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THE UNFROZEN WATER CONTENT IN FROZEN COHESIVE SOILS IN THE LIGHT OF DSC RESULTS.

ZAWARTOŚĆ WODY NIEZAMARZNIĘTEJ W ZAMARZNIĘTYCH GRUNTACH SPOISTYCH W ŚWIELE WYNIKÓW OTRZYMANYCH PRZY UŻYCIU KALORYMETRII SKANINGOWEJ DSC.

Summary: Results of determination of the unfrozen water function in frozen soil-water system involving analysis of the DSC signal in terms of convolution has been presented. Four homoionic forms of bentonite (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and two homoionic forms of kaolin (Ca^{2+} and Na^+) were used in the experimental program. Analysis of the obtained results suggests that the process of the ice melting in the soil-water system is not a continuous phase change. The existence of five separate stages of the phase change process during warming from -28°C has been indicated. Three of them, I, III and V, are characterised by quite a vanishing of the phase effects. The intensity of the phase effects during stage IV near the melting point T_f is almost two orders of magnitude greater than in the low-temperature stage II. Additionally, many micro-stages without any phase changes were observed and among them, a characteristic significant stage III directly before the final melting called "the plateau".

Streszczenie: W pracy przedstawiono wyniki wyznaczenia zawartości wody niezamarzniętej jako funkcji temperatury w zamarzniętych systemach woda-grunt. Analizę sygnału różnicowej kalorymetrii skaningowej DSC przeprowadzono przy założeniu, że stanowi on konwolucję szukanego rozkładu rzeczywistych efektów termicznych $q(T)$ i funkcji aparaturowej $a(T)$. Porównując wyniki konwolucji zbioru hipotetycznych rozkładów z funkcją aparaturową, znajdowano taki rozkład impulsów $q(T)$, który w konwolucji z funkcją aparaturową dawał najmniejsze odchylenie od obserwowanego sygnału DSC. Tym samym stało się możliwe precyzyjne wyznaczenie krzywej zmian zawartości wody niezamarzniętej w funkcji temperatury. W programie badawczym wykorzystano cztery monojonowe formy bentonitu bentonite (Ca^{2+} , Mg^{2+} , Na^+ , K^+) i dwie monojonowe formy kaolinu (Ca^{2+} i Na^+). Analiza otrzymanych krzywych sugeruje, że proces topienia lodu w systemie wodno-gruntowym w nie jest ciągłą przemianą fazową. Wykazano istnienie pięciu osobnych etapów zmiany składu fazowego w trakcie ogrzewania od -28°C . Trzy z nich, I, III i V, charakteryzuje całkowity zanik efektów fazowych. Natomiast intensywność efektów fazowych na etapie IV w pobliżu punktu rozmarzania T_f jest dwa rzędy wielkości większa niż na niskotemperaturowym etapie II. Dodatkowo obserwowano wiele mikro-etapów bez przemiany fazowej, a wśród nich charakterystyczny etap III, nazwany „plateau”, bezpośrednio przed końcowym rozmrożeniem.

INTRODUCTION

The effects of frost on soils have been widely described since the first observations of Beskow (1935). It has been showed by many authors that it is an important pedogenetic agent, influencing soil structural development, consolidation, deformation and particle translocation. Reviewing the main factors influencing frost effects in soil, one can conclude that moisture is the most important (Washburn, 1979). Frost can be considered as a peculiar type of thermally oriented desiccation (Van Vliet-Lanoe, 1998). Most cryogenic fabrics can be related to shrinkage, frost heave pressure and gravitational sliding (Van Vliet-Lanoe, 1985). To allow precise paleoclimatic interpretation of periglacial features in Quaternary paleosols, it is necessary to compare them with soil features formed in active periglacial environments (Van Vliet-Lanoe, 1998). Knowledge of the basic processes, and their effects on the microfabric induced by repeated freeze–thaw cycles, allows us to understand the dynamics of frost in soils.

The phase composition of soil water predetermines its specific physical and mechanical properties and the pattern of occurrence of cryogenic-geological processes. The ice is an important soil-forming mineral and monomineral rock in the permafrost regions. Its present in the frozen ground takes the form of ice cement, ice inclusions and masses of concentrated ice. However, in contrast to typical solid materials which undergo a phase change at a fixed temperature, soils exhibit a specific temperature zone of phase change below the freezing point T_f , the latter being only the boundary temperature of phase change. At any temperature below freezing point, unfrozen water and ice in a soil-water system remain in a thermodynamic equilibrium state. It has been widely understood for many years, that the presence and phase changes of unfrozen water strongly influence the heat and mass transport processes in frozen soils and other porous media. Nevertheless, the nature of the unfrozen water phenomenon still remains unclear. The liquid phase of water in the frozen sediments can be in different energetic and structural states ranging from the state of free water to the substantially modified structure in the immediate vicinity of the surface of mineral particles. Water is strongly adsorbed onto the surfaces of colloids, both mineral and organic, remaining unfrozen at several degrees below zero (Anderson and Tice 1971). In clay-rich soils adsorbed water is able to migrate at temperatures as low as -40°C (Burt and Williams, 1976; Push, 1979). The structure, composition and properties of unfrozen water in the frozen soils have not been explored thoroughly, having a complex nature. It was found experimentally that the amount of unfrozen water in the frozen soil is a function of the soil composition and structure which, in turn, are determined by the origin and age of deposits. Phase equilibrium of moisture in the frozen soils is also influenced by the thermodynamic conditions (temperature and pressure) as well as by various physical fields. A variety of characteristics of the composition of the frozen soil and structure that determine phase composition of the moisture can be reduced to a few physical-chemical factors such as specific active surface, structure of void space, concentrations and type of ions and the pore solution, as all these factors are in functional dependence. Mineral composition is to a great extent a key factor determining the ratio of liquid and solid phases in the frozen soil. Because of the high values of the specific surface area, the role

of the clay minerals as montmorillonite, illite and kaolinite is regarded as the most important.

METHOD

Measurements of the unfrozen water contents in frozen soils have been made by dilatometry (Push 1979), adiabatic calorimetry (Kolaian and Low 1963), isothermal calorimetry (Anderson and Tice 1971, 1973), x-ray diffraction (Anderson and Hoekstra 1966), nuclear magnetic resonance NMR (Tice et al. 1982, Kujala 1989, Turov and Leboda, 1999; Watanabe and Mizoguchi, 2002), the neutron spin-echo NSE (Swenson et al., 2002), differential scanning calorimetry (Horiguchi, 1985; Kozlowski, 2003), the time domain reflectometry TDR (Yoshikawa and Overduin, 2005), Raman scattering and Fourier-transform infrared FT-IR (Crupi et al., 2005) and the dielectric capacity method (Fen-Chong and Fabbri, 2005; Fabbri et al., 2006).

Determination of the function $u = f(T)$ was usually made by means of approximation of several points obtained in a series of experiments. Such a procedure is not very precise and cannot explain details of the freezing and thawing process. Only two new techniques, nuclear magnetic resonance NMR and differential scanning calorimetry DSC enable the monitoring of the continuous phase changes during freezing or thawing of an individual soil sample. The unfrozen water in frozen soil can be divided into two forms: so called non-freezable water u_n (Horiguchi 1985) and the water the quantity of which depends on temperature. The former does not freeze down to at least -30°C (Anderson and Tice 1971) and its content can be successfully determined by the differential scanning calorimetry technique (DSC). Warming a soil sample from a low temperature of about -20°C gives an endothermic peak, the integration of which in relation to time or temperature determines the thermal effect connected with the melting of ice contained in soil. The amount of the non-freezable water corresponds to the difference between the total amount of water and the amount of ice. However, problems appear while using the DSC technique to determine the unfrozen „freezable” water content. Beginning the calorimetric warming run from a temperature at which some quantity of the freezable water already exists (e.g. -5°C) makes it impossible to get the calorimetric base line fixed, because the phase transition of ice starts simultaneously with the scanning process. Therefore, the starting point of the warming run must be established possibly low, before the beginning of the phase transitions. The curve of the unfrozen water content could be obtained by analysis of the whole of the warming endothermic peak recorded. An example of such an analysis was given by Horiguchi (1985). He assumed that real thermal flux connected with melting a quantity of ice in a small temperature interval ΔT_i corresponds to the part of the endothermic peak in this interval, and only with this part. Unfortunately, this assumption is not reasonable, even at low scanning rates about $0.1\text{K}/\text{min}$. Furthermore, the melting point of the sample, which is the parameter of particular importance, cannot be determined by that method. The DSC (differential scanning calorimetry) technique makes it possible to record thermal effects attributed to ice melting in a frozen soil sample precisely, but the highest temperature at which thermal effects are observed cannot be indirectly attributed to the melting point. Regardless of the apparatus construction, thermograms obtained during

the DSC run are not real thermal flux curves connected with the investigated process. The existence of thermal resistance between the sample and a heat sensor leads to the effect of broadening of the experimental peak. However, with a method presented lately (Kozłowski, 2003a), it is possible to obtain the melting point from experimental data. The method, using the DSC, consists in determining the real heat flux function $q(T)$ absorbed by the frozen soil sample during the warming DSC run. It is based on searching for a distribution of "heat impulses" in relation to temperature, which, convoluted with the apparatus function $a(T)$, gives a minimal deviation from the observed heat flux function $h(T)$. The function $q(T)$ can be easily related to the function of unfrozen water content $u(T)$. The latter determines such important parameters of the soil freezing process as the content of "non-freezable" water u_n and the melting point T_f , comprehended as the temperature of the last non-zero thermal impulse on warming. The accuracy of such determination equals the length of the temperature intervals ΔT_i , into which the observed function of heat flux $h(T)$ (or the calorimetric peak) was divided. In the reported research, it was 0.1K.

Table 1. Soil properties

Type of soil†	Major cation		Salt conc. Cl ⁻ [g/100g]	Fraction <2 μ m [%]	Spec. surface [m ² /g]		Number of samples
	[meq/100g]	[% C.E.C]			External	Total	
B-Ca ²⁺	104.15	96	0.02	34	122	732	23
B-Mg ²⁺	105.22	96	0.06	34	122	732	25
B-Na ⁺	90.49	81	0.62	92	110	644	23
B-K ⁺	38.12	76	0.43	30	56	336	24
K-Ca ²⁺	4.61	77	0.02	51	8	48	23
K-Na ⁺	3.57	60	0.02	54	10	60	23

† The symbols B and K in the soil type column mean bentonite and kaolin respectively

MATERIALS AND EXPERIMENTAL PROCEDURE

For this study, homoionic forms of bentonite (with particularly high content of montmorillonite, > 90 %) and kaolinite were used. The forms had been obtained from natural bentonite from Chmielnik in Poland and kaolin from Sedlec in Czech by repeated saturation of the fraction less than 0.063mm and subsequent purifying from solutes by diffusion. The soil pastes were then dried at room temperature to a required total water content and stored in closed vessels for about three weeks before the

experiment. The total water contents varied approximately between $w=0.5w_p$ and $w=1.5w_L$. Basic properties of the soils are given in Table 1.

Aluminum sample pans were weighed and filled with the soil pastes, sealed hermetically and weighed again. The masses of the soil samples were determined by differentiation and numbered approximately 10 mg. A thin layer of the soil paste covered only the bottom of the pan which ensured a very good exchange of heat. A quasi-uniform thermal field within the sample is the necessary condition of the presented method. The Unipan-Thermal differential scanning calorimetry system Model 607 with an LN₂ cooling system was used in the experiments. The samples were cooled with the scanning rate 1K/min to -28°C and then warmed with the scanning rate 0.5 K/min to +10°C at a calorimeter sensitivity of 5 mW. After the experiment, pinholes were punched in the sample covers and the total water content was determined by drying to a constant mass at 110°C.

Only results obtained during warming DSC run were analyzed. Thus the non-equilibrium phenomena connected with supercooling has been excluded.

RESULTS AND ANALYSIS

The Curves of the Unfrozen Water Content

For each soil sample, the comprehensive numerical analysis was applied to the observed heat flux function $h(T)$ and the real heat flux function $q(T)$ in the range between -28°C and +10°C were determined (Fig.1). Subsequently, the unfrozen water content curves were calculated. Actually, such a method assumes the fact that the process of ice melting in the soil-water system includes a set of distinct phase transitions occurring below the freezing point.

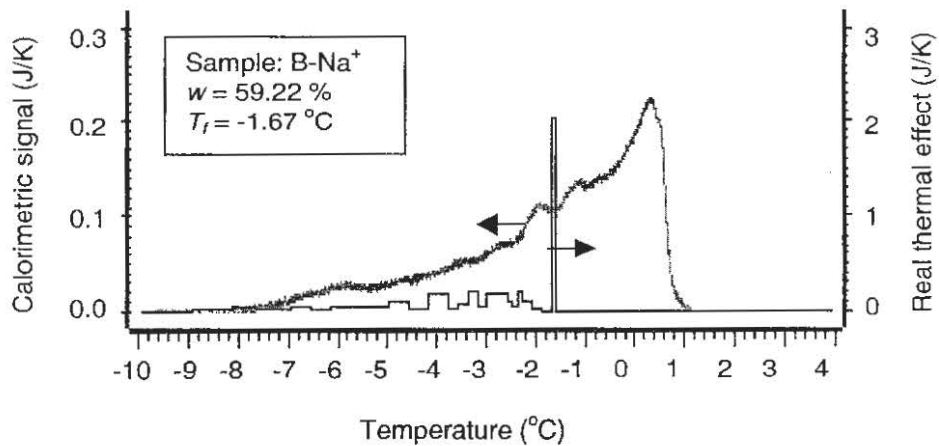


Fig. 1. An example of determining the plot of real thermal impulses distribution $q(T)$; $h(T)$ is the observed calorimetric thermogram corrected in relation to the base line.

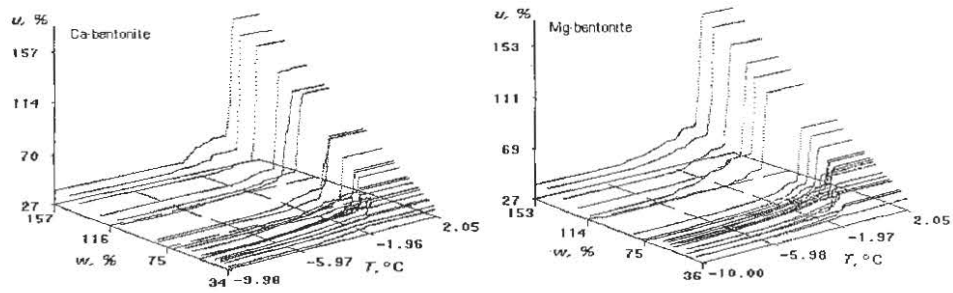


Fig. 2 The curves of the unfrozen water content vs. temperature and the total water content obtained for Ca- and Mg-bentonite.

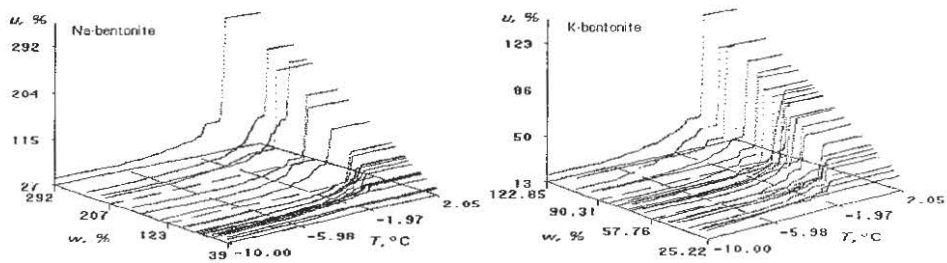


Fig. 3 The curves of the unfrozen water content vs. temperature and the total water content obtained for Na- and K-bentonite.

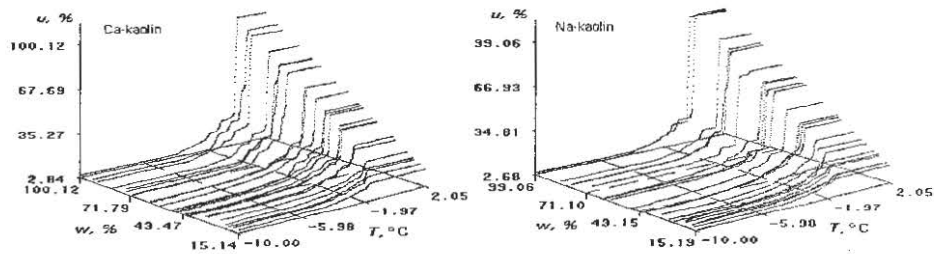


Fig. 4 The curves of the unfrozen water content vs. temperature and the total water content obtained for Ca- and Na-kaolin.

In Figs. 2-4, the curves of the unfrozen water content obtained for the six tested soils are shown. The presentation has been restricted to the temperature interval between $-10\text{ }^{\circ}\text{C}$ and $+2\text{ }^{\circ}\text{C}$, because in most of the investigated samples any phase effect down below $-10\text{ }^{\circ}\text{C}$ has not been observed and the process of ice melting finished below $0\text{ }^{\circ}\text{C}$ as a rule. Most of the curves, independently of the soil type and total water content, indicate a similarity of shape. A qualitative analysis of the typical curve $u=f(T)$ at constant water content will be done on base of one of the plots obtained for a sample of

magnesium bentonite B-Mg²⁺ (Fig. 5). The shape of the unfrozen water content curves suggests that the process of the ice melting in the soil-water system is not a continuous phase change. Absorption of the heat occurs at distinct temperature intervals and it is not strictly increasing the function of temperature. Almost all obtained curves have shown the interval of the vanishing of the phase effects before the final intensive impulses near melting point.

Generally, some characteristic temperature zones of the phase composition diagram have been distinguished. This is illustrated by Fig. 5. Initially, any measurable phase changes do not occur and the unfrozen water content u corresponds to the constant and temperature-independent value of non-freezable water u_n (zone I). At the temperature T_m , the melting of ice begins and the unfrozen water content increases roughly exponentially (zone II). Next, one can observe another stage without phase changes (zone III). Finally, the remaining portion of ice melts almost stepwise (zone IV). As the thaw process is completed, the unfrozen water content equals the total water content of the sample (zone V).

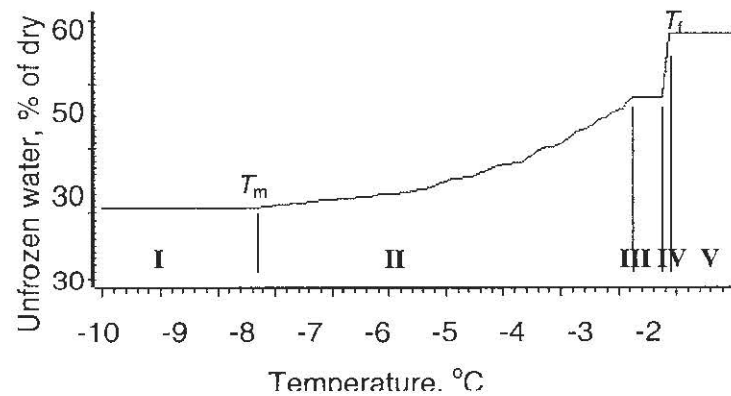


Fig. 5. Experimentally determined plot of unfrozen water content with the characteristic stages of the phase composition change process

Table 2. Characteristic zones of the phase composition change process

№ of zone	Lower limit	Upper limit	Relative variability of phase composition (%/K) for			
			B-Ca ²⁺ †	B-Na ⁺	B-K ⁺	Kaolins ‡
I		T_m	0	0	0	0
II	T_m		1.4	2.8	1.5	1.6
III			0	0	0	0
IV		T_f	140	95	244	166
V	T_f		0	0	0	0

† - calcium and magnesium form of bentonite behaved similarly, ‡ - no statistically essential differences were observed between the two investigated forms of kaolin

The five zones are characterized in Table 2 by the average values of relative variability of phase composition (or, in other words, local slope of the curve) defined by

$$\left[\frac{\Delta u}{\Delta T} \right] = \frac{u_2 - u_1}{T_2 - T_1} \quad (1)$$

where the indices 1 and 2 refer to the beginning and the end of a given zone respectively (the temperatures T_1 and T_2 correspond to the lower and upper limits of a zone, respectively).

Hence, the relative variabilities observed for zone IV are about 100 times greater than those observed for zone II. Besides, two zones without measurable phase changes have been distinguished, among which stage III, called "the plateau", seems to be the most interesting. Its occurrence was to be explained by the fact that all cohesive soils are characterised by the relatively high values of the specific surface at a significant contribution of the micropores less than 10 μm to the total porosity (Kozłowski, 2003b).

The freezing point depression

The freezing point T_f was comprehended as the initial temperature of the last non-zero thermal impulse in the plot of real thermal impulses distribution (Kozłowski 2004). Strictly speaking, the term "melting point" should be used instead. Actually, such a method assumes the fact that the process of ice melting in the soil-water system includes a set of distinct phase transitions occurring below the freezing point.

Generally, the results confirm the strong dependency on total water content (Fig. 6). Assuming that such a dependency is statistically significant, a model with the total water content as the independent value was searched. Over ten such models have been examined. At last, the following empirical relationship has been proposed:

$$T_f = -0.0729 w_p^{2.462} w^{-2} \quad (2)$$

where T_f is the freezing point, $^{\circ}\text{C}$, w_p is the plastic limit, %, and w is total water content, %. The correlation coefficient $R = 0.933294$ (in relation to all 137 observed values of T_f).

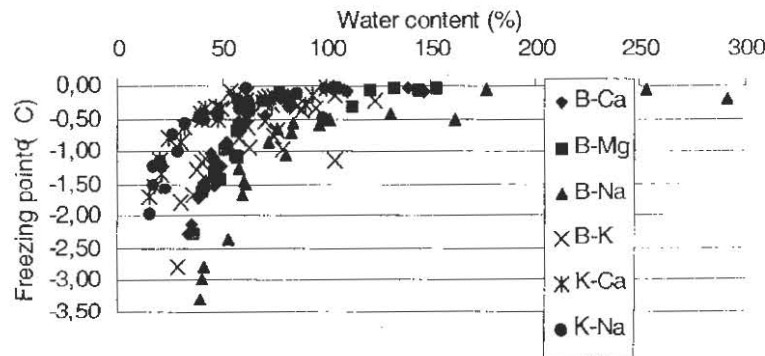


Fig. 6. The freezing point vs. the total water content.

The content of the non-freezable water

Independently of the method, using the convolution analysis to obtain the curve of the unfrozen water content (Kozłowski 2003a), the content of the non-freezing water w_{nf} can be straightforwardly determined from calorimetric data as a function of the total calorimetric effect associated with thawing or freezing the soil sample:

$$w_{nf} = w - \frac{100 \cdot \Delta h}{L \cdot m_s} \quad (3)$$

where w is the total water content, Δh is the total thermal effect associated with the freezing or thawing of the sample, L is the latent heat of fusion and m_s is the mass of the dried soil sample.

Detailed analysis showed that the differences between the values obtained for freezing and thawing are statistically insignificant. Only the potassium bentonite was an exception to the rule. However, because the small differences between the non-freezable water obtained on cooling and warming proved to be dependent on the total mass of the sample, the deviation could be explained by lowered kinetics of the freezing in this system compared with the others under investigation.

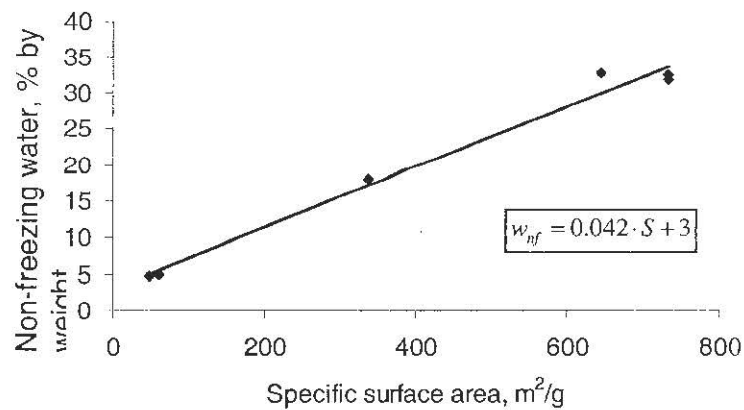


Fig. 7 Average non-freezing water content vs. specific surface area for six model soils

Looking at the experimental diagram of average non-freezing water content vs. specific surface area (Fig. 7), a strong correlation with the specific surface area is expected. Indeed the value of the correlation coefficient $R = 0,99279$ has been obtained for the empirical relationship as follows:

$$w_{nf} = 0,042 \cdot S + 3 \quad (4)$$

where w_{nf} is the content of non-freezing water in percent of dry mass, S is the total specific surface area in square meters per gram of dry soil.

Such a high correlation between w_{nf} and S proves that the non-freezing water corresponds to the water adsorbed on flat surfaces of clay minerals. Thus the non-

freezing water content can be determined experimentally as the hygroscopic water content, for example by sorption under 10 % solution of sulphur acid for 10 days.

CONCLUSIONS

- 1) A method able to construct the full curve of the soil phase composition during a warming run of an individual soil sample from -28°C to $+10^{\circ}\text{C}$, including such parameters of the process as the melting point and the non-freezable water content has been presented. The method appeared more precise and comprehensive than the others used before and enables one to analyse the melting process in details.
- 2) Analysis of the obtained real heat flux thermograms as well as the curves of the unfrozen water content suggests that the process of the ice melting in the soil-water system is not a continuous phase change. Absorption of the heat occurs at distinct temperature intervals and it is not a strictly increasing function of temperature so the melting of soil ice is a multi-stage process. Many micro-stages without any phase changes were observed and among them, a characteristic significant stage directly before the final melting called "the plateau".
- 3) The kind of exchangeable cation of a clay soil and its mineral composition determine parameters of a phase composition curve such as the melting point in relation to the total water content, the non-freezable water content and characteristic parameters of the plateau. However, the existence of the five distinctive stages of the melting process concerns all investigated soils.

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