	36.37	3.27
29	-1.6	33.72	13.06	72	-19.2	36.74	2.46
30	-1.6	33.73	10.72	73	-19.2	36.92	3.99
31	-1.6	35.33	11.61	74	-19.2	37.74	2.49
32	-1.6	35.60	12.52	75	-19.2	83.45	0.64
33	-1.6	35.81	11.74	76	-19.2	84.41	1.43
34	-1.6	36.97	10.98	77	-19.2	84.51	1.75
35	-1.6	37.55	11.30	78	-19.2	87.18	1.09
36	-1.6	80.62	10.10	79	-19.5	66.35	0.69
37	-1.6	81.34	10.81	80	-19.5	66.49	2.13
38	-1.6	81.75	10.31	81	-19.5	67.76	0.71
39	-1.6	83.54	8.29	82	-19.5	67.79	1.84
40	-1.6	85.86	10.41	83	-19.5	68.27	2.05
41	-1.6	87.12	9.54	84	-19.5	69.36	1.59
42	-1.6	87.58	9.28	85	-19.5	70.57	1.79
43	-1.6	89.00	10.67	86	-19.5	71.40	3.03

Table 7. Parameters of empirical equations (14-16)

Parameter	Eq. (14)	Eq. (15)	Eq. (16)
Number of samples	97	100	86
Corr. coeff. r	0.973	0.993	0.982
a	3.450	95.770	4.414
b	-0.014	-0.069	-1.092
c	1.622	-0.279	1.978
d	-0.203	0.201	0.010

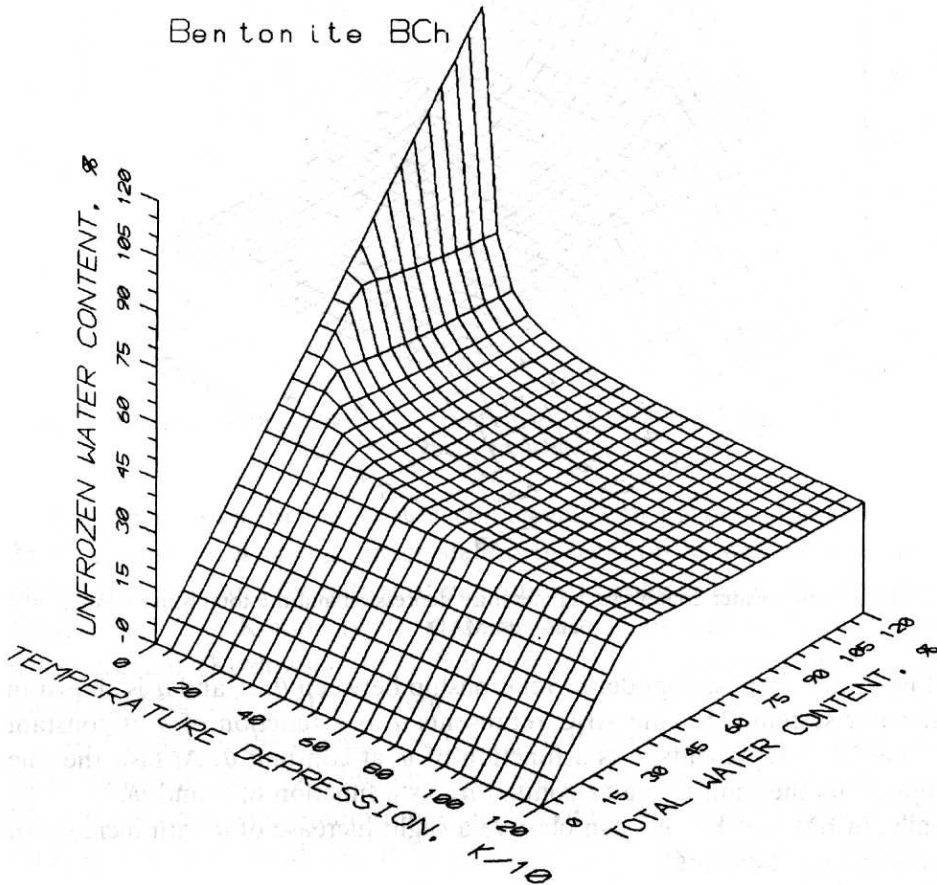


Fig. 4. The unfrozen water content vs. temperature depression and the total water content - bentonite from Chmielnik

$$w = u \quad (17b)$$

where $u = f(w, \theta)$ is one of functions given by Eqs. (14–16). The curve of u_L in the system of coordinates (θ, w, u) is visible as a “ridge” in Figs. (4–6).

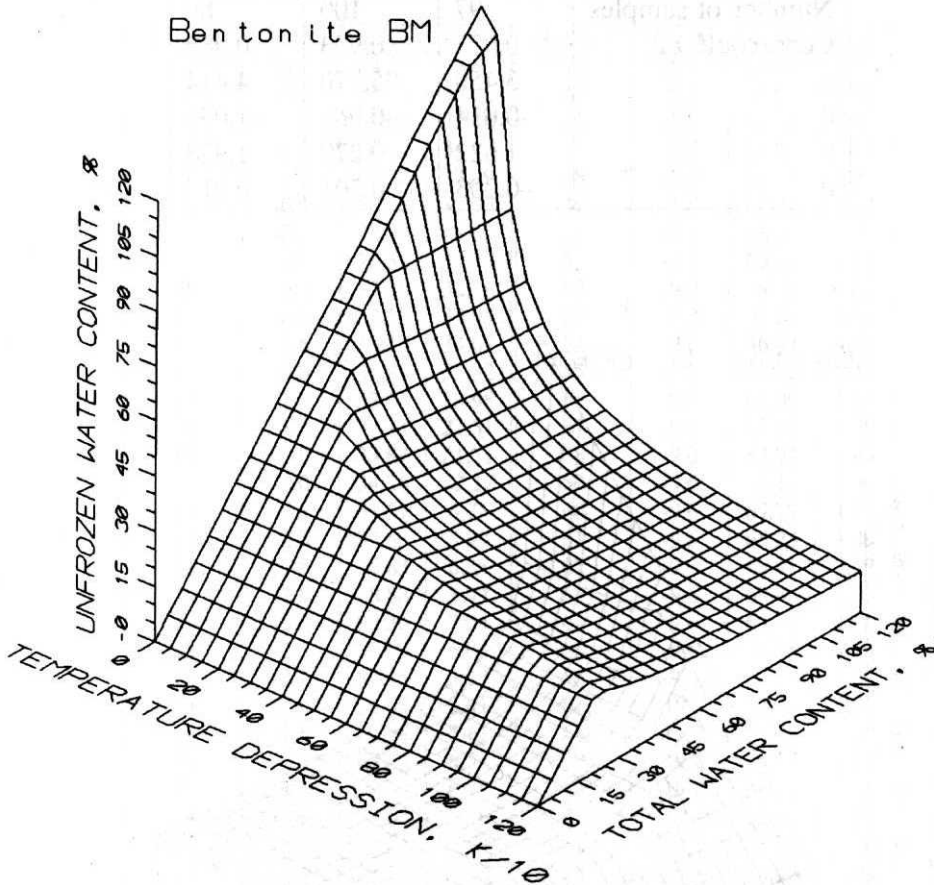


Fig. 5. The unfrozen water content vs. temperature depression and the total water content – bentonite MAD

In Fig. 7, the proposed model of relationship between θ , w and u is shown in the soil-water system. The line ABC represents u as a function of θ at constant w . The line EBD represents u as a function of w at constant θ . At last, the line FBG represents the limiting water content u_L as a function of θ and w .

Finally, in BM and KS one can observe a slight increase of u with increase of w at temperatures near 0°C .

In the author's opinion, a group of factors affecting a decrease in the unfrozen water content with an increase in the total water content can be distinguished, as well as a group of factors affecting the opposite. The former set of factors consists of the following:

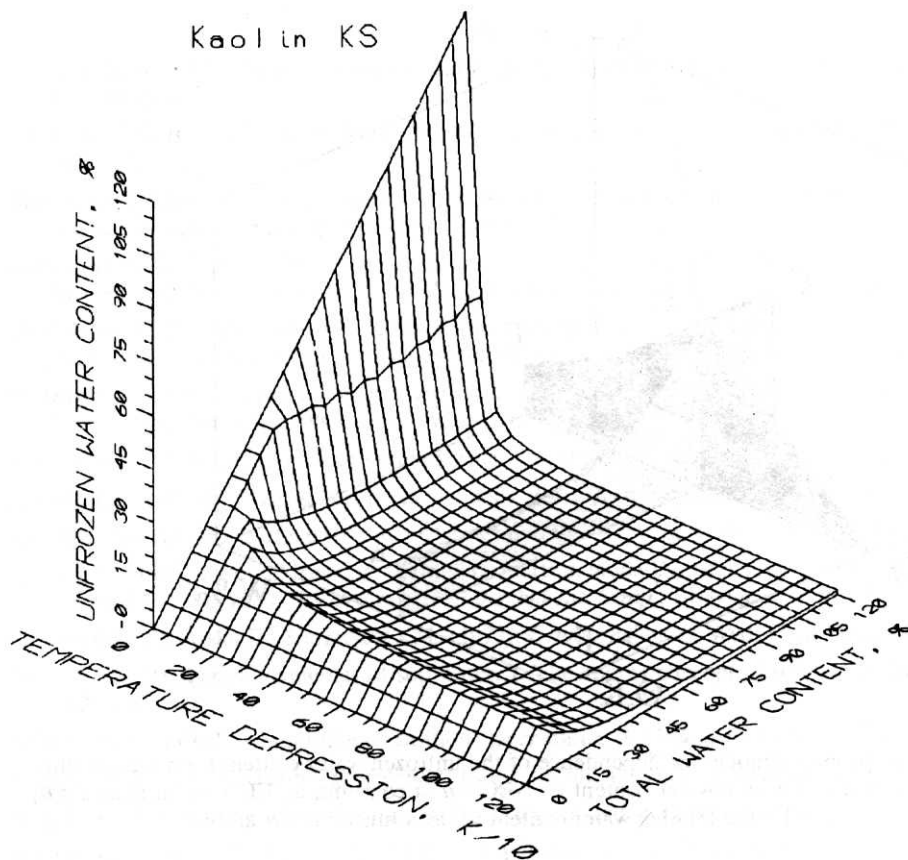


Fig. 6. The unfrozen water content vs. temperature depression and the total water content – kaolin from Sedlec

(a) Changes in microstructure connected with previous freezing down to -35°C , consisting in change in crystallite orientation as well as in increasing in partial thickness and formation of macropores (Yong et al. 1985, Stępkowska and Skarzyńska 1989, Kumor 1989), that should lead to a decrease in the unfrozen water content (Kozłowski 1987). The intensity of these processes is probably a function of the total water content.

(b) Change in the chemical potential of the surface of ice crystals connected with changes in their sizes (which in soil are dependent on its total water content). Then thermodynamic equilibrium (equality of the chemical potentials of adjacent phases) can be reached only through a change in the number of unfrozen water layers.

(c) A decrease in the internal pressure in unfrozen water, connected with an increase in the thickness of ice crystals (perpendicular to the mineral surface), which is a consequence of the energy concept of ground water (Iwata 1972).

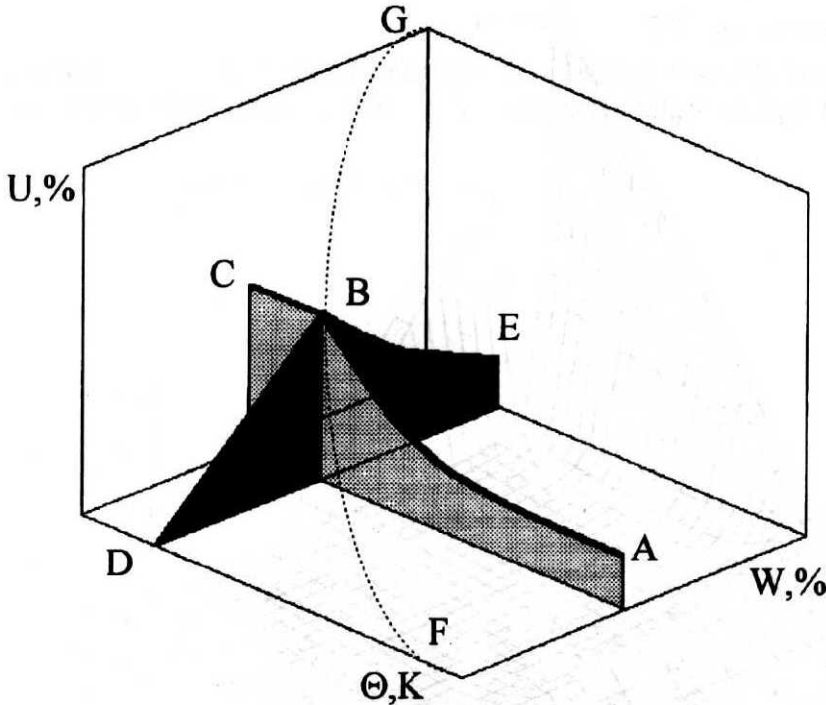


Fig. 7. The proposed model for dependence of the unfrozen water content u on temperature depression θ and the total water content w : ABC - u at constant, w , EBD - u at constant θ , FBG - the limiting water content u_L as a function of θ and w

A set of factors, which can be responsible for an increase in the unfrozen water content while increasing the total water content, is as follows:

(a) The existence of a liquid-like transition layer on ice crystals (Jellinek 1968), the thickness of which increases considerably close to 0°C . Probably, in some classes of soil microstructure, the specific surface of ice crystals can increase with an increase in the total water content. The opposite is also possible - increase in the total water content would cause a decrease in the specific surface of ice crystals as a result of their association. In this case, the contribution of the liquid-like layer to the general unfrozen water content would decrease with an increase in the total water content, and this factor would belong to the first group mentioned.

(b) An increase in the quantity of "non-freezing" interlamellar water with an increasing total water content in expanding materials (Ershov et al. 1979) would explain the behaviour of strongly expanding sodium bentonite MAD and poorly expanding calcium bentonite from Chmielnik near 0°C (Figs. 4 and 5).

Superposition of the above-mentioned factors, the result of which depends on soil structure, mineral composition and temperature, is the cause of the complicated dependence of the unfrozen water content on the total water content.

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