

FAST ESTIMATION OF UNFROZEN WATER CONTENT IN FROZEN SOILS

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A new method is suggested for fast estimation of unfrozen water contents in frozen soils and sediments within a wide range of negative temperatures (up to -15°C). The method consists in measuring pore water potential (or water activity) at positive Celsius temperatures, with subsequent thermodynamic calculations of unfrozen water contents using the measured data. The method was used to estimate the amount of unfrozen water in frozen kaolinite and polymineral clay samples. The results showed good agreement with direct measurements by the contact method.

Frozen soil, unfrozen water, clay, pore water activity, contact method

INTRODUCTION

The presence of unfrozen pore water in frozen soils and sediments has important implications for their physicochemical and mechanical properties. Experimental evidence of incomplete pore water freezing was obtained in the first half of the 20th century. By the time being, different techniques have been proposed for experimental determination of unfrozen water contents in frozen natural materials: calorimetry, nuclear magnetic resonance, dielectric, cryoscopic, adsorption and contact methods [Yershov *et al.*, 1979; Akagawa, 1988; Ishizaki *et al.*, 1996; Cheverev, 2004; Yoshikawa and Overduin, 2005; Starostin, 2008]. In addition to experiments, researchers have tried to find predictive formulas for estimating the amount of unfrozen water in frozen soils at different negative temperatures [Anderson and Tice, 1972; Watanabe and Mizoguchi, 2002; Komarov, 2003].

With advance in experimental facilities, the interest to unfrozen water in frozen soils has increased markedly [Istomin *et al.*, 2009; Qin *et al.*, 2009; Dall'Amico *et al.*, 2011; Kozłowski and Nartowska, 2013; Starostin and Petrov, 2013; Painter and Karra, 2014; Kozłowski, 2016].

The ways of measuring unfrozen water contents require improvements to find fast and high-performance techniques and to overcome problems in comparing results of different methods.

Estimating the amount of unfrozen water from measured pore water activity: thermodynamic background

In our previous publication [Istomin *et al.*, 2009], we provided details on thermodynamics of pore water in fine-grained porous materials and suggested a method for calculating the amount of its unfrozen part from measured water potential (a parameter widely used in soil science), as a function of total moisture, at positive temperatures ($15\text{--}25^{\circ}\text{C}$). The results showed

good agreement with those of the contact method, within measurement error. The method reported in [Istomin *et al.*, 2009] can be simplified in the range of negative temperatures from 0 to -15°C (up to -20°C for some soils) and presented as a way of fast calculation of temperature-dependent unfrozen water contents (W_{uf}). The simplification is achieved by using pore water activity (a) instead of chemical potential, by applying simpler equations for thermodynamic calculations, as well as by neglecting the temperature dependence of pore water activity in many cases.

By analogy with aqueous solutions, the thermodynamic activity of pore water $a = a(T, W)$ in a soil system of the known moisture W is given by

$$a = \frac{p_{wpor}}{p_w}, \quad (1)$$

where p_{wpor} is the water vapor pressure on the tested sample with the bulk moisture content W (at atmospheric pressure); p_w is the vapor pressure of bulk water. Thus the pore water activity is a relative vapor pressure of bulk water in the sample.

According to (1), a is a dimensionless value, which depends on bulk moisture of the sample and, strictly speaking, on temperature, i.e., $a = a(T, W)$. It is $a < 1$ in the case of hydrophilic systems like soils and $a \rightarrow 1$ at increasing moisture contents.

The parameter of water potential ψ (MPa) used in soil science [Campbell *et al.*, 2007; Sudnitsyn and Kamanina, 2008] is related with the water potential (activity a)

$$\psi = RT \frac{\rho}{M} \ln \frac{p_{wpor}}{p_w} = RT \frac{\rho}{M} \ln a, \quad (2)$$

where R is the universal gas constant ($8.314 \text{ J/mol}\cdot\text{K}$); T is the sample temperature (K); M is the molecular weight of water (18.015 g/mol); ρ is the water density (1.0 g/cm^3).

The thermodynamic activity of pore water is calculated from measured water potential in a sample of known bulk moisture content from (2) as follows:

$$\begin{aligned} a(W, T) &= \exp\left[\frac{M\psi}{RT\rho}\right] = \exp\left[\frac{18.015\psi}{8.314T\rho}\right] = \\ &= \exp\left[\frac{2.167\psi(W, T)}{T}\right]. \end{aligned} \quad (3)$$

Thermodynamic calculations [Istomin *et al.*, 2015, 2017] show that the temperature dependence of pore water activity can be neglected in many cases for the temperature range 0 to -15°C , i.e., a can be assumed to be just a function of W (according to (3)), $\psi(W, T)/T$ is independent of temperature in this case). The absence of temperature dependence means that the enthalpy of pore water coincides with that of bulk water. Strictly speaking, this assumption is valid only for very moist samples about the saturation maximum. Note that temperature dependence of pore water activity is relevant for bound water, as well as for interstitial water in collapsible clay (i.e., at high percentages of montmorillonite or hydromica).

Experimental data on pore water activity in a soil sample with a given bulk moisture (W , measured in percent of dry weight) can be used to calculate the temperature of bulk ice – pore water equilibrium T_{eq} ($T < 273.15\text{ K}$), in the same way as in the case of temperature dependence of unfrozen water contents found by the contact method. At this temperature, the bulk moisture W becomes equal to the content of unfrozen pore water: $W = W_{uf}$. The thermodynamic calculations use an empirical relationship for Gibbs free energy (chemical potential) difference between liquid (supercooled water) and bulk ice phases [Istomin *et al.*, 2009]. Then, equating the chemical potentials of pore water and bulk ice, we obtain the dependence of the pore water activity on the temperature T_{eq} of the water-bulk ice equilibrium:

$$\begin{aligned} -RT \ln a &= \\ &= 6008(1 - T/T_0) - 38.2 \left[T \ln \frac{T}{T_0} + (T_0 - T) \right], \end{aligned} \quad (4)$$

where $T_0 = 273.15\text{ K}$; $T = T_{eq}$ ($T < T_0$) is the temperature (K) corresponding to the pore water-bulk ice equilibrium (at the given sample moisture W and the water activity a).

However, in practice it is more convenient to use an inverse pore water activity dependence of the equilibrium temperature ($^\circ\text{C}$) instead of (4). Using equation (4), we obtained the t_{eq} equation for the measured pore water activity $a = a(W)$ in the range $0.6 \leq a \leq 1.0$:

$$t_{eq} = 103.25 \ln a + 5.57(1 - a)^2. \quad (5)$$

Equation (5) relates the bulk moisture content (via pore water activity) and equilibrium temperature t_{eq} , $^\circ\text{C}$ (at which pore water in a sample of the given moisture W is in thermodynamic equilibrium with bulk ice). To put it different, equation (5) gives the temperature dependence of unfrozen water content because it relates the water activity (amount of unfrozen water W_{uf}) and the negative temperature of a sample.

Measurements of soil pore water potential and thermodynamic activity

Water potential (ψ , MPa) is widely used in soil physics to describe thermodynamic properties of pore water in fine-grained porous materials [Shein, 2005; Trofimov, 2005]. It can be estimated using different methods and instruments, e.g., a Decagon Devices WP 4T water potential meter (USA) [Campbell *et al.*, 2007]. In this case, the water potential ψ of a sample is measured automatically by the dew point method, in natural soils (sediments) with different moisture contents. The instrument allows measuring water potential within 5 to 43°C , at an accuracy of $\pm 0.1\text{ MPa}$ (0 to -10 MPa) to $\pm 1\text{ MPa}$ (for the range -10 to -50 MPa). The WP 4T meter can also measure the thermodynamic activity a of pore water (one value is converted to another using (3)). With all kinds of uncertainty, the error is ~ 0.025 at $0.7 \leq a \leq 0.9$ and no more than 0.01 at $0.9 < a < 1.0$.

The samples we used are $\sim 3.8\text{ cm}$ in diameter and $0.5\text{--}1.0\text{ cm}$ in height, with moisture contents from 0–1 % to full saturation. Data acquisition, storage, and processing can be run automatically by connecting the WP 4T instrument to a PC using the standard *Hyper Terminal* software. Measuring of water potential starts with maximal water saturation of samples. Then the samples are dried stepwise (1–2 %) in a desiccator, with calcium chloride, and their moisture content and water potential are determined at each step. At least six or seven measurements are run at different bulk moisture contents. The moisture content W is monitored by weighing the samples on analytical scales to an accuracy of 0.001 g, before and after the water potential determination. This gives empirical moisture and temperature dependences of water potential for the samples. Water potential can be measured at room temperature ($\sim 25^\circ\text{C}$), as well as in the range $+15$ to $+40^\circ\text{C}$, which allows obtaining temperature dependence of pore water activity. Testing showed that this dependence is weak; it has to be taken into account only for clay samples with bound (adsorbed) water [Istomin *et al.*, 2017] and can be neglected in other cases (at a specified bulk moisture).

Samples

The studies were applied to samples of natural polymineral (Kudinov Fm.) [Istomin *et al.*, 2009] and

Table 1. Particle size distribution, mineralogy and salinity of natural kaolinite and polymineral clay

Type of sediment	Particle size distribution, wt. %							Mineralogy (%)	Salinity, %
	1–0.5 mm	0.5–0.25 mm	0.25–0.1 mm	0.1–0.05 mm	0.05–0.01 mm	0.01–0.005 mm	>0.005 mm		
Polymineral clay	1	2	13	15	22	13	34	Quartz (45) Microcline (9) Illite (8) Kaolinite (5) X-ray amorphous phase (28)	0.19
Kaolinite clay	1	1	0	3	19	11	65	Kaolinite (92) Quartz (6) Muscovite (2)	0.04

monomineral (kaolinite) clay. Their grain sizes were determined by hydrometer testing and the mineral composition by X-ray diffraction (Table 1). Polymineral clay is composed mostly of quartz (45 %) with lesser amounts of microcline (9 %), illite (8 %), kaolinite (5 %), hydromica (2 %), and an X-ray amorphous phase (28 %). Its grain size distribution is: 69 % of silt and clay in total and 34 % of clay particles (<0.005 mm). Kaolinite clay (kaolin) consists mainly of kaolinite (92 %) with 92 % of silt-clay size particles, while the percentage of clay particles (<0.005 mm) reaches 65 %.

The soil samples contain minor amounts of dissolved salts: 0.04 % and 0.19 % (dry residue) in kaolinite and polymineral clay, respectively. The specific active surface areas of the clay samples defined by nitrogen adsorption are 12 m²/g for kaolinite and 26 m²/g for polymineral clay.

The unfrozen water contents in the samples were preliminarily determined by the contact method implying measurements of water contents in equilibrium with ice in a dried sediment plate placed in close contact with two ice plates under isothermal conditions [Grechishchev and Yershov, 1983; Yershov, 1985], for about two weeks (Table 2).

Table 2. Contents of unfrozen water W_{uf} in clay samples measured by contact method

$T, ^\circ\text{C}$	$W_{uf}, \%$	Reference	$T, ^\circ\text{C}$	$W_{uf}, \%$	Reference
Polymineral clay			Kaolinite clay		
-1.7	9.4	[Istomin et al., 2009]	-3.0	7.0	[Istomin et al., 2015]
-2.5	8.8		-4.0	6.6	
-4.0	7.3		-5.0	5.6	
-7.0	6.5		-7.0	3.9	
-10.0	5.4		-10.0	3.1	
-14.0	4.4		-3.0	7.0	[Grechishcheva and Motenko, 2015]
-1.6	9.1	This study	-6.5	4.3	
-2.8	7.7		-14.8	2.6	
-3.7	6.4		-19.9	2.3	
-6.5	5.4		-22.5	2.2	
-22.0	4.2		-27.6	2.1	

Calculating unfrozen water content from measured water potential

The amount of unfrozen water is estimated from empirically found thermodynamic activity of pore water in two steps. First, the dependence of pore water activity a on bulk water content W (wt.%) of the fine-grained water-saturated porous samples is measured at room temperature (by WP 4T in our case). Then, the equilibrium temperature t_f of the samples is determined by using the measured water activity and equation (5) for each water activity value for the sample (and hence for each moisture value W).

This makes it possible to estimate the water content W in equilibrium with the bulk ice phase as a

Table 3. Pore water potential ψ and water activity a at different bulk water contents W , at $t = 25 ^\circ\text{C}$

$W, \%$	ψ, MPa	$a, \text{u.f.}$
<i>Polymineral clay</i>		
3.7	-45.36	0.719
4.5	-32.53	0.790
5.0	-15.53	0.893
5.8	-12.46	0.913
7.0	-4.81	0.966
7.9	-4.01	0.971
9.5	-2.19	0.984
9.9	-1.86	0.987
<i>Kaolinite clay</i>		
1.8	-34.37	0.776
2.6	-20.68	0.860
3.5	-10.21	0.928
4.0	-9.32	0.935
5.0	-6.24	0.956
5.5	-4.48	0.968
6.0	-3.73	0.973
9.0	-2.96	0.979
9.5	-2.55	0.982
12.5	-1.59	0.989
17.0	-0.95	0.993
21.0	-0.55	0.996

Table 4. Calculated equilibrium temperatures t_{eq} for polymineral and kaolinite clay samples with different water contents W

$W, \%$	$a, \text{u.f.}$	$t_{eq}, \text{°C}$
<i>Polymineral clay</i>		
3.7	0.719	-33.6
4.5	0.790	-24.2
5.0	0.893	-11.6
5.8	0.913	-9.3
7.0	0.966	-3.6
7.9	0.971	-3.0
9.5	0.984	-1.6
9.9	0.987	-1.4
<i>Kaolinite clay</i>		
1.8	0.776	-25.9
2.6	0.860	-15.4
3.5	0.928	-7.6
4.0	0.935	-7.0
5.0	0.956	-4.7
5.5	0.968	-3.4
6.0	0.973	-2.8
9.0	0.979	-2.2
9.5	0.982	-1.9
12.5	0.989	-1.2
17.0	0.993	-0.7
21.0	0.996	-0.4

function of negative Celsius temperatures and thus calculate the content of unfrozen pore water (W_{uf}) in a range of negative temperatures. The method was applied to two clay soil samples and the results were compared with those of the contact method.

The experimental water potential and water activity data for the kaolinite and polymineral clay samples at different moisture contents (W , wt.%) are presented in Table 3. The measurements were performed using a scale precise to 0.001 g, which allows measuring water contents of porous fine-grained materials to an accuracy of 0.1 %. Calculations by equation (5) gave dependence of bulk moisture content (W , wt.%) on the negative temperature (t_{eq} , °C) at which the amount of pore water is in equilibrium with the bulk ice phase (Table 4). Thus, the temperature (t_{eq} , °C) dependence of equilibrium pore water content in ice-bearing porous soils W_{uf} at negative temperatures is found from water activity. This dependence for the analyzed clay samples is plotted in Fig. 1.

The contents of unfrozen water in polymineral and kaolinite clay samples calculated by the suggested fast method and measured by the contact method agree well (Fig. 1), in a large range of negative temperatures, to as low as -27 °C. The difference does not exceed 0.5 %, which is commensurate with the accuracy of the contact method.

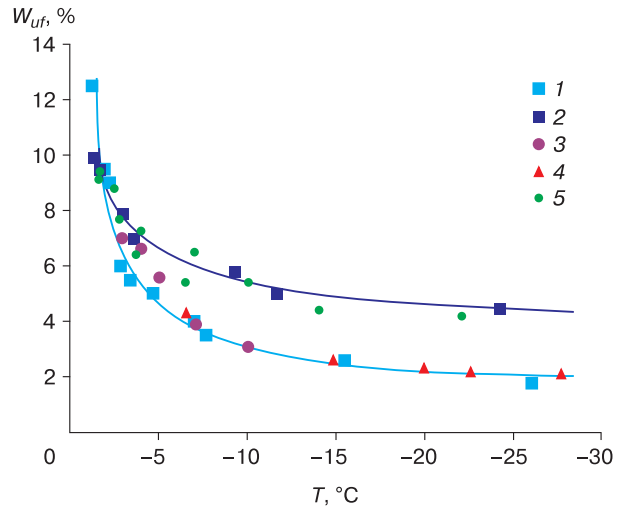


Fig. 1. Temperature-dependent variations of unfrozen water content in clay soils.

1, 2 – fast calculations using pore water activity for kaolinite and polymineral clay samples, respectively; 3, 4 – measured directly by the contact method for kaolinite clay by Istomin et al. [2015] and by Grechishcheva and Motenko [2015], respectively; 5 – results of measurements by contact method. Solid lines are approximations of unfrozen water contents found using the fast method.

It should be noted that the new method allows estimating unfrozen water contents in sediments frozen to -15 °C for 7–8 h. It is faster than other techniques and no less accurate than the contact method.

CONCLUSIONS

A new fast method is suggested to determine the temperature dependence of unfrozen water content in porous fine-grained materials. It consists in measuring thermodynamic activity of pore water at positive (room) temperatures and subsequent thermodynamic calculations for negative Celsius temperatures.

The suggested method was used to estimate the amount of unfrozen water in kaolinite and polymineral clay samples in a large range of negative temperatures (to -15 °C). The contents of equilibrium unfrozen pore water calculated from water potential data show a good fit to the results of direct contact measurements in natural clay sediments, within the uncertainty of the methods.

Further research in this line will include estimating the effect of temperature on pore water activity, checking the accuracy of the new method for materials of different grain sizes and porosities, and extending it to saline, organic-bearing, and oil-contaminated soils.

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