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UNFROZEN WATER CONTENT FROZEN SOILS AND SOIL MOISTURE SUCTION

BY

P. J. WILLIAMS

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UNFROZEN WATER CONTENT OF FROZEN SOILS
AND SOIL MOISTURE SUCTION

by

P. J. WILLIAMS*

SYNOPSIS

The unfrozen water content of various soils has been measured by calorimeter. The suction-moisture content characteristics of the same soils were also determined at room temperature, with conventional pressure plate and pressure membrane apparatus. Using the values of unfrozen water content measured during freezing, and the suction characteristics obtained during drying, a relation was found between the two sets of results. The relationship approximates that of Schofield, between suction and initial freezing point, of soils at various moisture contents. Knowledge of the relationship permits prediction of the amount of water remaining unfrozen in a soil at negative temperatures down to -1.0°C and often somewhat lower. Such prediction requires only determination of suction-moisture content characteristics by conventional methods together with a simple determination of the freezing point of an extract of the soil solution. In many cases, the accuracy of the prediction is apparently as great as can be obtained using even complex calorimetric methods. Using these relatively easily determined values of unfrozen water content at various temperatures, realistic estimates can be made of the apparent specific heats of frozen soils. The observed relationship provides a basis for studies of the effects of both load and temperature, on the proportions of ice and water in frozen soils and on the state of stress within the ice and unfrozen water.

La teneur en eau non gelée de divers sols, a été mesurée par calorimètre. Les caractéristiques des teneurs eau-suction des mêmes sols furent aussi déterminées à la température ambiante, avec plaque conventionnelle de pression et appareil à membrane de pression. En utilisant les valeurs des teneurs en eau non gelée mesurées pendant la congélation, et les caractéristiques de suction obtenues pendant le séchage, un rapport fut trouvé entre les deux séries de résultats. Le rapport se rapproche de celui de Schofield, entre la suction et le point initial de congélation de sols de diverses teneurs en eau. La connaissance du rapport permet de prédire la quantité d'eau restant non gelée dans le sol à une température descendant jusqu'à -1.0°C et souvent quelque peu plus basse. Une telle prédiction nécessite seulement la détermination des caractéristiques de la teneur eau-suction par les méthodes conventionnelles, ainsi qu'une détermination simple du point de congélation d'un prélèvement de solution du sol. Dans beaucoup de cas, l'exactitude de la prédiction est apparemment aussi grande que celle qui peut être obtenue même en utilisant des méthodes calorimétriques complexes. En utilisant ces valeurs déterminées d'une manière relativement facile de teneur en eau non gelée à diverses températures, on peut faire des évaluations réalistes des chaleurs spécifiques apparentes des évaluations réalistes des chaleurs spécifiques apparentes des sols gelés. Les rapports observés fournissent une base pour les études des effets à la fois de charge et de température, sur les proportions de glace et d'eau dans les sols gelés et sur l'état des contraintes dans la glace et l'eau non gelée.

INTRODUCTION

Early studies of the freezing of soil moisture were mainly concerned with the determination of a freezing "point", that is, the temperature at which freezing commences in a sample (Bouyoucos and McCool, 1916). More recently it has been realized that the freezing of water in finely porous materials takes place over a range of temperatures (Lovell, 1957; Institut Merzlot., 1953-57); and that the equilibrium freezing temperature varies in different parts of the soil water. The greatest depression of the freezing point below 0°C presumably occurs in water that is most firmly held and is closest to the soil particles.

Schofield (1935) showed that as the moisture content of soil samples is reduced the freezing point is depressed further below 0°C . Schofield carried out investigations on the suction with which water is held in soil and showed clearly that as the water content of the sample is reduced the suction to be applied to a column of water in contact with the soil (as in the suction plate apparatus) must be increased if water is not to enter it. He argued that this

* Research Officer, Snow and Ice Section, Division of Building Research, National Research Council Ottawa, Canada. Research Fellow, Norwegian Geotechnical Institute, Oslo, 1963, 1964.

"pressure deficiency" or suction of the soil water is mainly responsible for the freezing point depressions observed; and proposed and verified experimentally that a relationship exists between the pressure deficiency at a given moisture content and the temperature at which the water in the soil (in the absence of supercooling) begins to freeze.

Comprehensive calorimetric investigations of the freezing of a variety of soils have recently been carried out; some are described in this Paper. They allow calculation of the amounts of unfrozen water present in the soils at various negative temperatures. These amounts may be said to have freezing points (i.e. to start to freeze) at those temperatures. Accordingly there might be expected (as pointed out by Croney, Coleman, and Black 1958), a relationship similar to that proposed by Schofield, between the temperature associated with a certain content of unfrozen water and the suction associated with the same moisture content in the soil (measured at room temperature). The establishment of such a relationship would have theoretical and practical interest and would allow, without the necessity for elaborate calorimetric tests, prediction of the unfrozen water contents of a soil at temperatures below 0°C (on the basis of determination of the moisture-content-suction characteristics of the soil). This Paper gives observations, determined calorimetrically, on the unfrozen water content of soils and on the suction-moisture content characteristics of the same soils. A relationship between these two quantities is shown to exist and is discussed.

EXPERIMENTAL METHODS

The determination of unfrozen water content in freezing soils

A calorimeter was constructed that permits the determination of the heat quantities required to raise or lower the temperature of soils by a measured amount. When expressed as calories/g/ $^{\circ}\text{C}$ this value is the specific heat. If freezing temperatures are involved, it is usually markedly temperature-dependent, and in this Paper is called "apparent specific heat" because it includes some latent heat of fusion. A full description of the apparatus, together with observations on the apparent specific heat of soils, has been given recently (Williams, 1964(a)).

The soil sample (about 120 cc volume) is contained in a sample holder inside an outer container. During warming tests heat is supplied to the sample at a measured rate through a heating coil wound onto the sample holder. The outer container is maintained at the same temperature as the sample holder so that there is no loss of heat externally. During cooling tests the outer container is maintained at a temperature lower by a constant amount than that of the sample holder. There is then a steady and known passage of heat from the sample holder to the outer container and the exterior.

Such measurements permit the calculation of the amount of unfrozen water present in a frozen soil at various negative temperatures. The method has been outlined (Williams, 1963). The unfrozen water content at a given temperature is dependent on whether the temperature is reached by cooling or warming. The present Paper is concerned only with the former case.

In calculating the unfrozen water content of a frozen soil the time/temperature record (obtained during warming or cooling of a specimen) is divided into increments, ΔT , of 0.13°C (other values occasionally being used). The quantity of heat associated with the change of temperature of the sample holder, soil, ice and water is subtracted from the quantity of heat removed from the sample in the time taken for this temperature change. The remainder is the latent heat involved in freezing or thawing of water. By adding the quantities of ice formed in each increment of temperature change (starting with the temperature of initial freezing), and by making appropriate corrections for the changing proportions of ice and water, the amount of ice present at any temperature can be calculated. This quantity is deducted from the total moisture content to give the unfrozen water content. These calculations can be expressed as:

Unfrozen water content of sample (g):

$$\text{total mc (g)} = \sum_{T_{\text{in}}}^{T_x} \frac{\Delta H - (K_s + \text{cal const})\Delta T_c + (K_w - K_i)I\Delta T_c}{79.68} \quad (1)$$

where

ΔH = quantity of heat removed to lower temperature of sample by ΔT_c

ΔT_c = temperature change of sample

K_s = specific heat of wet soil (from determinations in unfrozen state)

cal const = heat required to change temperature of sample holder, cal/°C

K_w = 1 cal/g/°C (i.e. specific heat of water)

K_i = 0.508 cal/g/°C (average value of specific heat of ice)

T_{in} = temperature at which freezing commences

T_x = temperature at which unfrozen moisture content is required

I = amount of ice present at temperature of warm end of interval ΔT_c (change in the amount of ice present as the temperature changes through ΔT_c was ignored; the resulting error in the expression $(K_w - K_i)I\Delta T_c$ is not significant)

79.68 = latent heat of freezing of water, cal/g.

The results of observations on several soils are given in Figs 2 to 5, where the unfrozen moisture content expressed as a percentage of the dry weight is shown as a function of temperature during cooling (freezing). The grain size composition and a brief description of each soil are given in Fig. 1.

In compressible soils at a given temperature the unfrozen water content of a sample that has been frozen previously differs from that observed during the first freezing. The observations, therefore, include both cases. In determinations carried out on soils previously frozen and thawed (Figs 2(b), 3(b), and 4(b)) the lowest temperatures reached during prior freezing varied somewhat (although always lower than those in the determinations themselves). The unfrozen water content subsequently determined did not appear to be affected by these variations.

Accuracy of the calorimetric investigations

In calibration tests with water a standard deviation of 4% from the true value for specific heat was found in five tests; the average of the five results was within 1%. In tests with frozen soils further considerations are necessary. The greater part of the 4% error is due to an unmeasured loss or gain of heat in the sample during tests (Williams, 1964(a)). During prolonged tests it was often possible to rectify this so that a value better than $\pm 4\%$ could be expected. The calculated quantities of ice formed or melted should also be accurate to well within these limits. When the ice quantity, and subsequently the unfrozen water, is expressed as a percentage of dry weight, the latter may be in error by a maximum of 0.5 to 2% dry weight (depending on the total moisture content) at, for example, -5°C . The error does not accumulate as lower temperatures are reached, except insofar as I in the expression $(K_w - K_i)I\Delta T_c$ may be in error, and this expression has only a small effect on the whole calculation.

This accuracy is also indicated by a series of repetitive, though not entirely similar, tests on Leda clay (Fig. 4(b)). More serious are the errors associated with measurement of the

sample temperature, especially within the temperature range 0° to -1°C , on account of the rapid change of unfrozen water content with temperature. The sample temperatures were usually measured to an accuracy of $\pm 0.05^{\circ}\text{C}$, but occasionally to an accuracy of -0.075°C . The curves can be displaced by this amount, and this will result in possible errors in unfrozen water content of about 2 to 3% dry weight and occasionally more. Most of the curves given in this Paper are more accurate than these figures indicate because they are based (as noted in each figure) on more than one test.

Repeated tests on the same sample (Fig. 4(b)) showed no difference, within the limits of experimental error, in unfrozen water content for a wide range of freezing rates. The temperatures, therefore, can be regarded as true equilibrium freezing temperatures. Temperature differences within the sample were very small and always less than 0.05°C .

Fig. 1. Grain size composition and other characteristics of soils investigated:

- NS — Niagara silt
- WCB — Undisturbed, mottled, montmorillonite clay; Winnipeg
- LC-GCS — Undisturbed Leda (marine) clay, mainly illite (for analysis, see Lambe and Martin, 1956); Green's Creek, Ottawa
- LC-KNB — Remoulded Leda (marine) clay, mainly illite
- IO — Haematitic iron ore, friable; Schefferville, P.Q.

The determination of the suction-moisture-content characteristics

In the simplest form of apparatus for determining the suction-moisture-content characteristics of a soil, the sample rests on a porous plate to the underside of which is attached a column of water (Croney, Coleman, and Bridge, 1952). Various suctions are applied to this water, usually by means of a mercury manometer. At each suction the soil is allowed to establish its equilibrium moisture content, which is then determined. Because of the limitation on the suction that can be applied to a column of water, this method can be used only over a very limited range of soil moisture content.

In the present investigations, therefore, pressure plate and pressure membrane apparatus were used (Richards, 1947). Instead of placing the water source under reduced pressure, it is maintained at atmospheric pressure and the air pressure around the sample is raised. It is generally assumed that the air pressures are numerically equivalent to the suction* that would

* The word "suction" is now generally used in soil studies, to describe the property of the soil water system being measured here (ISSMFE, 1961). It does not imply, however, that the "pressure deficiency" of the water in the soil is limited to between 0 and 1 atmosphere. Furthermore, there is controversy (discussed later) as to the nature of the stresses giving rise to the observed suctions.

have to be applied to a column of water to produce the same moisture content in similar samples in the suction plate apparatus. As in the suction plate apparatus, water passes out of the sample through the plate or membrane until equilibrium is reached. Air does not escape from the chamber in significant quantity because of the small size of the pores in the pressure plate, which can be used at pressures up to about 1.02 kg/sq. cm, or of the pores of the membrane in the pressure-membrane apparatus, which can be used at pressures up to 14 kg/sq. cm. In the case of the pressure membrane apparatus a rubber diaphragm is pressed down by an additional air pressure of about 0.3 kg/sq. cm on to the soil sample, which is thus maintained in close contact with the membrane.

Fig. 2. Unfrozen water content during freezing of Leda clay GC-8: (a) during first freezing (based on observations during two tests); (b) following previous freeze and thaw

Fig. 3. Unfrozen water content during freezing of Winnipeg Clay B: (a) during first freezing; (b) following previous freeze and thaw

The thickness of the specimens was normally about 3 mm, and tests indicated that equilibrium was reached in 4 or 5 days. Moisture contents were determined by drying at 105°C. In the observations of Coleman and Marsh (1961) equilibrium was reached in 5 to 6 days, about 1% dry weight moisture content loss occurring during the last 1 or 2 days; but these specimens were about 5 mm thick. The results of the experiments are shown in Figs 6

and 7, where the pF of the soil is given as well (Schofield, 1935).^{*} The samples for the calorimeter and suction tests should be as similar as possible. In the case of undisturbed samples, they should be adjacent parts of a single soil specimen. The same sample cannot be used for both tests, as the test procedure changes the character of the soil.

The suction-moisture-content characteristics of a given soil are known to vary with degree of consolidation, previous wetting or drying (Croney and Coleman, 1954). It was found in this investigation that a freeze/thaw cycle also resulted in similar changes. The figures give as well, therefore, determinations of suction-moisture-content characteristics of the soils following a freeze/thaw cycle.

Interpretation and accuracy of observations of suction-moisture-content characteristics

Suction-moisture-content characteristics were determined at room temperature (approximately 20°C). Gardner (1955); Wilkinson and Klute (1962); and Coleman, Croney, and Bridge (1952) have pointed out a dependence of suction on temperature. The question arises, therefore, of whether the suction values determined at room temperature should be corrected to a temperature near 0°C before comparison with the unfrozen moisture content/temperature observations. Gardner's experiments, which involved suctions up to 0.32 kg/sq. cm (pF 2.5), indicate a change of suction of about 0.14 kg/sq. cm between 20 and 0°C. Such a change corresponds to about 0.16 pF units at pF 2.5, but would correspond to only 0.06 units at pF 3, and to 0.01 pF units at pF 3.5. It will be shown, subsequently, that pF 's lower than about 3 are of relatively little significance in the present investigation. It is apparent, therefore, that no serious error will result if the temperature correction is ignored in all cases. Tests by Penner (1958) lead to the same conclusion.

In previously frozen and thawed samples the lowest temperature to which they were subjected in prior freezing varied between -5 and -18°C . These variations appeared to have no significant effect on the subsequently observed suction-moisture content characteristics, and a single line was used to represent all points for a given soil.

Water from soils collected after passing through the membrane has a depressed freezing point (Table 1) and contains a quantity of dissolved salts. In the porous plate apparatus and certain of the pressure membrane apparatus fresh water is periodically circulated below the membrane to remove air bubbles; this procedure may reduce the salt concentration of the water in the soil. In the present experiments, however, moisture contents obtained with this technique did not differ significantly from those where the lower side of the membrane was always in contact with solution from the soil.

Effects of salts on freezing temperatures

Salts dissolved in the soil solution are partly responsible for depression of the temperature of freezing and for the associated unfrozen water content of freezing soils (Ayers and Campbell, 1951). To investigate this the soil solution was extracted and collected with the pressure membrane apparatus at various air pressures up to 4.2 kg/sq. cm. In this application the air pressures are applied entirely above the rubber diaphragm and are thus not exactly comparable with those used in the suction-moisture-content investigations. This procedure is necessary to avoid air leakage through the membrane (it is not possible to keep the membrane saturated by circulation of water below it—this would dilute the extracted solution). Using a mercury thermometer, simple freezing point determinations accurate to about $\pm 0.02^{\circ}\text{C}$

^{*} pF is a widely accepted symbol to refer to the convenient value, the logarithm of the suction. It is used in this Paper solely in that sense and without reference to the "free energy" of the soil water.

Table 1
Freezing point determinations on extracted soil solutions

Soil	Air pressure used for extraction: kg/sq. cm	Initial moisture content: % dry wt	Freezing point: Δt_s , °C	Remarks
Winnipeg clay B	4.2	48	- 0.29	{ Same sample subjected to two air pressures
Leda clay GC-8	4.2	57	- 0.22	
Leda clay KNB	4.2	31	- 0.10	
Leda clay KNB	14.2		- 0.10	
Iron ore		30 approx.	taken as: -0.30 (see text and footnote *)	

(Table 1) were made on the solution obtained. Within this accuracy it was found that for each soil the freezing points were similar for water extracted at any pressure up to 14 kg/sq. cm. In the absence of ice, therefore, that part of the soil water of interest in the present investigation is assumed to have a uniform concentration of dissolved salts.

As the ice (which does not contain any significant amount of dissolved salts) is formed during freezing of the soil, the salts become increasingly concentrated in the unfrozen water. Because the increase in freezing point depression due to salts in solution is approximately proportional to the concentration, the effects of dissolved salts on the freezing temperature associated with each quantity of unfrozen water are easily calculated:

$$\Delta T_{sx} = \frac{\Delta T_s \text{ total moisture content}}{\text{unfrozen water content at temperature } x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

 ΔT_s = the observed freezing point depression of the extracted solution °C

ΔT_{s_x} = the calculated freezing point depression °C of the unfrozen water content at temperature x (on account of dissolved salts)

The observed temperature corresponding to each quantity of unfrozen water must therefore be raised (giving a smaller negative temperature) by the amount, ΔT_s , before comparison with suction-moisture-content observations.

The freezing point depression of the extracted solutions is quite similar to the temperature at which ice first appears in the calorimeter samples (i.e. the highest temperature on the unfrozen water content-temperature graphs). They are not expected to be exactly the same because the calorimeter samples were usually not saturated. At their total moisture content, therefore, the pF value is not 0, and their freezing temperature is somewhat below that of the extracted solution.*

There is a possibility that the membranes used are semi-permeable with respect to some of the salts in the soil solution. The similarity in freezing point of the extracted solution and the initial freezing temperature of the calorimeter sample indicates, however, that this does not occur to any significant extent.

* For one soil, iron ore, the reverse was found to be the case, the calorimeter sample commencing to freeze at -0.026°C ; the extracted solution froze at -0.13°C . Different samples were used for the calorimeter test and for extraction of the solution, however, and the difference in freezing temperature is almost certainly due to the variable nature of the material. In this case only, therefore, the calorimeter value, -0.026°C ., was taken as a better value for ΔT_s .

Fig. 4. Unfrozen water contents during freezing of Leda clay KNB: (a) during the first freezing (based on observations during two tests) (b) following previous freeze and thaw; the five tests were carried out at different rates of freezing as indicated; in one test the total moisture content was 19%, while in four it was approximately 35%; it may be seen that the different total moisture content has no significant effect on the unfrozen water content

Fig. 5. The unfrozen water content during freezing of: (a) Iron ore (based on two tests); (b) Niagara silt

COMPARISON OF THE OBSERVATIONS OF UNFROZEN WATER CONTENT AND SUCTION-MOISTURE-CONTENT CHARACTERISTICS OF THE SOILS

As already noted, the moisture content at a given suction and the unfrozen water content at a given temperature are both affected by previous freezing and thawing. This must be borne in mind when comparing results.

Unfrozen water contents on first freezing, and suction-moisture-content characteristics of soil not previously frozen

For the first comparisons, freezing tests (Figs 2(a), 3(a), 4(a), and (5)) were completed on samples of several soils that had not been previously frozen (all samples were from deposits below the maximum annual frost penetration and from areas where permafrost has almost certainly never occurred). Further samples were taken from the same soils and the suction-moisture-content relationships determined (Figs 6(a), 6(c), 7(a), 7(c), 7(d)). To compare these

Fig. 6. Suction-moisture content curves for soils investigated calorimetrically: For the soils previously frozen, the following symbols are used in this Figure and Fig. 7 to indicate the lowest temperature for each sample:

▲	- 5.0	●	- 12.0
△	- 6.5	□	- 15.0
■	- 9.5	×	- 18.0

two sets of results a graph was drawn (Fig. 8) showing negative temperature and suction values. These were obtained by selecting a temperature and finding the unfrozen moisture content corresponding to it for a particular soil. The suction value corresponding to an equal moisture content in the unfrozen soil was then obtained from the appropriate graph in Fig. 6 or 7. To allow for the effects of dissolved salts a correction (as described in the previous section) was made to each freezing temperature before plotting. From the curves obtained (Fig. 8) it is quite clear that there is a strong relationship between the suction and the equilibrium freezing temperature.

Unfrozen moisture contents during second and subsequent freezing of a soil, and the suction-moisture-content characteristics of soils also previously frozen and thawed

For these next comparisons, freezing tests were carried out on soil samples previously frozen and thawed (Figs 2(b), 3(b), 4(b)). Suction-moisture content characteristics were also determined for samples of the same soil similarly pretreated (Figs 6(b), 6(d), 7(b)). These two sets of information were again used, with appropriate correction for the influence of salts, to give the curves shown in Fig. 9. It is clear that the relationship previously found also holds in this case. In view of the difference between observations made on the same soil, with and without prior freezing, it is equally clear that the relationship will only apply if the suction-moisture content and temperature-unfrozen water content measurements are made on samples of soil treated similarly with respect to previous freezing.

Fig. 7. Suction-moisture-content curves for soils investigated calorimetrically (symbols as in Fig. 6 except that ● is used for soils not previously frozen)

DISCUSSION

The results described above have important theoretical and practical implications. This Paper is not primarily concerned with the causes of the observed relationships, but a brief theoretical discussion is appropriate.

Theoretical

When a uniform pressure (above atmospheric) is applied to ice and water in contact, the freezing point is lowered below 0°C. Conversely, if the pressure is reduced below atmospheric, the freezing point is raised above 0°C. If the measured suctions in soils imply that the water is under pressure lower than atmospheric, it might be supposed that freezing would take place at temperatures above 0°C. Even when allowance is made for dissolved salts and the necessity for an ice nucleus, however, it has been frequently observed that this does not

occur. Edlefsen and Anderson (1943) proposed that very little, if any, of the soil water is under reduced pressure. They believed that most of the water in a fine-grained soil is under the influence of adsorption forces acting normally to the particle surface and resulting in raised pressures in the adjacent water. Ice present would also be subjected to these pressures, and the result would be a depression of freezing point. They believed such adsorption forces could also be responsible for the "suction" of the soil.

Schofield, on the other hand, thought that much of the soil water was really under tension or reduced pressures, but that the ice first formed would be under atmospheric pressures. If such were the case the freezing point would again be depressed according to the relationship:

$$H = \frac{L}{Tg} \cdot \Delta T \quad \dots \dots \dots (3)$$

Fig. 8. Relationship for soils investigated between suction for a given moisture content, at room temperature, and temperature (after correction for dissolved salts) at which a similar amount of unfrozen water occurs in the freezing soil. (For descriptions of soils see Fig. 1)

where

H = suction expressed as height of a column of water, cm

L = latent heat of freezing of water 3.336×10^9 ergs/g

T = temperature °K

g = gravitational acceleration, 981 cm/sec²

ΔT = freezing point depression °C

In Schofield's (1935) paper, errors have apparently occurred in the printing of the equation, which is given here correctly. No derivation for the equation is given, but this may be followed in the work of Poynting (1881) and Hudson (1906).

Schofield and Botelho da Costa (1938) found that the initial freezing points for samples with various moisture contents (and hence various suction values) fitted this relationship well. The relationship has been plotted on Figs 8 and 9 ($\Delta T = T'$), and corresponds also to the experimentally observed relationship shown there.

Experimental

With respect to the present investigations the following should be noted:

(1) The various curves determined experimentally in Figs 8 and 9 coincide remarkably closely. The relationship cannot be fortuitous, because the soils differ substantially in both nature and experimental behaviour. The theoretical curve from equation (3) is also very similar, although it differs slightly from the curve that would most nearly approximate all the experimentally determined curves. Theoretical values calculated from an equation based on the work of Edlefsen and Anderson (1943), on the contrary, deviate significantly from the experimentally obtained curves.

(2) The agreement between the observations and the curve given by equation (3) implies that even when large quantities of ice are present for temperatures down to at least -1°C the pressure on the ice is different from that on the water. Probably, as visualized by Schofield, the pressure on the ice approaches atmospheric and that on the water is appropriate

Fig. 9. Relationship for soils investigated between suction for a given moisture content, at room temperature, and temperature (after correction for dissolved salts) at which a similar amount of unfrozen water occurs in the freezing soil. (For descriptions of soils see Fig. 1)

to the remaining water content, as is shown by the suction-moisture-content characteristics of the soil in question. Alternatively, the pressure on the ice may rise somewhat. That on the water must then be assumed to rise by approximately the same amount (i.e. with respect to the suction-moisture-content curve, the pF values must decrease) to give the observed relationship.*

(3) The correspondence between the curve from equation (3) (which was experimentally verified by Schofield and Botelho da Costa (1938) as relating initial freezing points of water in

* According to the usual relationship:
$$\Delta P = \frac{L\Delta T}{(V_2 - V_1)T}$$

where

ΔP = change of pressure, relative to atmospheric

V_1 = spec. vol. of ice

V_2 = spec. vol. of water

other symbols as in equation (3)

pressures applied uniformly to ice and water give a change in freezing point of 0.0073°C for each 1,000 g/sq. cm. If the pressure on ice and water in the soil changes by a uniform amount, the temperatures for each unfrozen water content will differ from those predicted by equation (3). Pressures of even 10 kg./sq. cm, however, would produce a temperature change so small as to be barely significant experimentally.

soil to suction at various total moisture contents) to the curves derived in the present investigation leads to an important conclusion: the equilibrium freezing temperature associated with a particular (unfrozen) water content is not greatly affected, if at all, by the amount of ice (formed at higher temperatures) already present.

The observed correspondence thus provides some theoretical justification for the experimental observations already made (Fig. 4(b), and Williams, 1962 (b)) that the unfrozen water content for a soil at a given negative temperature is independent of the total (water and ice) moisture content (so long, of course, as the total moisture content is not less than the appropriate unfrozen water content).

It should be remembered that this statement will not be strictly true if the different total moisture contents are associated with different amounts of soluble salts per unit weight of dry materials: in such cases ΔT_{sx} will vary somewhat, causing differences (whose magnitude will depend on that of ΔT_{sx}) in the temperature associated with a given unfrozen moisture content.

(4) Although the agreement between the curves (Figs 8 and 9) is generally good, it is useful to speculate on the causes of the deviations that do occur, because they have significance in regard to the discussion in the next section.

There are margins of error to be expected in the temperature/unfrozen water content and in the pF moisture content determinations discussed earlier. Especially where the pF increases rapidly with decrease in moisture content (as in Figs 7(a) and 7(b)), a quite small error in the curve will result in rather large errors in moisture content values for given pF values. The error in moisture content will also be proportionately greater where the soil moisture contents are always relatively low (as in Figs 7(c) and 7(d)).

Errors in determination of the freezing point of the extracted solutions (ΔT_s) are important, particularly where the moisture contents are always relatively low. They are especially important when the decrease in moisture content with increasing pF is rapid.

Another explanation for part of the deviations lies in the possible pressure changes resulting from some confinement of the freezing and expanding sample within the sample holder. The sample does not completely fill the holder, but various stresses might be set up in both the ice and pore-water that could cause some of the observed deviations.

There is no obvious explanation for the fact that four of the five soils illustrated in Fig. 8 lie below the theoretical curve in a consistent manner. It may be that with further observations on other soils, this pattern will cease to be apparent.*

CONSEQUENCES OF THE OBSERVED RELATIONSHIP

Prediction of unfrozen water contents

The most direct result of the relationship established is that it permits prediction of the unfrozen water present in frozen soils at temperatures from 0 to -1.0°C , and often somewhat colder, without the necessity of elaborate calorimetric tests. Although the relationship has not been established for temperatures much colder than -1°C , soil temperatures in seasonally frozen layers and in islands of sporadic permafrost (situations of major practical significance) most frequently lie within the range 0 to -1°C . Prediction of unfrozen water content in this way requires careful determination by conventional methods (as described in this Paper) of the appropriate suction-moisture-content characteristics. The unfrozen moisture contents for the temperatures desired are then found by finding the corresponding suction values from the relationship as represented by the theoretical curve (of equation (3)) in Figs. 8 and 9.

* Very recent work, as yet unpublished, indicates that the difference between interfacial energy for ice-water, and air-water is partly responsible (see Miller, 1964; Williams, 1964(b)).

It is essential that the soil sample be typical for that for which the unfrozen water content is to be determined, particularly with respect to previous freezing and thawing or drying and rewetting. For soils with significant amounts of dissolved material, determination of the freezing point of the extracted solution is necessary.

To illustrate the procedure it will be assumed that the unfrozen moisture content of Leda clay KNB at a temperature of -0.7°C is required. The clay has not been previously frozen. The steps involved are:

- (1) The total moisture content of a sample of (unfrozen) soil is found to be 33.4% dry weight.
- (2) The suction-moisture-content characteristics are determined for suctions up to about $pF\ 4$ (as in Fig. 7(a)).
- (3) A specimen of the soil solution is extracted in a pressure membrane apparatus using an air pressure of between 4 and 14 kg/sq. cm. The freezing point ΔT_s of this solution is found to be -0.10°C (as in Table 1).
- (4) Using the theoretical curve representing equation (3) on the graph (Fig. 8) read off the suction appropriate to a temperature $T'^{\circ}\text{C}$, which should be less than that temperature for which the unfrozen water content is required by at least the value ΔT_s . Taking T' as -0.5°C , for example, the pF value is 3.8.
- (5) From the suction-moisture-content curve (Fig. 7(a)) read off the moisture content corresponding to this suction (in this case 24.5% dry weight). This gives a rough value of the unfrozen water content required.
- (6) The freezing point depression ΔT_{sz} caused by dissolved salts concentrated in the amount of unfrozen water found in § 5 is then calculated as $33.4 \times 0.1/24.5 = -0.14^{\circ}\text{C}$.
- (7) The quantity of unfrozen water, 24.5% dry weight, is thus that to be expected at temperature of $T' + \Delta T_{sz} = -0.64^{\circ}\text{C}$.

Reference to the curve obtained calorimetrically for this soil shows that 22.7% dry weight unfrozen water content occurs at -0.64°C , so that agreement is close.

If the curve of unfrozen water content versus temperature is required (for example, to obtain a value for -0.7°C exactly) a number of points can be obtained in a similar manner.

If the procedure used to obtain the points in Figs 8 and 9 is followed through, it will be seen that when salts are dissolved in a soil solution the curve for that soil will always terminate short of -1.2°C (corresponding to the highest measured pF 's for a salt-free soil, according to equation (3)). The amount by which the curve falls short of -1.2°C depends on the value of ΔT_s , the suction moisture content relationship, and of course on any errors in the pF and unfrozen water content determinations.

The experimental data obtained do not at first sight verify the relationship for T' further than -0.5°C for some of the soils, but it is reasonable to assume that they do in fact apply also for those soils at temperatures of -1.0°C and even somewhat lower. If, for example, the graph (Fig. 8) is entered at -1.0°C , a pF value of 4.09 is obtained (from the Schofield curve). Assuming that Winnipeg Clay B is considered, and proceeding from paragraph (5) above, an unfrozen moisture content of 36.75% dry weight is found to occur at -1.38°C . As the calorimetrically determined value is 34.9% dry weight at -1.38°C , the agreement is again close.

It appears that even for soils for which the pF temperature relationship (Fig. 8) deviates considerably from that of equation (3) a useful estimate can be obtained. For example, for Leda clay KNB that has been previously frozen, a value of 20.75% unfrozen moisture content would be predicted at -1.16°C . According to the calorimetric tests, the value is

16.2% unfrozen moisture content at that temperature. An approximation accurate to this extent is likely to be of more use for the practical purposes outlined below than estimates based on grain size analysis or other simple appraisal. This appears especially true if the very large variations in unfrozen water contents between different soils are recalled.

Prediction of thermal properties

In an earlier paper, calorimetric measurements made during these and other tests were used to calculate values for actual and apparent specific heats of frozen soils (Williams, 1964 (a)). Most soils in a range of temperature to several degrees below 0°C have apparent specific heats largely composed of latent heat.

Estimation of these apparent specific heats (if calorimetric tests are not feasible), based on visual or grain size tests, is often not very satisfactory. The apparent specific heats can be calculated with reasonable accuracy if the corresponding unfrozen water contents are calculated from determinations of the suction-moisture-content characteristics. The difference in unfrozen water content between any two temperatures gives the latent heat involved in such a temperature change. Because the apparent specific heats change very rapidly with temperature, it is necessary that they be calculated for small increments of temperature change. For each such temperature change the latent heat component of the corresponding apparent specific heat can be calculated directly from the change in unfrozen moisture content.

To obtain apparent specific heat there must be added the heat involved in changing, by an equal amount, the temperature of soil solids, water, and ice present. These heats can be estimated with satisfactory accuracy using values for specific heat of dry soil from for example, Kersten (1948), water and ice, if the total moisture content is known. Determination of apparent specific heats in field problems may involve a number of variables (e.g. externally applied stresses, the effects of which are the subject of continuing investigations).

Strength properties of frozen soil

Relatively few studies of the strength of freezing or thawing ground and its consolidation properties have been carried out (Lovell, 1957; Vialov, 1955; Inst. Merzlot, 1953-57). Some of these are of an entirely empirical nature and the general applicability of the results is correspondingly limited. It is apparent that the change in proportions of frozen and unfrozen water, and especially the effects of loading, are of fundamental significance in this respect. The present investigation has shown the thermodynamic equation which relates the unfrozen water content of frozen soils to temperature and pressure. A basis is thus provided for studies of the effects of load and pore-water pressure on the deformation behaviour of frozen soils.

CONCLUSIONS

(1) The unfrozen water content of various soils during freezing has been determined calorimetrically. The suction-moisture-content characteristics of the soils at room temperature have also been determined. When allowance for experimental error is made and a correction applied for depression of the freezing point by dissolved salts, a unique relationship is found to exist between the negative temperature at which a given unfrozen moisture content occurs and the suction corresponding to a similar moisture content at room temperature.

(2) This relationship is similar to that given by Schofield (1935) and Schofield and Botelho da Costa (1938) as existing between the initial freezing temperatures of soils at various moisture contents and the suctions associated with those moisture contents.

(3) The correspondence of the observed relationship with that of Schofield provides theoretical justification of the earlier observed independence of unfrozen water content, at a given temperature, from the total moisture content.

(4) The observed relationship permits prediction, from the suction-moisture-content characteristics, of the unfrozen water content of a given soil at various negative temperatures down to -1.0°C , and often somewhat lower, without the need for calorimetric studies.

(5) Such predictions permit calculation of the apparent specific heats of frozen soils, also without calorimetric tests.

(6) Establishment of the relationship between suction and unfrozen water content provides a basis for studies of the effects of pressure as well as temperature, and thus of applied loads, on the unfrozen water content of frozen soils.

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