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The freezing point depression of soil water as a function of mineral composition and physical properties

1. Introduction

In spite of the fundamental part played by the freezing point depression in most problems of frozen ground mechanics, there are no useful solutions in the references (Andersland and Anderson 1978, Cytowicz 1973, Farouki 1986, Jumikis 1977).

It is known that it is possible to describe the freezing point depression of soil water θ_o as an approximating function of the object:

$$\theta_o = f(w, x_1, x_2, \ldots, x_n) \tag{1}$$

where w is the soil water content. Determination of the function (1) using direct measurements is very time-consuming and a special equipment and an experienced investigator are also needed. It would be therefore advisable to derive universal formulae making it possible to calculate θ_o with sufficient accuracy as a function of w and other easily determinable geotechnical parameters. In other words, the function (1) should be presented in a form, where chosen geotechnical parameters consitute a subset X_1 of the set X of parameters of Eq. (1) ($X = x_1, x_2, \ldots, x_n$) whereas a set of constant coefficients is the complement of X_1 in X. The present paper gives a proposal of solving the question.

2. Problems related to a physicochemical approach

Low et al. (1968) tried to find a theoretical form of the function (1) in terms of thermodynamics and physico-chemistry. Despite many simplifications assumed, the

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authors obtained a complicated equation involving the negative of the relative partial molar heat content of soil water $(H_l^o - H_l)$, the relative molar free energy of soil water $(F_l - F_l^o)$ and the freezing point depression θ_o at some assigned water content. There is a possibility of determination of the value of $(H_l^o - H_l)$ on the ground of the differential heat of desorption and the value of $(F_l - F_l^o)$ is a function of the swelling pressure. As anyone can see, the solution undoubtly very interesting from a theoretical point of view is of a little practical value; determination of the value of θ_o at some given water content (including an error on account of the simplifications) needs two self-dependent investigations what takes not less time than a direct measurement.

It seems that a strict thermodynamical approach cannot yield useful solutions. Generally, change in the chemical potential of soil water is a function of such parameters as electric and magnetic forces associated with charged mineral particles, radius of curvature, pressure, concentration of solutes, temperature. The quantities are not always easily determinable. Therefore, it would be reasonable to distinguish a number of geotechnical parameters which seem to be connected with the thermodynamical parameters mentioned above. In the author's opinion, there are two groups of such soil parameters.

1. Water content (particularly as a number of monomolecular water layers per a specific area unit).

2. Factors connected with the structure and composition of the mineral matrix:

   a) mineral composition

   b) geometrical parameters of mineral particles

   c) geometrical parameters of pores

3. Chemical factors independent or insufficiently dependent on mineral composition:

   a) kind of the exchangable cations

   b) concentration and kind of pore solutes.

One should expect that not all the mentioned factors exert considerable influence on the value of freezing point depression. Therefore, on the faith of results of own investigation, the author has gone by a postulate of maximum simplicity and usefulness of the solutions.

3. Universal semi-empirical equations

The author has reported (Kozłowski 1990) methodics and results of investigation of the freezing point depression θ_o vs. total water content w in three almost monomineral model soils: Ca-bentonite from Chmielnik (BCh), Na-bentonite MAD (BM) and kaolinite from Sedlec (KS). The results are shown in Fig. 1. It has been found that the freezing point depression equal to 20 K occurs at water content relative to about one (exactly 1.3) conventional monomolecular layer of bounded water in the bentonites and to about three monomolecular layers in the kaolinite. Thus, it has been assumed that
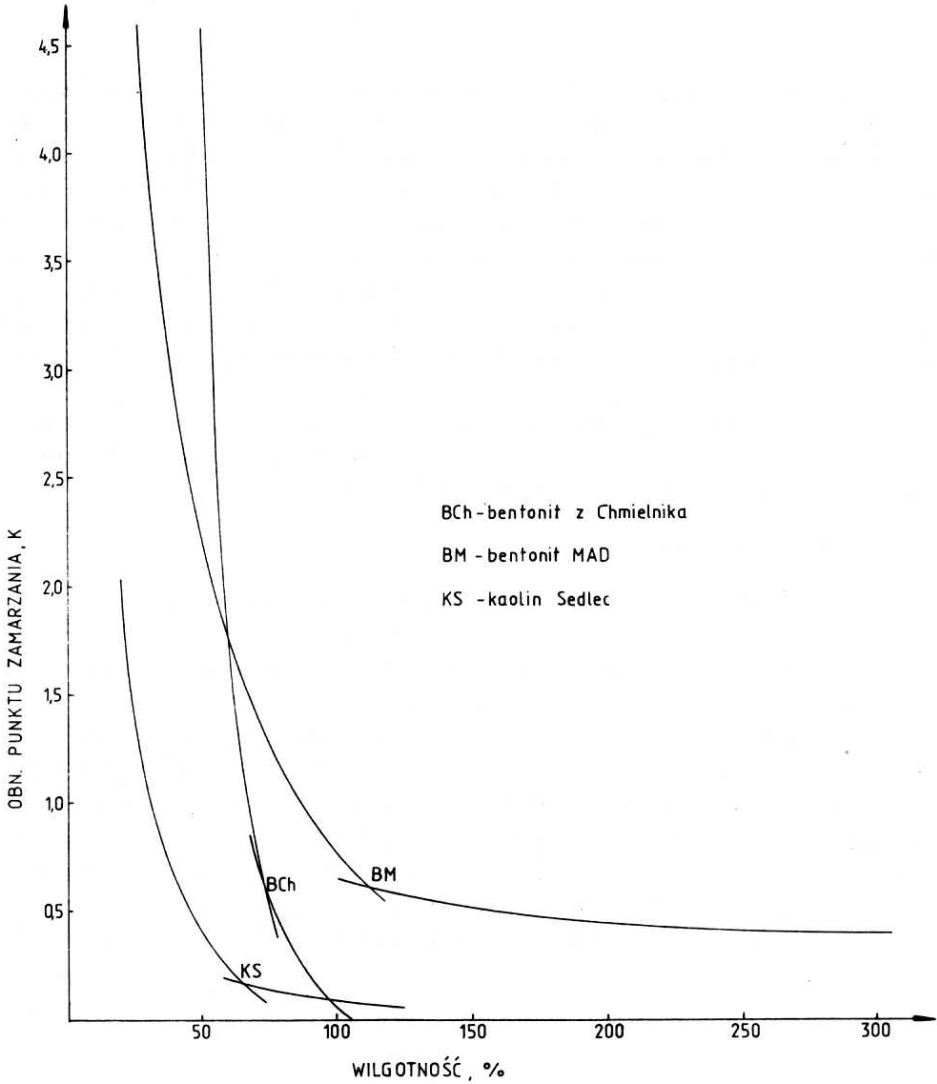
Fig. 1. Empirical relationship between the freezing point depression and water content for three clayey soils under investigation (best fitting curves of regression)

the freezing point depression equal to 20K depends only on mineral composition of a soil. In that instance, the maximum water content at which freezing does not begin at -20°C can be describe by following equation:

$$w_{\text{max},20} = 0.035 Sm \tag{2}$$

where $w_{\text{max},20}$ is the maximum water content, at which ice can be absent in the system at temperature -20°C (%). So $w_{\text{max}.20}$ is slightly less than the water content at which freezing point depression numbers 20K. In Eq. (2), S is specific surface area (m²/g), m is a coefficient being the number of monomolecular layers and it depends on mineral composition. The value 0.035 is the water content relative to one monomolecular water layer covering 1 m² of mineral surface (thickness of monomolecular layer 2.76×10^{-10} m x average density of the bound water 1.27×10^6 g/m³ × 100%). The value 1.27×10^6 g/m³ is density of sorbed water constituted of bimolecular layer (Martin 1962) and in present writer's opinion it can be regarded as an approximate density between 1.3 and 3.0 monomolecular layers.

The value of m numbers 1.3 in case of montmorillonite and 3.0 in case of kaolinite. Basing on the data indicating full additivity of surface properties of mineral components in mixture (Grabowska-Olszewska 1968), one can obtain:

$$m = 3k + 1.3(1 - k) \tag{3}$$

where k is the content of kaolinite as a fraction of the dry soil mass.

At temperature depressions near 0°C the value of „maximum content of non-freezing water" $w_{u,\text{max}}$ is affected by the grain size distribution and kind of the main exchangeable cation. Little number of soils in the investigation did not allow for making generalisations directly relative to the dispersion and the exchangeable complex. However, it is known that the parameters are connected with the values of consistence limits w_p and w_l. Looking for observable relations, the author noticed the values of freezing point depression θ_o at water contents equal to the consistence limits in the given soil. It appeared that the value of θ_o increased with increasing the plasticity index I_p (Fig. 2). Values of θ_o from the correlation diagrams θ_o/w relative to $w = w_p$ and $w = w_l$ are shown in Table 1. The values from Table 1 were possible to approximate by power functions:

$$\theta_o(w_p) = 0.049 I_p^{0.812} \tag{4}$$

$$\theta_o(w_l) = 0.023 I_p^{0.513} \tag{5}$$

Correlation coefficients for Eqs (4) and (5) number respectively 0.99998 and 0.99941. The zero of the functions occurs for zero value of the independent variable I_p, what agrees with experimentally confirmed fact that non-cohesive salt free soils are lacking in the freezing point depression.

The author appreciated the fact that Eqs (4) and (5) describe the freezing point relation only in the three soils under investigation. However, the assumption that the formulas are valid with reference to other cohesive soils is not baseless. The values of
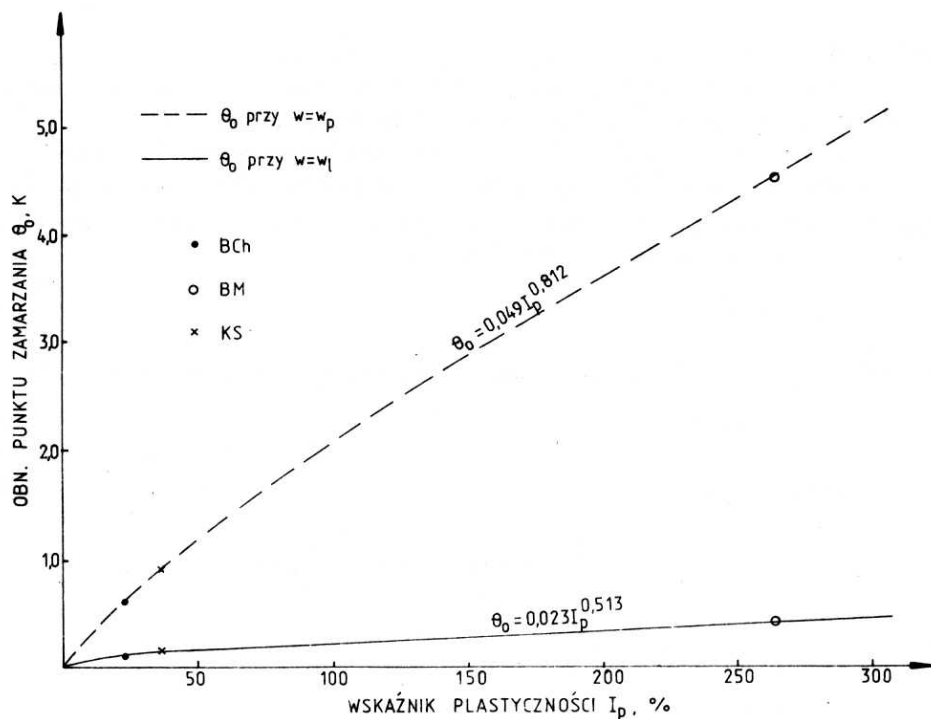
Fig. 2. Relationship between the freezing point depression at $w = w_p$ and $w = w_l$ and the value of plasticity index I_p

Table 1

Freezing point depression $\theta_o(w_p)$ at the plasticity limit and $\theta_o(w_l)$ at the liquid limit

Parameter	Bentonite Chmielnik	Bentonite MAD	Kaolin Sedlec
w_p, %	74,10	27,00	33,70
w_l, %	96,00	290,60	70,40
I_p, %	21,90	263,60	36,70
$\theta_o(w_p)$, K	0,60	4,50	0,90
$\theta_o(w_l)$, K	0,11	0,40	0,15

consistency limits in cohesive soils depend on mineral and granulometric composition, shape of mineral particles, kind of exchangeable cations as well as on chemical composition and concentration of pore solution (Grabowska-Olszewska 1977). Thus, information about most of the factors mentioned in section 2 of the paper is contained by the values of w_p and w_l. Therefore, the assumption was made that Eqs (2), (4) and (5) have an universal sense. On the grounds of the equation, two methods of predicting the freezing point depression θ_o have been worked out.

Method A

The soil data required are: approximate mineral composition (content of kaolinite), specific surface area S in m^2/g and consistence limits w_p and w_l in %.

An equation of a curve $\theta_o = f(w)$ well representing empirical data about θ_o in the three soils was sought for, when two points belonging to the curve were known: $(w_{max,20}, 20)$ and $(w_l, \theta_o(w_l))$. Test calculations have shown that good approximation can be expected of the following power function:

$$\theta_o = \theta_A = a_1 w^{b_1} \tag{6}$$

Substituting Eqs (2) and (5) into (6) and rearranging gives a system of equations

$$20 = a_1(0.035Sm)^{b_1} \tag{7a}$$

$$0.023I_p^{0.513} = a_1 w_l^{b_1} \tag{7b}$$

the solution of which gives values of the coefficients in Eq. (6):

$$b_1 = \frac{6.768 - 0.513\ln J_p}{\ln(0.035Sm/w_l)} \tag{8}$$

$$a_1 = 0.023J_p^{0.513} w_l^{-b_1} \tag{9}$$

The value of m in Eq. (8) is given by Eq. (3).

Method B

If data refered to mineral composition and specific surface are not available, the function $\theta_o = f(w)$ can be estimated on the grounds of the soil consistence limits w_p and w_l. The curve in request runs through two points: $(w_l, \theta_o(w_l))$ and $(w_p, \theta_o(w_p))$. It has been found that the power function (6) is not useful in this instance because of great errors at extrapolation for $w < w_p$. A better fitting is showed by the hyperbolic function:

$$\theta_o = \theta_B = a_2 + b_2/w \tag{10}$$

Combining Eqs (4), (5) and (10) yields a system of equations

$$0.049I_p^{0.812} = a_2 + b_2/w_p \tag{11a}$$

$$0.023I_p^{0.513} = a_2 + b_2/w_l \tag{11b}$$

the solution of which determines values of the parameters of Eq. (10):

$$b_2 = (x_1 I_p^{x_2} - x_3 I_p^{x_4})w_p w_l \tag{12}$$

$$a_2 = x_3 I_p^{x_5} - b_2/w_l \tag{13}$$

where $x_1 = 0.049$, $x_2 = -0.188$, $x_3 = 0.023$, $x_4 = -0.487$, $x_5 = 0.513$.

4. Verification of the methods

Adequacy of the presented methods has been verified on the grounds of available data from the references and results of own investigation. Additionally, the freezing point depression was computed by use of following empirical equation given by Fedorov (1989):

$$\theta_o = \theta_F = 0.045 \left(\frac{w}{w_l}\right)^{-4} \tag{14}$$

The present writer had at his disposal two sets of soil data. The first one comprised full information about given soil including specific surface area S. In the set, the data about freezing point depression of Morin clay from American center of frost investigations CRREL are especially reliable. Results of computations of θ_A – according to the method A, θ_B – according to the method B, θ_F – according to the Fedorov equation (14) are given in Table 2. In Table 3, results of computations of θ_B and θ_F are given for soils the specific surface area of which is unknown. The values of plasticity limit w_p of soils investigated by Fedorov (only the values of liquid limit w_l are given in the Fedorov's paper) were calculated using the empirical Casagrande equation (Dumbleton and West 1966):

$$I_p = 0.73(w_l - 20) \tag{15}$$

Assuming, with the purpose of the analysis, that the measured values of freezing point depression θ_{oe} are free from errors, the average absolute error d_1 was calculated for the values θ_A, θ_B, θ_F in the range of water content $w > 0.8w_p$ and the average absolute error d_2 in the restricted range of water content $w > w_p$. For all the methods is $d_1 > d_2$. The fact is a consequence of existence of a point of discontinuity on the empirical curve θ_o vs. w (Fig. 1), what renders a succesful one-function approximation impossible. On that score, the method A proved best ($d_1 = 0.22$K, $d_2 = 0.13$K). It makes use of the approximating function (6) definite in wide domain of w. Instead, error of the method B, insignificant one at $w > w_p$ ($d_2 = 0.08$K), quadruples in the wider range of w ($d_1 = 0.32$K). Both proposed methods seem to be suitable for an approximate calculating the freezing point depression of soil water. An accuracy of 0.1K at $w > w_p$ and 0.2 – 0.3K at $w > 0.8w_p$ is sufficient in most thermal computations. Instead, the Fedorov method proved decidedly worse ($d_1 = 1.88$K, $d_2 = 0.36$K). The degree of agreement between the calculated values of freezing point depression θ_A, θ_B, θ_F and the measured values θ_{oe} is shown in Fig. 3.

The author points out that Eqs (6) and (10) describe only a state of phase equilibrium before appearance of ice crystals in the system. They will yield overestimated values of the unfrozen water content u after rearranging and substituting u instead of w and any temperature depression $\theta > \theta_o$ instead of θ_o (Kozłowski 1989).
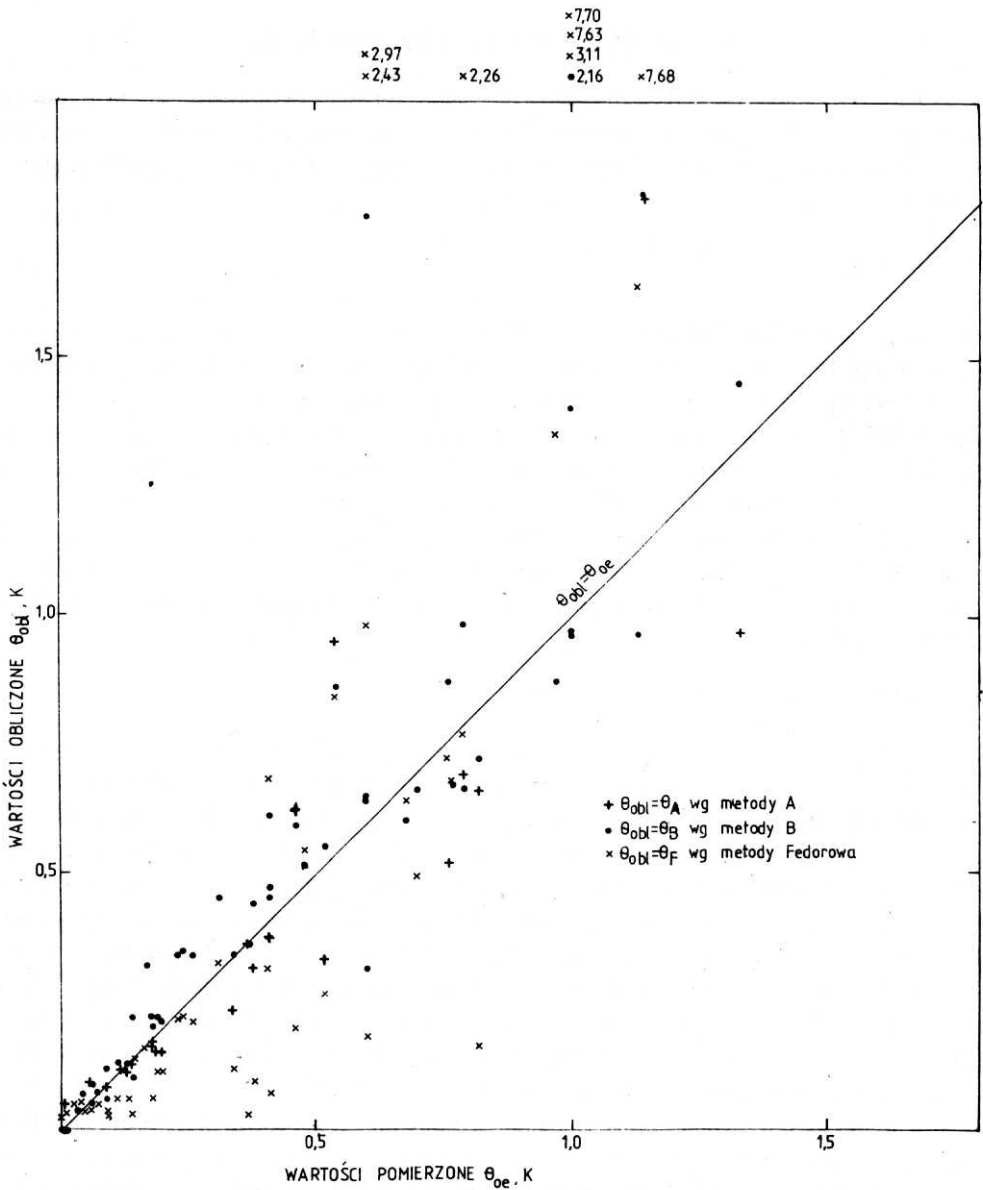
Fig. 3. Plot of the calculated values of freezing point depression θ_A, θ_b θ_F vs. the experimentally observed values of freezing point depression θ_{oe}

Table 2

Comparison of observed values of freezing point depression (θ_{oe}) and values calculated according to the author's methods (θ_A, θ_B) and from Fedorov's equation (θ_F)

Name of soil	Source of data	w_p %	w_l %	S m²/g	w %	θ_{oe} K	θ_A K	θ_B K	θ_F K
Bentonite Chmielnik	A	74.1	96.0	838	110.0	0.01	0.05	0.00	0.03
					100.0	0.06	0.09	0.05	0.04
					90.0	0.18	0.16	0.22	0.06
					80.0	0.38	0.31	0.44	0.09
					70.0	0.82	0.66	0.72	0.16
					60.0	1.85	1.58	1.10	0.29
Bentonite MAD	A	27.0	290.6	226	320.0	0.37	0.36	0.36	0.03
					260.0	0.41	0.46	0.45	0.07
					200.0	0.46	0.62	0.59	0.20
					140.0	0.54	0.95	0.86	0.84
					80.0	1.14	1.82	1.51	7.88
					20.0	8.37	9.21	6.12	?^{x}
Kaolin Sedlec	A	33.7	70.4	46	75.0	0.14	0.13	0.10	0.03
					65.0	0.18	0.17	0.20	0.06
					55.0	0.34	0.23	0.34	0.12
					45.0	0.52	0.33	0.56	0.26
					35.0	0.76	0.52	0.87	0.72
					25.0	1.35	0.97	1.45	2.77
Morin Clay	B, C	22.8	38.3	60	41.16	0.09	0.08	0.06	0.03
					36.07	0.11	0.11	0.13	0.06
					30.90	0.19	0.15	0.22	0.11
					25.77	0.24	0.21	0.35	0.22
					19.44	0.41	0.37	0.61	0.68
					14.38	0.79	0.98	0.69	2.26
					9.26	2.04	1.68	1.77	13.17
					4.81	7.02	6.36	3.80	?^{x}
Leda Clay	D, E, F	20.8	37.2	54	35.0	0.13	0.11	0.13	0.06
					30.0	0.20	0.15	0.21	0.11

^{x} – values incommensurably overestimated (up to 200K) and not taken into account in calculation of the average errors (Table 4)

The sources:

A – own investigation

B – Xiaozu et al. (1985a)

C – Xiaozu et al. (1985b)

D – Dillon and Andersland (1966)

E – Williams (1964a)

F – Williams (1964b)

Table 3

Comparison of observed values of freezing point depression (θ_{oe}) and values calculated according to the author's method $B(\theta_B)$ and from Fedorov's equation (θ_F)

Name of soil	Source of data	w_p %	w_l %	w %	θ_{oe} K	θ_B K	θ_F K
Sandy loam	G	20.7	22.7	22.4	0.03	0.04	0.05
				17.0	0.14	0.22	0.14
				12.2	0.48	0.51	0.54
Loam	G	22.4	28.8	28.2	0.04	0.07	0.05
				19.3	0.23	0.34	0.22
				14.8	0.68	0.60	0.64
Loam	G	23.0	31.1	30.9	0.07	0.07	0.05
				21.1	0.26	0.34	0.21
				15.3	0.79	0.66	0.77
Loam	G	24.3	35.8	49.0	0.00	0.00	0.02
				41.1	0.06	0.09	0.04
				29.7	0.17	0.32	0.16
				25.1	0.41	0.47	0.31
				20.7	0.77	0.67	0.68
				16.6	1.13	0.96	1.64
				10.2	1.97	1.88	11.52
Loam	G	25.6	40.8	36.6	0.04	0.07	0.04
				22.0	0.31	0.45	0.32
				15.3	0.97	0.87	1.35
Clay	G	30.2	57.8	58.2	0.09	0.12	0.04
				31.8	0.70	0.66	0.49
				23.9	2.03	1.06	1.54
Sandy silt	H, I	13.7	21.7	8.0	0.60	0.65	2.43
				6.0	1.00	0.96	7.70
Kaolin	H, I	21.7	39.7	28.0	0.60	0.31	0.18
				11.0	1.00	1.40	7.63
Clay	H, I	19.6	34.6	16.0	0.60	0.64	0.98
				12.0	1.00	0.96	3.11
Bentonite	H, I	43.6	114.0	40.0	0.60	1.78	2.97
				34.5	1.00	2.16	5.36
				29.0	3.00	2.70	10.75

The sources:
G – Fedorov (1989)
H – Akimow (1978)
I – Jerszow (1979)

Average absolute errors in calculation of freezing point depression at different ranges
of water content (from data shown in Tables 2 and 3)

Method of calculation	$08w_p < w < 1.2w_l$		$w_p < w < 1.2w_l$	
	Amount of points	Error d_1 K	Amount of points	Error d_2 K
A	28	0.22	21	0.13
B	59	0.32	37	0.08
after Fedorov (1989)	57^x	1.88	37	0.36

^{x} – two particulary unfavorable values were not taken into account

5. Conclusions

1. In the face of difficulties of a physico-chemical analysis, two semi-empirical methods have been worked out enabling one to calculate the equilibrium freezing point depression θ_o as a function of soil water content and other soil physical properties.

2. The method A based on the approximating power function (6) takes into account mineral composition, specific surface area, and the values of soil consistence limits. The method B making use of the approximating hyperbolic funtion (10) needs only knowing of the consistence limits w_p and w_l.

3. Verification of the methods proved that the values of θ_o are estimated at water contents w from the interval $(w_p; 1.2w_l)$ with an average absolute error equal to 0.13 K (method A) and 0.08 K (method B). The average absolute error at w from the interval $(0.8w_p; 1.2w_l)$ numbers 0.22 K and 0.32 K, respectively for method A and method B. One can admit the above values to be acceptable in most cases of engineering computations.

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Summary

A possibility of estimation of the equilibrium freezing point depression in a soil without necessity of direct experimental determinations would be very useful for many practical and theoretical reasons. A strict theoretical approach does not seem to be full of promise, therefore the author elaborated two universal computational methods on the grounds of own experimental results. Relationships existing in three investigated model soils between their mineral composition and a quantity of monomolecular water layers non-freezing at -20oC (253K) (eq. 2) as well as well as between freezing point depression at water content equal to the plasticity limit or the liquid limit of a soil and a number of the plasticity index (eqs 4,5).

The method A (eqs. 6, 8, 9) needs knowledge of water content, approximate content of kaolinite, specific surface and the Atterberg limits of a soil. The method B (eqs 11, 13,

14) needs only knowledge of water content and the Atterberg limits. On the grounds of experimental data from the references, the proposed methods have been verified. Average differences between the measured values and the calculated ones are equal to 0,1K and 0,22K (for two different ranges of the total water content) in the case of method A and 0,08K and 0,32K in the case of method B.

Streszczenie

Z wielu względów praktycznych i teoretycznych przydatna byłaby możliwość szacowania obniżenia punktu zamarzania równowagowego wody w gruncie bez konieczności przeprowadzania badań bezpośrednich. Podejście stricte teoretyczne nie wydaje się być obiecujące, dlatego autor opracował dwie uniwersalne metody obliczeniowe w oparciu o wyniki własnych badań laboratoryjnych. Wykorzystano związki występujące w trzech badanych gruntach modelowych między ich składem mineralnym a ilością warstw monomolekularnych wody nie zamarzającej przy $-20°C$ (253K) (równanie 2) oraz między obniżeniem punktu zamarzania przy wilgotności równej w_p lub w_l a wartością wskaźnika plastyczności (równania 4 i 5).

Metoda A (równania 6, 8, 9) wymaga znajomości wilgotności całkowitej, zawartości kaolinitu, powierzchni właściwej i granic konsystencji. Metoda B (równania 11, 13, 14) wymaga znajomości jedynie wilgotności i granic konsystencji gruntu. Wykorzystując dostępne dane eksperymentalne z literatury przeprowadzono weryfikację proponowanych metod, otrzymując średnie odchylenia wartości pomierzonych od obliczeniowych równe 0,1K i 0,22K (dla dwóch zakresów wilgotności) w przypadku metody A oraz 0,08K i 0,32K w przypadku metody B.