

PREDICTING UNFROZEN WATER CONTENTS IN FROZEN SOILS FROM SURFACE AREA MEASUREMENTS

Duwayne M. Anderson and Allen R. Tice,
U. S. Army Cold Regions Research and Engineering Laboratory

An empirical equation relating the unfrozen water content of partially frozen soils to temperature and specific surface area has been devised. In spite of the simplifying assumptions involved, this prediction equation is of sufficient accuracy for normal engineering requirements. Predicted unfrozen water contents (phase composition) computed from this equation are compared with experimentally obtained values for nine soils and two surface-active soil constituents and are found to be in good agreement, particularly at temperatures below -5 C (23 F). Possession of this prediction equation permits more refined calculations of frost and thaw penetration under natural or disturbed conditions and calculation of the time-dependent temperature distributions associated with foundations, footings, production oil wells, and pipelines.

•THE evidence establishing the existence of a continuous, unfrozen water phase separating ice from the mineral or organic matrix in frozen soils has come from many sources and is now a widely accepted fact (3, 4, 6, 16-19, 20, 23-25, 27-31). Questions regarding the mobility of the interfacial water, the nature of the ice phase, and the factors governing the quantity of water remaining unfrozen under given conditions, at least in qualitative terms, have been answered. The unfrozen, interfacial water behaves as a two-dimensional liquid, with water molecules and solutes freely mobile in this zone (13, 14, 15, 22). NMR spectra show decreasing, but significant, molecular mobility down to -40 C . Although it was once claimed that anomalous ice phases might exist in frozen soil, in all instances so far reported the ice formed is normal, hexagonal ice I (2). The principal factor determining the quantity of water remaining unfrozen in frozen soil is temperature (23). Pressure is a less important, but significant, factor; at a given temperature, an increase in pressure increases the unfrozen water content in a predictable way (18, 26, 29). Solute concentration in the interfacial zone seems to exert an effect roughly equal to that predicated from the freezing point depression (5, 8, 18). In addition to these factors, Bouyoucos (9) has pointed out that the geometrical arrangement of soil particles and the manner in which freezing was accomplished also are important.

During freezing or thawing, the associated latent heat of phase change does not appear instantaneously; instead, it is evolved or absorbed progressively as freezing or thawing proceeds. One of the major problems in performing calculations of frost penetration, or the thawing of permafrost due to heat transferred from foundations and footings, wells, and pipelines, has been a lack of understanding of how to treat the latent heat term that eventually appears. A particularly troublesome aspect of this problem has been the lack of a suitable function to adequately represent phase composition data. In this paper, we suggest a functional form and an equation that we believe will be found useful and adequate until further refinement becomes possible.

During the past decade, the various ways in which phase composition curves (unfrozen water contents as a function of temperature) could be obtained or derived from direct, experimental measurements as well as from other observations by indirect methods have been investigated (3, 7, 11, 20, 23, 28, 29, 30). In general, these methods yield comparable values for samples of a given soil, provided that sample histories are the same. Although several important questions remain to be investigated before it

can be said that our understanding is sufficient for present needs, an important and perhaps basic relationship has emerged: the dependence of unfrozen water contents on the specific surface area of the sample. The beginning of this idea can be traced back to Bouyoucos' (9) early work in which he related unfrozen water contents to the general classification of soil water, which in turn was known to be related to soil particle size. It seems first to have been considered explicitly by Nersosova and Tsytoich (23), who listed the following as the main factors determining the phase composition of frozen soil: (a) temperature, (b) pressure, (c) specific surface area of the solid phases, (d) chemical and mineralogical composition of the soil, (e) other physicochemical characteristics, especially the nature of exchangeable cations, and (f) solute content and composition. Of these, temperature was established as the dominant factor for a given soil, but the relative importance of those remaining was left undetermined. Dillon and Andersland (11) were next to focus on the importance of the interfacial area. They constructed a prediction equation that explicitly involved the specific surface area of the soil matrix, the plasticity index, and a defined "activity ratio." Although they did not emphasize it, the latter two parameters are closely related to the specific surface area of the soil mineral grains. Thus, it has become clear that specific surface area is a major determinant of the phase composition of frozen soils.

In an earlier paper (7), we reported unfrozen water content (phase composition) data that were determined by using the isothermal calorimeter method and unit surface area normalization. We have continued these measurements and now report complete phase composition data for ten representative soils and soil constituents (Figs. 1 and 2.) These data are well represented by the power curve

$$W_u = \alpha\theta^\beta \quad (1)$$

where W_u is given in percentage of dry sample weight, θ is the temperature below freezing in degrees C, and α and β are parameters characteristic of each soil. Values of α were obtained by using a least-squares regression of the experimentally measured values of W_u versus θ . These, together with the respective correlation coefficients and experimentally measured specific surface areas, are given in Table 1.

Figures 1 and 2 show the degree to which the normalization of unfrozen water content data to unit surface area unifies the results. In some respects, specific surface area is seen to be a more important factor than temperature in determining the water phase composition. This can be seen by examining Eq. 1 for silt and clay soils. The primary factors governing phase composition would be written in order of importance as

$$W_u = f(S, \theta, P, \Pi) \quad (2)$$

where S is the specific surface area, θ is temperature in degrees below 0 C (32 F), P is the confining or overburden pressure, and Π is the osmotic potential of the soil solution. In addition to these four primary factors, a complete consideration would involve such secondary factors as the nature of the fine pore geometry of the mineral grains, particle packing geometry, surface charge density and the suite of exchangeable, adsorbed ions. In this investigation, P and Π were held constant as the calorimetric, unfrozen water data shown in Figures 1 and 2 were obtained. Hence, the degree to which the curves in Figures 1 and 2 do not coincide indicate the combined effect of these secondary factors. A careful examination of the data for kaolinite and the two bentonites reveals that the data are better fit by segments of two different curves having the form of Eq. 1 (shown as dashed lines in Figs. 1 and 2). When this fact was discovered, the extensive data of Nersosova and Tsytoich were examined with the same result: segments of two power curves are required for a good fit of the data for kaolinite and montmorillonite. The basic significance of this observation is not readily apparent and is under continuing study. It is evident, in general, however, that the representation of phase composition data by a single power curve is quite satisfactory for most purposes (note the correlation coefficients given in Table 1); Eq. 1 should, however, be regarded as a first approximation, with the expectation that further refinements may become possible. There are no fundamental data on the influence of the secondary and tertiary

Figure 1. Phase composition plots (unfrozen water contents W_u versus temperature below freezing θ) for five representative soils.

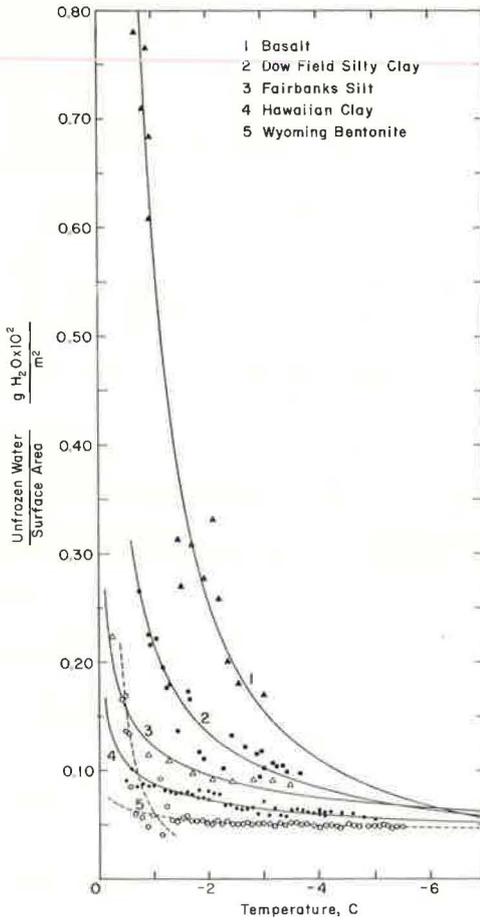


Figure 2. Phase composition plots (unfrozen water contents W_u versus temperature below freezing θ) for five representative soils.

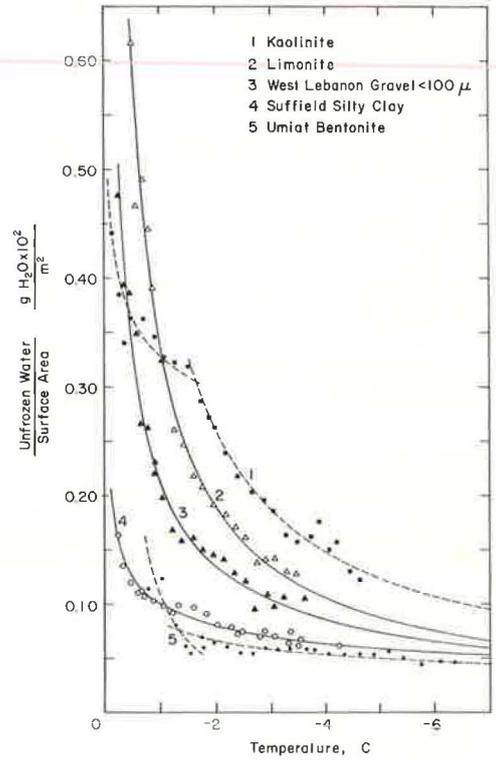


Table 1. Values of α and β , experimentally measured specific surface areas, and correlation coefficients.

Soil	Surface Area (m ² /g)	α	β	r
Basalt	6	3.45	-1.13	0.96
Rust	10	11.05	-0.80	0.95
West Lebanon gravel, <100 μ	18	3.82	-0.64	0.94
Limonite	26	8.82	-0.83	0.99
Fairbanks silt	40	4.81	-0.33	0.96
Dow Field silty clay	50	10.35	-0.61	0.94
Kaolinite	84	23.80	-0.36	0.90
Suffield silty clay	140	13.92	-0.31	0.98
Hawaiian clay	382	32.42	-0.24	0.93
Wyoming bentonite	800	55.99	-0.29	0.72
Umiat bentonite	800	67.55	-0.34	0.83

factors that influence phase compositions, and it is clear that their acquisition will be a laborious and lengthy process. In the absence of the basic relationships needed for thoughtful refinement of Eq. 1, let us explore some additional empirical correlations. Two interesting relationships appear when the values of α and β (Table 1) are regressed against the specific surface areas, S . It is found that

$$\ln \alpha = 0.5519 \ln S + 0.2618 \quad (3)$$

with a correlation coefficient of 0.90 and

$$\ln(-\beta) = 0.2640 \ln S + 0.3711 \quad (4)$$

with a correlation coefficient of 0.86.

Additional phase composition data are not likely to alter significantly the two relationships expressed in Eqs. 3 and 4. Therefore, one can use Eqs. 1, 3, and 4 to obtain

$$\ln W_u = 0.2618 + 0.5519 \ln S - 1.4495 \ln \theta^{-0.264} \quad (5)$$

a convenient computation form of a general phase composition equation.

An indication of the accuracy of unfrozen water contents predicted by Eq. 5 is given in Table 2, which contains unfrozen water contents calculated for $\theta = 1$ and $\theta = 10$. The differences in the observed values (obtained from Eq. 1 and the appropriate values of α and β from Table 1) and the calculated values (obtained from Eq. 5) are seen to be relatively large in only a few cases, notably, Umiat bentonite, kaolinite, and rust, at $\theta = 1$. At lower temperatures, $\theta \geq 10$, the differences diminish rapidly and eventually become practically insignificant.

A family of water phase composition curves calculated for the range of specific surface areas encompassing all naturally occurring soils is shown in Figure 3. The curves provide a quick estimate of W_u for any soil when its specific surface area is known or can be estimated. The expansion of certain clay minerals when wetted, which exposes an "internal" surface area, must be accounted for in S . Methods are available for measuring the total (internal and external) surface, S (10, 12, 21); when measured values of S are not available, it is possible to derive a "geometric" specific surface area from grain size distribution curves to obtain good estimates of W_u (11). (Specific surface areas derived from nitrogen adsorption isotherms are unsatisfactory because they are a measure of "external" surface only.)

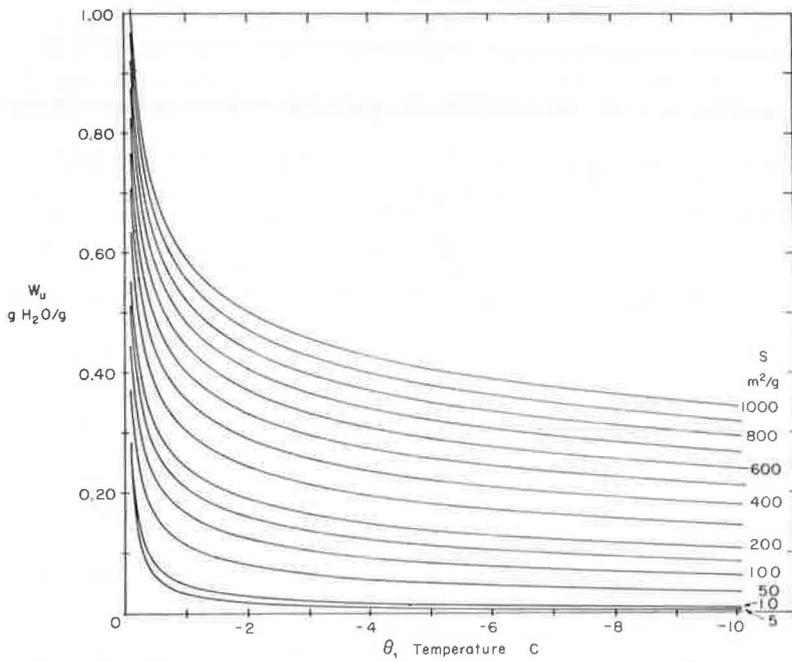
Equation 5 is similar to one proposed by Dillon and Andersland. However, Eq. 5 is considerably simpler and more convenient in that it requires that only one soil parameter, S , be known. In terms of accuracy of predicted values of W_u , Eq. 5 is probably equal to the Dillon and Andersland equation, but this cannot be verified at present because the data required for a complete test are not yet available. Because Eq. 5 rests on correlations obtained from a very extensive body of water phase composition data, we believe that it can be used effectively in frost penetration calculations to predict thaw and degradation of permafrost under natural and disturbed conditions and to calculate the time-dependent temperature distributions associated with foundations, footings, production oil and water wells, and buried or overhead pipelines. In such calculations it is necessary to consider the term

$$\int_{\theta_1}^{\theta_2} L (\partial W_u / \partial \theta) d\theta$$

in a heat capacity Eq. 3. This term, in which L is the latent heat of phase change, accounts for the heat involved as the relative amounts of ice and unfrozen water change in the temperature interval $(\theta_2 - \theta_1)$. Usually, L is taken as a constant equal to 79.7 cal/g, which is satisfactory in all but exceptional cases. However, it is known that the latent heat of phase change is not constant but varies with $W_u(1)$. The manner in which this complication may be dealt with is treated in a subsequent paper.

Table 2. Unfrozen water contents.

Soil	Observed W_u (percent)		Calculated ΔW_u (percent)	
	$\theta - 1$	$\theta - 10$	$\theta - 1$	$\theta - 10$
Basalt	3.45	0.25	0.04	0.19
Rust	11.05	1.75	-6.29	-0.96
West Lebanon gravel, <100 μ	3.82	0.87	2.58	0.47
Limonite	8.82	1.29	-0.97	0.62
Fairbanks silt	4.81	2.27	5.14	0.55
Dow Field silty clay	10.35	2.52	0.91	0.91
Kaolinite	23.80	10.30	-8.81	-4.98
Suffield silty clay	13.92	6.75	5.95	1.28
Hawaiian clay	32.42	18.53	2.15	-1.27
Wyoming bentonite	55.99	28.66	-4.00	0.70
Umat bentonite	67.55	30.66	-15.56	-1.30

Figure 3. Calculated phase composition curves for various values of specific surface area.

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