

## EQUILIBRIUM AND NON-EQUILIBRIUM FREEZING OF WATER IN CLAY-WATER SYSTEMS

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The temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  were determined for six monomineral, homoionic clayey soils by use of the Differential Scanning Calorimetry (DSC) technique. The temperature of spontaneous nucleation  $T_{sn}$  was determined on the cooling run, as the initial temperature of the observed exothermic peak. The temperature of equilibrium freezing (or melting)  $T_f$  was comprehended as the initial temperature of the last non-zero thermal impulse in the diagram of real thermal impulses distribution  $q(T)$  obtained on warming. The supercooling  $\Psi$  was calculated as the difference between  $T_f$  and  $T_{sn}$ . The obtained results testify the strong dependency of the equilibrium freezing point  $T_f$  on the water content  $w$ . It has been proved that  $T_f$  can be expressed as a power function of water content  $w$  and the limit of plasticity  $w_p$  with a high correlation coefficient ( $R = 0.933$ ) showing a good fit to the experimental data. In contrary, a scatter of results was observed for  $T_{sn}$  and  $\Psi$ , which could be related to the effect of factors other than the water content. The diagrams of the supercooling vs. the water content suggest a relationship with an extreme. The critical water content,  $w_{cr}$ , at which the supercooling reaches a maximum, was found by use of a quadratic empirical model. For all the clay-water systems, the critical water content  $w_{cr}$  occurs between the plastic limit  $w_p$  and the liquid limit  $w_L$ .

### 1. INTRODUCTION

The freezing or melting of pure normal water under ordinary conditions proceeds at  $0^\circ\text{C}$  at the ice-water interface until ice formation stops. The presence of solutes, high pressure, or dispersal in fine pores causes the water to freeze at temperatures below  $0^\circ\text{C}$  (the so-called freezing point depression). However, water freezing cannot be comprehended as the reverse of ice melting. Melting occurs steeply at the melting point as ice is heated whereas freezing of liquid water on cooling involves [ice crystal nucleation](#) and crystal growth that is generally initiated a few degrees below the melting point even for pure water in bulk. In other words, some supercooling is needed to initiate the process of freezing. In soil-water system, the freezing point is comprehended as the

temperature,  $T_f$ , at which the equilibrium freezing of liquid soil water (i.e. its solidification) begins. This temperature corresponds to the  $0^\circ\text{C}$  for pure free water and in the case of the soil-water system is lower than  $0^\circ\text{C}$ . According to thermodynamic considerations by Low et al. (1968), the main macroscopic parameter affecting the phenomenon is the water content  $w$ . Similarly to the case of pure free water, the freezing process in the soil-water system does not start, as a rule, at  $T_f$  and some supercooling below the freezing point is needed. Fig. 1 shows the time-temperature relationship for freezing (the so called cooling curve) of pure water (A'B'C'D'E') and the clay-water system (ABCDE). The systems below their equilibrium freezing point, from A to B or from A' to B', remains in non-equilibrium, metastable state. Under normal atmospheric pressure, pure water can be easily supercooled down to  $-25^\circ\text{C}$  and with difficulties down to  $-41^\circ\text{C}$ , depending on the droplet diameter (Fletcher, 1970). At the temperature of spontaneous nucleation,  $T_{sn}$ , below the equilibrium freezing point, embryo nuclei form and grow to the critical sizes, and crystallization, initially a non-equilibrium one, begins (Anderson, 1968). As the result of the release of the latent heat  $L$ , the temperature of the system rises to the value of  $T_f$ , at which it stabilizes for a period, from C to D or from C' to D'. It should be stressed that the temperature  $T_f$  can be reached only if the latent heat is sufficient to increase the system temperature to  $T_f$ . Such a liquid, supercooled so deeply that the latent heat is not sufficient to raise its temperature to  $T_f$  is referred to as being hypercooled (Akyurt *et al.*, 2002). In the case of pure free water, all the liquid crystallize at this stage and further heat extraction leads to the decrease in temperature of ice from D' to E'. However, in the clay-water system, B is not equal to B', since the presence of additional

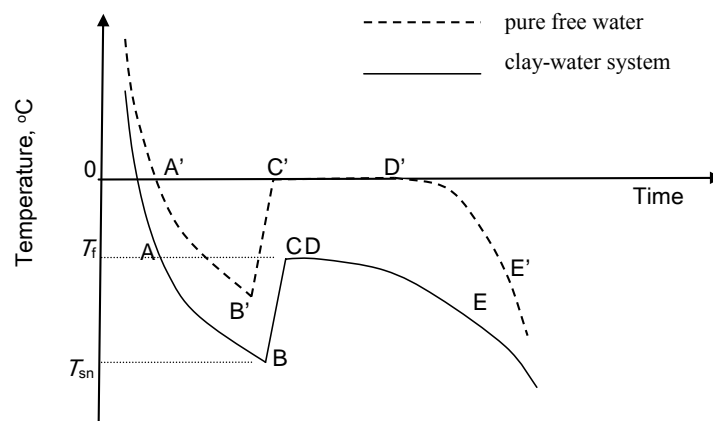


Fig. 1. Cooling curves for pure free water and the clay-water system ( $T_f$  – the freezing point for clay-water system,  $T_{sn}$  – temperature of spontaneous nucleation for the clay-water system)

factors promoting (or inhibiting) nucleation. The time line from C to D is shorter in this instance, because not all the “freezable” water solidifies at the freezing point. During freezing of the clay-water system, extraction of heat leads to successive freezing of the remaining unfrozen water. At temperatures well below the initial freezing point, some liquid, thermodynamically stable water remains and undergoes successive phase changes as the temperature is lowered.

Let supercooling be defined as the difference between the temperature of equilibrium freezing and the temperature of spontaneous nucleation:

$$\Psi = T_f - T_{sn} \quad (1)$$

According to a few previous investigations of the spontaneous nucleation in soils (Anderson 1968, Bozhenova 1953) and in the analogy to the facts relative to the supercooling of pure free water (Fletcher, 1970; Franks, 1983), it is possible to determine a set of factors affecting the value of supercooling. For a given kind of soil, they are as follows: the water content  $w$ , the mass of water in sample (or total mass of a sample), an intensity of heat removal and the thermal history. The dependency on masses means that the temperature of spontaneous nucleation, in contrary to the freezing point, is a function of extensive

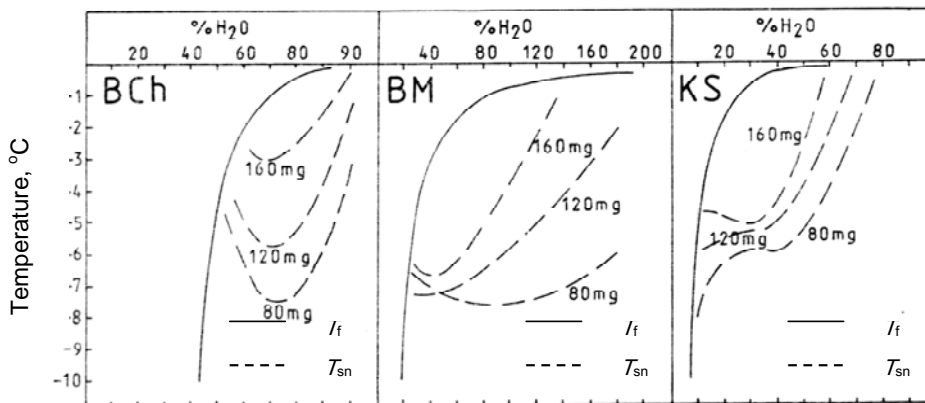


Fig. 2. The freezing point  $T_f$  and the temperature of spontaneous nucleation  $T_{sn}$  (the latter at three masses of sample) vs. the water content (BCh – bentonite from Chmielnik, BM – bentonite MAD, KS – kaolin from Sedlec) (Kozłowski, 1989)

parameters of the system. However, the effect of the water content seems unclear. In the previous investigation of the present author (Kozłowski, 1989), carried out on three model soils by use of the “classic” cooling curve method, a critical water content  $w_{cr}$  was observed, at which  $\Psi$  reached a maximum value (Fig. 2.) It was at variance with previous data reported both by Bozhenova

(1953) and Anderson (1968). The authors maintained that the temperature of spontaneous nucleation decreased monotonically with a decreasing water content, similarly to the temperature of equilibrium freezing  $T_f$ .

The problem of the relationship between the supercooling and the extensive parameters of a sample, such as the total mass of water or the dry mass, also remains unexplained, although it is an important question in relation to the thermal modeling of natural conditions and artificial ground freezing. However, as it was mentioned above, there are only a few papers dealing with this problem. In the present paper, the analysis of the supercooling phenomenon was done for data obtained by use of the Differential Scanning Calorimetry, which made it possible to use soil samples much smaller than those used in the cooling curve or DTA methods.

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

The DSC experiments was conducted using homoionic forms of bentonite and kaolinite. 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 0.063 mm and subsequent purifying from solutes by diffusion. The properties of the soils are given in Table 1.

Table 1. Soil properties

Type of soil†	The Atterberg limits		Fraction <2 $\mu$ m [%]	Spec. surface [m <sup>2</sup> /g]		Number of samples
	w <sub>p</sub> , %	w <sub>L</sub> , %		External	Total	
B-Ca <sup>2+</sup>	69,7	106,8	34	122	732	23
B-Mg <sup>2+</sup>	75,8	105,9	34	122	732	25
B-Na <sup>+</sup>	86,5	253,7	92	110	644	23
B-K <sup>+</sup>	66,0	93,2	30	56	336	24
K-Ca <sup>2+</sup>	33,8	61,2	51	8	48	23
K-Na <sup>+</sup>	36,8	62,9	54	10	60	23

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

The Unipan-Thermal differential scanning calorimetry system Model 607 with an LN<sub>2</sub> cooling system was used in the experiments. Basal parameters of the system are as follows:

- sensitivity: 5 mW to 180 mW
- scanning rate: 0.1 K/min to 20 K/min
- working temperature: -80°C to +400°C
- noise level:  $\leq 3$  mJ/K at scanning rate 0.5 K/min

A PC was interfaced with the system for the scanning rate control and real-time data storage. 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 ranged between 4 and 18 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 samples were cooled with the scanning rate 1K/min to  $-28^{\circ}\text{C}$  and then warmed with the scanning rate 0.5 K/min to  $+10^{\circ}\text{C}$  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  $110^{\circ}\text{C}$ .

The temperature of spontaneous nucleation  $T_{\text{sn}}$  was determined on the cooling run, as the initial temperature of the exothermic peak observed (Fig. 3).

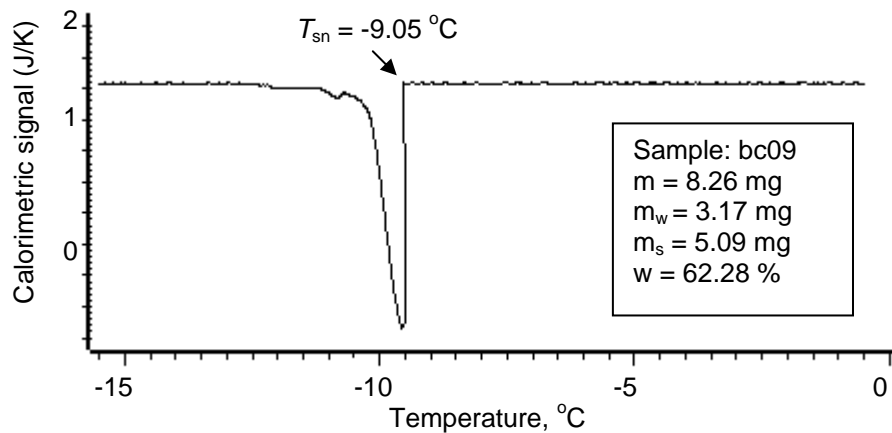


Fig. 3. An example of the exothermic DSC peak obtained during cooling run for a sample of calcium bentonite.

For each soil sample, the unfrozen water content curves were determined on warming in the range between  $-28$  and  $+10^{\circ}\text{C}$  by use of a comprehensive numerical analysis, presented elsewhere in detail (Kozłowski, 2003). A total of 159 tests were carried out, of which in 141 phase effects were detected. The method makes it possible to monitor the continuous phase changes during freezing or thawing of an individual soil sample. The freezing point  $T_f$  was calculated together with the curves, as their immanent parameter.

The freezing point  $T_f$  is the initial temperature of the last non-zero thermal impulse in the plot of real thermal impulses distribution  $q(T)$  (Fig. 4). 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. Theoretically, a thermal impulse related to a phase transition is infinitely

short, what can be described by use of the Dirac delta-function defined as follows:

$$\left\{ \begin{array}{l} \delta(x - x_1) = \infty \text{ for } x = x_1 \\ \delta(x - x_1) = 0 \text{ for } x \neq x_1 \\ \int_{-\infty}^{\infty} \delta(x - x_1) dx = 1 \end{array} \right. \quad (2)$$

Now, the thermal impulse associated with a phase transition in temperature  $T_0$  can be written as

$$q(T) = Q \cdot \delta(T - T_0) \quad (3)$$

latent heat of the phase transition.

However, for the obvious reason, the heat impulses created during the process of the numerical analysis of the DSC thermograms could not be infinitely short and the widths of 0.1 K were assumed. Therefore, the actual freezing point is in the range between  $T_f$  and  $T_f + 0.1$  K.

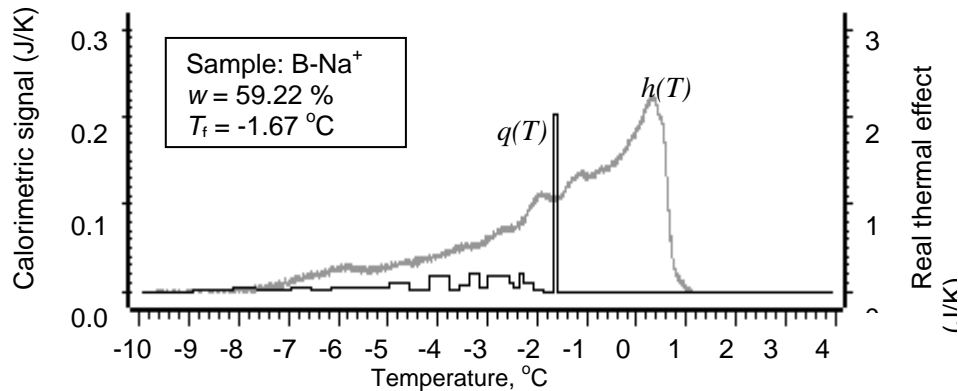


Fig. 4. An example of determining the freezing point  $T_f$  as the initial temperature of the last non-zero thermal impulse in the plot of real thermal impulses distribution  $q(T)$ ;  $h(T)$  is the observed calorimetric thermogram corrected in relation to the base line.

Strictly speaking, the term of “melting point” should be used instead. However, in the writer’s opinion, such a distinction is not necessary for the time being. Similarly,  $0^\circ\text{C}$  is referred to as either the „freezing” or „melting” point of pure water. Of course, in the case of a soil-water system, the possibility of a hysteresis still exists despite the lack of evidence. It is an interesting topic that definitely deserves further investigation. In this paper, the widely accepted term

„freezing point” will be used. Exact analysis presented by Kozłowski (2004) speaks in favor of the thesis that the hypothetical difference between the freezing and melting points is of little significance.

The supercooling was calculated according to Eq. (1), as the difference between the equilibrium freezing point  $T_f$  and the temperature of spontaneous nucleation  $T_{sn}$ .

### 3. RESULTS AND DISCUSSION

The results confirmed the strong dependency of the freezing point  $T_f$  on the total water content (Fig. 5-8). Assuming that such a dependency is statistically significant, a model with the total water content as the independent variable was searched. Over ten such models have been examined. At last, the following empirical relationship has been proposed:

$$T_f = -0.0729w_p^{2.462}w^{-2} \quad (4)$$

where  $T_f$  is the freezing point, °C,  $w_p$  is the plastic limit, %, and  $w$  is total water content, %. The correlation coefficient  $R = 0.933$  (in relation to all 137 observed values of  $T_f$ ).

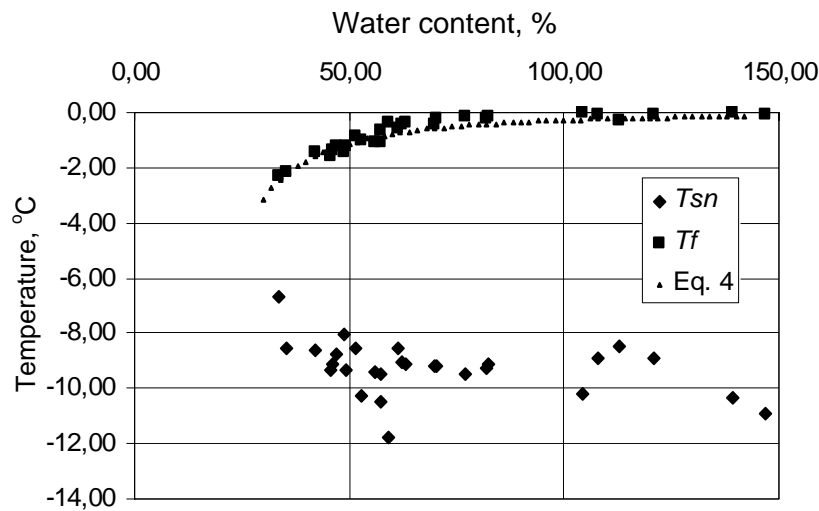


Fig. 5. The temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  vs. water content in bentonites with bivalent cations (B-Ca<sup>2+</sup> and B-Mg<sup>2+</sup>)

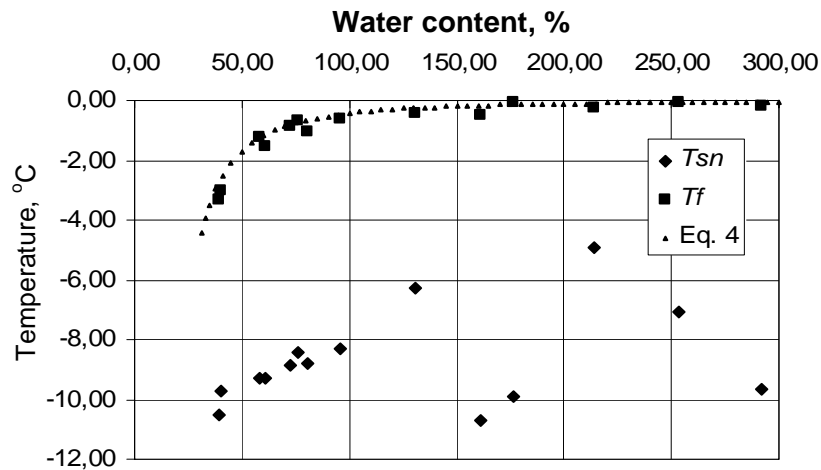


Fig. 6. The temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  vs. water content in sodium bentonite (B- $\text{Na}^+$ )

The model represented by Eq. (4) is well fitted to the experimental data obtained on melting. The verification of the model included comparison of the freezing point determined by the use of Eq. (4) with values observed in the laboratory by other investigators on cooling (Kozłowski, 2004). The empirical model proved to fit to the 33 results reported in references, giving the root mean square error in the order of 0.3K. It indicates that Eq. (4), despite its simplicity, could be taken as a general empirical equation, useful at typical computational problems when knowledge of the soil freezing point is needed.

Apparently, a simple relationship between the temperature of spontaneous nucleation  $T_{sn}$  and the water content is not as evident as in the case of the freezing point  $T_f$  (Fig. 5-8). Because the error of determination of the nucleation temperature  $T_{sn}$  should be expected to be much less than the error of estimation of the freezing point  $T_f$  (the latter being a product of a quite complicated computation, involving data collected on the whole of the warming run), the much larger scatter of the values  $T_{sn}$  than of the values of  $T_f$  in Figs. (5-7) must be a result of an influence of factors other than the water content. The results of investigations on the supercooling in pure free water (Pruppacher, 1967; Usu & Sano, 1965; Fletcher, 1970) allow us to distinguish several significant factors:

1. sample volume,
2. cooling velocity,
3. the presence and concentration of solutes,
4. the presence of solid impurities,
5. an effect of external fields (ultrasounds, impulse waves, electromagnetic radiation, nuclear radiation).



In the present investigations, the factor #2 was constant, but the variation in the water content affected some changes of the factor #3. Similarly, the variation in the water mass corresponds to changes of the factor #1 and the variation in the dry mass (after excluding the correlation with the water content) corresponds to changes of the factor #3. In homogeneous nucleation, the factor #1 proves to be most significant; the probability of the creation of a stable embryo nuclei increases with increasing the potential region of nucleation. Hence the factors are probably some extensive sample parameters like the total mass, the mass of water or the dry mass (all being strongly correlated with each other). The correlation matrix shown in Table 2 speaks in favor of this hypothesis. In the case of monovalent bentonites (B-Na<sup>+</sup> and B-K<sup>+</sup>), the correlations coefficients for masses are higher than those for the water content, both for  $T_{sn}$  and  $\Psi$ . This is not so evident in the case of kaolins and bivalent bentonites, although bivalent bentonites showed a significantly higher correlation between  $T_{sn}$  and mass of water  $m_w$  than between  $T_{sn}$  and the water content  $w$ .

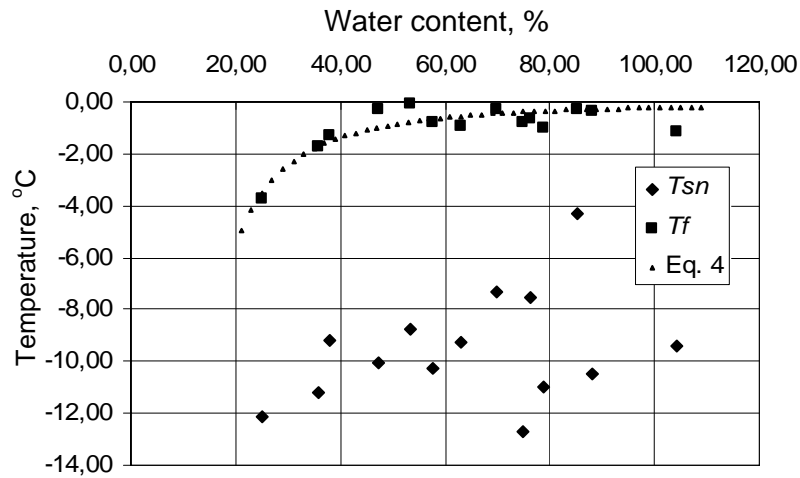


Fig. 7. The temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  vs. water content in potassium bentonite(B-K<sup>+</sup>)

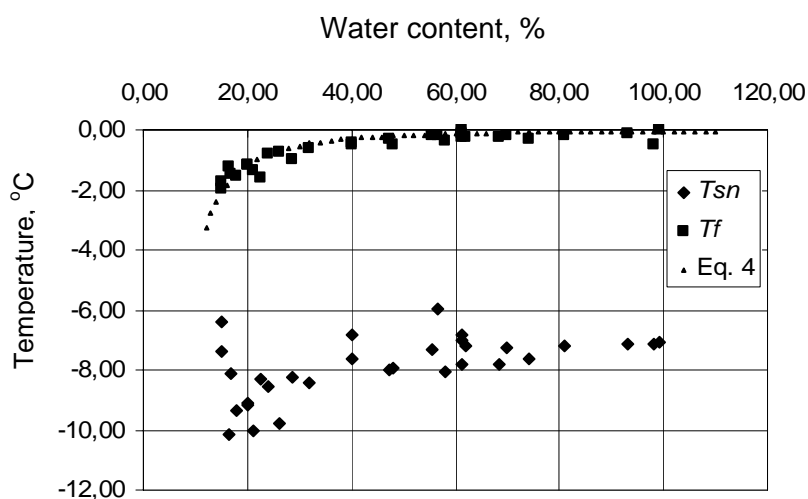


Fig. 8. The temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  vs. water content in kaolins (K- $\text{Ca}^{2+}$  and K- $\text{Na}^+$ )

Table 2. Matrix of correlation between parameters of supercooling ( $T_{sn}$ ,  $\Psi$ ) and the extensive parameters of the samples ( $m$ ,  $m_w$ ,  $m_s$ ) as well as the water content  $w$

R for correlation with	B- $\text{Ca}^{2+}$ & B- $\text{Mg}^{2+}$ †		B- $\text{Na}^+$		B- $\text{K}^+$		Kaolins‡	
	$T_{sn}$	$\Psi$	$T_{sn}$	$\Psi$	$T_{sn}$	$\Psi$	$T_{sn}$	$\Psi$
$w$	-0,15	0,50	0,37	0,37	0,13	0,28	0,73	-0,28
$m$	-0,17	0,05	-0,46	-0,42	0,48	-0,35	-0,44	0,23
$m_w$	-0,34	0,50	-0,36	0,23	0,63	-0,19	0,56	-0,11
$m_s$	-0,06	-0,18	-0,42	-0,51	0,35	-0,38	-0,64	0,26

† - no statistically essential differences were observed between calcium and magnesium bentonites

‡ - no statistically essential differences were observed between calcium and sodium kaolins

As mentioned above, the relationship between the supercooling and the water content observed by the present author in previous investigation (Kozłowski, 1989) involved a maximum for a “critical water content”  $w_{cr}$  (Fig. 1). The supercooling at water contents both higher and lower than  $w_{cr}$  was less. This observation was in contrary to the observations reported by Bozhenova (1953) and Anderson (1968). Therefore, in this study, the problem deserves special attention.

Table 3. Parameters of Eq. (5) and the calculated critical water content  $w_{cr}$  (for the purpose of comparing, the Atterberg limits  $w_p$  and  $w_L$  are given)

	B-Ca <sup>2+</sup> & B-Mg <sup>2+</sup> †	B-Na <sup>+</sup>	B-K <sup>+</sup>	Kaolins‡
<i>R</i>	0,76944	0,46770	0,50941	0,32248
<i>A</i>	-0,001350	-0,000117	-0,000871	-0,000169
<i>B</i>	0,234809	0,036800	0,124944	0,010996
<i>C</i>	-0,482080	5,704825	5,392631	7,332562
$w_{cr}$ , %	87	157	72	44
$w_p$ , %	73	87	66	35
$w_L$ , %	106	254	93	62

† - no statistically essential differences were observed between calcium and magnesium bentonites

‡ - no statistically essential differences were observed between calcium and sodium kaolins

First observations related to  $T_{sn}$  can be done on the grounds of the plots in Figs. 5-8. Undoubtedly, there is no strict and monotone relationship between the temperature of spontaneous nucleation and the water content, otherwise than between the freezing point and the water content. Similarly, the diagrams of the supercooling vs. the water content (Figs. 9-12) rather preclude the existence of a relationship given by a monotonous function. Instead, they suggest a relationship with an extreme. Therefore, a model was searched in the quadratic form as follows:

$$\Psi = A \cdot w^2 + B \cdot w + C \quad (5)$$

The model is characterized in Table 3. Apparently, the correlation coefficients *R* are significantly higher in the case of a quadratic model than those corresponding to a linear relationship between  $\Psi$  and  $w$  in Table 2. It is very likely that the goodness of fit would be significantly improved after excluding the effect of the variation of masses from the model.

For all the soil-water systems, the critical water content  $w_{cr}$  calculated as the water content for which the function given by Eq. (5) reaches extreme is between the plastic limit  $w_p$  and the liquid limit  $w_L$ . This fact can support the explanation of the fact that the occurrence of the extreme was not observed by Bozhenova and Anderson. In both cases, the effect could not be observable because of too small a variability of water content in the soil samples under investigation. In Bozhenova's investigation the water contents were too high (the experiment was carried out on specimens with the water content  $w$  greater than the plasticity limit  $w_p$ ) and, in contrary, in Anderson's experiments the water contents were too low (as a rule below the plasticity limit) and, in

addition, the number of soil samples for each type of soil was too little and ranged between 6 and 11.

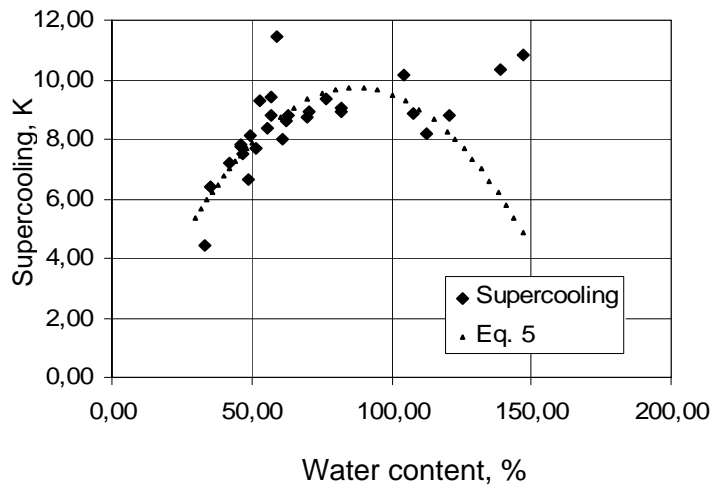


Fig. 9. Supercooling  $\Psi$  vs. water content in bentonites with bivalent cations (B- $\text{Ca}^{2+}$  and B- $\text{Mg}^{2+}$ )

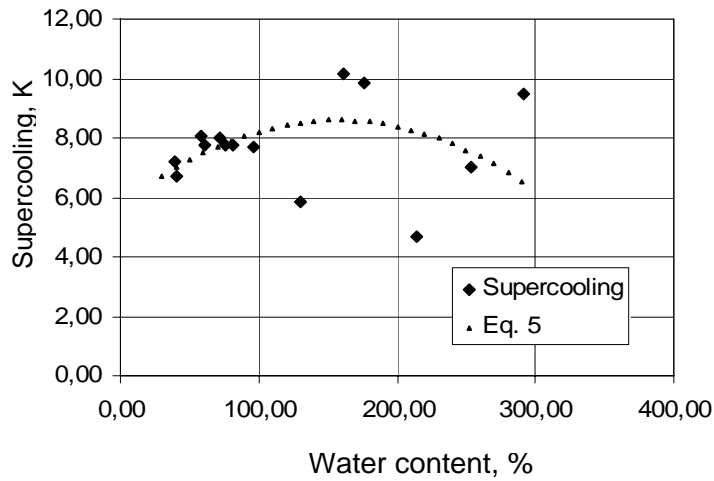


Fig. 10. Supercooling  $\Psi$  vs. water content in sodium bentonite (B- $\text{Na}^+$ )

It seems that the qualitative model of ice nucleation in soil-water system given by Anderson (1967, 1968) can be supported by the presented results (and *vice versa*). The model assumes existence of a very disrupted layer of initially

adsorbed water near the mineral surface where the nucleation is impossible. Embryos can form at a distance somewhat farther removed from the surface, in a zone of “extensive ordering effects”. In the present writer’s opinion, we deal with two kinds of nucleation in the soil water system. The heterogeneous one occurs at high water contents due to the presence of micro impurities in the pore solution (the factor #5 listed above). As the water content is lowered, the heterogeneous nucleation is less possible and the supercooling  $\Psi$  reaches a maximum value at the critical water content  $w_{cr}$ . Then at still lower water contents, in “Anderson’s zone”, the homogeneous nucleation begins to play an important part and supercooling decreases again. In other words, the existence of the extreme of  $\Psi$  can be explained as follows. Assuming that embryos of nucleation are coming into existence as a result of ceaseless thermal fluctuations, we can distinguish a set of factors hampering the process (e.g. reduction in mobility of water molecules as a consequence of a higher degree of ordering, changes in the concentration of solutes, the disruption of water structure near the solid surface) and a set of factors stimulating it (e.g. once again reduction in molecular mobility, presence of micro inclusions and other factors listed above). An interaction of the factors in the soil-water system results in the maximum of supercooling at the water content equal to the critical value  $w_{cr}$ .

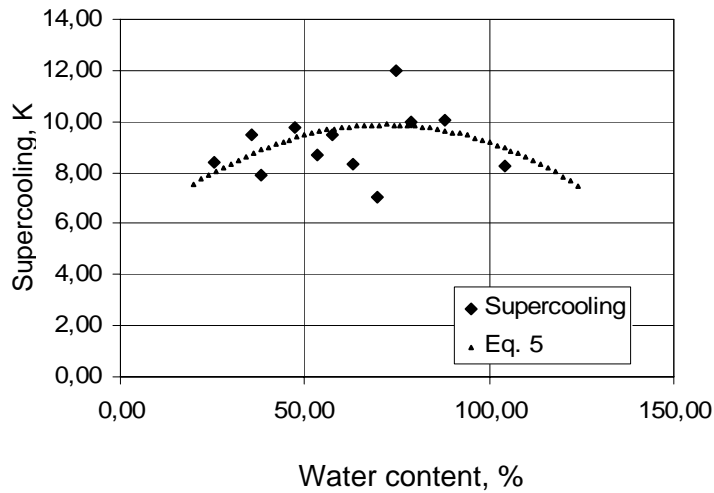


Fig. 11. Supercooling  $\Psi$  vs. water content in potassium bentonite (B-K<sup>+</sup>)

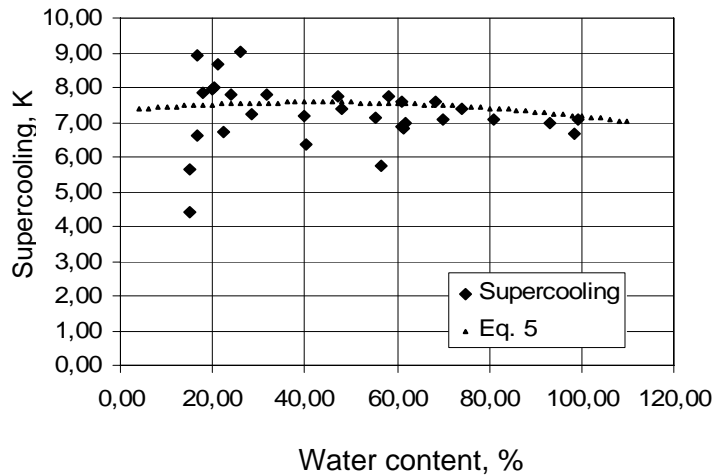


Fig. 12. Supercooling  $\Psi$  vs. water content in kaolins (K-Ca<sup>2+</sup> and K-Na<sup>+</sup>)

At a constant water content, the supercooling should increase with decreasing mass (the total one or the mass of water) due to decreasing the probability of growth of the embryo nuclei to critical sizes, being the consequence of a decrease in the total number of fluctuating molecules.

In the light of the presented results, the question of the absence or presence of supercooling in natural circumstances remains open. Every generalization of experiments on supercooling is very risky because of the part which is played in each test by its specific conditions.

#### 4. CONCLUSIONS

1. Both the temperature of spontaneous nucleation  $T_{sn}$  and the equilibrium freezing point  $T_f$  are possible to be determined by the Differential Scanning Calorimetry (DSC) technique, the former on the cooling run, as the initial temperature of the observed exothermic peak observed, and the latter on warming, as the initial temperature of the last non-zero thermal impulse in the plot of real thermal impulses distribution  $q(T)$ .
2. The obtained results confirm the strong dependency of the freezing point  $T_f$  on the total water content.  $T_f$  can be expressed as a power function of the water content  $w$  and the limit of plasticity  $w_P$  with a high correlation coefficient. In contrary, a scatter of results was observed for  $T_{sn}$ , which could be related to the effect of factors other than the water content.
3. The diagrams of supercooling (i.e. the difference between  $T_f$  and  $T_{sn}$ ) vs. the water content suggest a relationship with an extreme. A best fitted quadratic

model allowed us to find a critical water content,  $w_{cr}$ , at which the supercooling reaches a maximum. For the investigated clay-water systems, the critical water content  $w_{cr}$  occurs between the plastic limit  $w_P$  and the liquid limit  $w_L$ .

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