

II. 3. SPECIFIC HEATS AND UNFROZEN WATER CONTENT OF FROZEN SOILS

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It was observed many years ago that water in soils did not freeze until the temperature was lowered appreciably below 0°C (11). Subsequent experiments demonstrated that in natural soils there is no single freezing point but that the water freezes progressively as the temperature falls (1, 3). In fine-grained soils one-third of the water may remain unfrozen at several degrees below 0°C (8, 9). The stresses still existing in the soil-water system are generally regarded as the most important cause of this phenomenon.

The changing proportions of frozen and unfrozen water are significant in consideration of the strength and deformation of frozen ground (10, 15), and the freezing and thawing of water in soil at temperatures below 0°C has important effects on its thermal properties. Several soils have recently been studied by calorimetry as part of an investigation by the author of the unfrozen water content. The experimental observations and calculation of unfrozen water content from them are briefly described and discussed in this paper. It will be shown that the application of the results to field problems requires consideration of the factors influencing the freezing of water in soil.

CALORIMETRIC INVESTIGATIONS

A calorimeter has been constructed which permits measurement of the amount of heat added to or removed from a soil sample to raise or lower its temperature by a given amount. Three thermocouples inserted in the sample measure its temperature, which is continuously recorded. Temperature differences within the sample are normally less than $1/10^{\circ}\text{C}$.

During the warming of a sample, a measured heat input is supplied electrically by a coil wound around the holder containing the sample (Fig. 1). It is necessary that there be no significant exchange of heat with the soil sample other than that arising from the heating coil. To achieve this, the sample holder is suspended inside a brass container maintained at a temperature almost equal to that of the sample holder. There is thus no significant temperature gradient and negligible exchange of heat between them. The temperature of the brass container is regulated by a heater in the refrigerated ethylene glycol surrounding it. This heater is controlled automatically by a mechanism which operates when a small temperature difference occurs between the brass container and the surface of the sample holder.

From measured values of the time taken for the temperature of the soil to rise a given amount and rate of heat input to the sample, the quantity of heat supplied to cause the temperature rise is calculated. In the thawing curves of Figures 2 to 4 inclusive, results of this type are shown, as the specific heat of the soil (i.e. the amount of heat in calories required to raise the temperature of one gram of soil by 1°C) for various negative temperatures.

The specific heats during freezing are obtained in a similar way (Figures 2 to 4) except that the brass container is held at a temperature lower by a constant amount than that of the sample holder. The heating coil on the sample is not operated. There is then a steady extraction of heat from the holder, the magnitude of which is determined by prior calibration.

Were all the water to freeze at 0°C , one would expect that values of the specific heat below 0°C would be roughly constant and of much the same magnitude as those above 0°C . In fact, the latent heat released or absorbed as water is progressively frozen or thawed results in specific heats many times as great. For a given sample, the specific heats determined during cooling differ somewhat from those determined during freezing. Not only is the value of specific heat for a given temperature different in the two cases, but for one soil type (Figure 4), the values obtained for the case of cooling repeatedly showed an unexpected rise in the region of -1.1°C .

Instrumental Accuracy

The accuracy of the curves shown in Figures 2 to 4 inclusive, depends substantially on the quality of the temperature measuring and control equipment associated with the calorimeter. Calibration tests indicate that the specific heat values represented by the smoothed graph are correct to within a few per cent. The periodic fluctuations of points at lower temperatures are probably due to experimental error. The conspicuous peak at -1.1°C in Figure 4, exceeds by many times the value that would be expected should the curve in fact be smooth, and it cannot be regarded as an experimental error. On the other hand, the variations on the thawing curve at about -0.5°C represent deviations which, regarded as a percentage, are no greater than those appearing for the lower specific heats at lower temperatures.

CALCULATION OF THE PROPORTION OF ICE AND UNFROZEN WATER IN THE SOIL

The calorimeter results can be used to calculate the ice formation taking place in the soil. By deducting amounts corresponding

to the specific heat of the mineral components, ice and water present, from the heat involved in a given temperature change, a value for the heat involved in freezing or thawing water during that temperature change is obtained. Assuming the latent heat of freezing to have the same value as that of free water, a figure is obtained for the amount of ice formed or melted. By a process of summation between the temperature of initial freezing, or completed thawing, and temperatures below them, curves of the type shown (Figures 5 to 7) are obtained.

The finer-grained soils show higher unfrozen water contents. For each soil there is a marked hysteresis, such that the amount of unfrozen water present at a given negative temperature will depend on whether the soil is undergoing warming or cooling. Furthermore, during thawing the amount is also dependent on the lowest temperature reached in that freeze-thaw cycle (Figure 9).

Repeated tests on the same sample, and on different samples of the same soil, give results within 3.5% dry weight for the unfrozen moisture content at -4°C . Various rates of cooling were used. The time taken for cooling from -1° to -4°C was varied from 4 hours to 16 hours, and appeared to have no effect on the results (Figure 8). The unfrozen moisture content is shown to be independent of the total moisture content (Figure 9), so long of course, as it is greater than this.

PHYSICAL PROCESSES RESPONSIBLE FOR THESE OBSERVATIONS

The physical processes giving rise to these observations are incompletely understood, and the calorimetric results by themselves provide only limited information. Discussion of the processes is appropriate because they appear likely to have considerable relevance in the practical application of the calorimetric results.

Hypotheses Involving Stresses in Soil Water

When ice and water exist together under a pressure greater than atmospheric, the freezing point is lowered below 0°C . Edlefsen and Anderson point out also that if ice at atmospheric pressure is in contact with water at a pressure lower than atmospheric, this too will cause a freezing point depression (6).

That the water in unsaturated soils is not at atmospheric pressure is shown by the fact that water moves into such soils from a source at atmospheric pressure. This state of stress, or so-called "suction", of the water of soils is greater the lower the water content.

Several authors point out that, as ice forms in a soil, the remaining water will be under an increasingly different state of stress to that of free water at atmospheric pressure. Accordingly, to freeze such water requires progressively lower temperatures.

Different theories have been put forward as to the nature of the stresses in soil water that might be responsible for the lowering of the freezing point. Winterkorn (16), Jung (9) and Edlefsen and Anderson (6), have proposed that the adsorption forces of the soil particles acting on the adjacent water molecules result in pressures in the soil water that are higher than atmospheric. When these pressures exist at an ice/water interface, there will be a lowering of the freezing point. As the particle surface is approached, the pressure due to the adsorption forces increases, and the freezing point becomes lower.

In contrast, others (12) maintain that most of the water in unsaturated soils is because of capillary effects, under tension (sub-atmospheric pressure, or negative stress). This also can result in a lowered freezing point provided any ice present is under atmospheric or higher pressures (6) (this is also implicit in the equation used by Schofield (14), and Croney and Coleman (4)).

It is not known to what extent different pressures can occur in adjacent ice and water phases in a soil. Nor is it appropriate in this paper to discuss the relative importance in the soil water of stresses, greater, or less, than atmospheric pressure. Either of the situations outlined above can provide a reasonable explanation of the "suction" properties of soils. By using experimentally observed values of soil "suction" for particular moisture contents, values of freezing point depression may be calculated for these moisture contents (6, 14).¹ These freezing point values can then be compared with the temperatures found to give equal contents of unfrozen water in frozen soils. Depending upon which of the two situations discussed is accepted, somewhat different values are obtained for the freezing point depression. With the limited information at present available, both appear reasonable for certain ranges of moisture content. Investigations are at present being carried out to determine more precisely this relation between suction characteristics of soils and the amount of unfrozen water present at various negative temperatures.

¹In this paper a typographical error has apparently occurred in the equation which should read: -

$$H = \frac{(Lj)}{(Tg)} \times t \quad \text{where } H = \text{cm. of water; } T = \text{absol. temp.}$$

Lj = latent heat t = freezing point
of fusion; depression.

From the present experimental observations, and the observations and discussions of others, it can be concluded that the stresses in the soil in the pore water and solid phases have considerable influence on the course of freezing.

Depression of Freezing Point by Dissolved Salts

Bouyoucos (2) and others believed that the soil water contained sufficient salts such that, as freezing progressed, the concentration would rise sufficiently (because the salts are substantially excluded from the ice) to give lowered freezing temperatures of the magnitude observed. In fact, as pointed out by Edlefsen and Anderson, the salt concentration is far too low for this to be so in most soils. The soil solution extracted from the Leda clay at about 30% moisture content was found to freeze at approximately -0.1°C . When all but 5% moisture content is frozen, the depression of the freezing point on this account will be approximately 0.6°C .

Value Ascribed to the Latent Heat of Freezing

In calculating the amounts of unfrozen water, a value of 79.68 calories/gram was adopted for the latent heat of freezing. This is not strictly correct for freezing occurring below 0°C . Figures are available for the latent heat at freezing below 0°C occurring as the result of a pressure applied equally to both the ice and water (5). Were these figures used, the calculated values of unfrozen moisture content at, for example, -5°C might differ by about $1/2\%$ dry weight from those shown. Values are not known for situations where the pressures on the ice and water phases might differ, but such values are probably of similar magnitude.

When water is added to oven dried soils, measurable quantities of heat are liberated. This "heat of wetting" results, at least in part, from the adsorption of water on to soil particles. Such soil water, from which heat has been lost, might have a substantially lowered latent heat of freezing (7, 13). The heats of wetting have been determined (Figure 10) for the soils shown in Figure 5. The temperature rise occurring when a weighed quantity of the soil was mixed with a greater quantity of water was observed. For samples in which some moisture was already present, the heat liberated was much less than for oven dried soils (Figure 10). Already at quite low moisture contents, the addition of further water does not result in significant heat of wetting. It is reasonable to assume that the water from which significant heat is lost, because it includes the most strongly adsorbed, would only freeze at the lowest temperatures. When Figures 4 to 6 inclusive are compared with Figure 10, it is seen that the quantity of water remaining unfrozen, even at the lowest temperatures recorded,

probably includes all the water that is associated with the heat of wetting. The question of latent heat of such water does not therefore arise.

VALIDITY OF THE CALORIMETRIC RESULTS IN FIELD PROBLEMS

The calorimetric observations do not represent exactly the thermal properties of the soil under natural conditions. Especially where the overburden is thick, the stresses within the soil will be different from those in the calorimeter sample. The stresses in both ice and water phases may give rise to corresponding differences in the proportions of freezing and unfrozen water. The specific heats during freezing will often be apparently increased by migration of water and the associated ice lens growth. For many practical problems, however, involving near surface conditions, and where in any case the temperature and soil conditions are not very precisely defined, a useful qualitative evaluation may be obtained from the calorimetric observations.

GENERAL SUMMARY

The unfrozen water of frozen soils has been shown to be a significant and quite complex phenomenon. It is appropriate to summarize those aspects likely to be of general importance.

In most soils the freezing and thawing processes are progressive with the latent heat of freezing being involved through a wide range of temperature. For the sub-zero temperatures occurring in many field situations, a significant proportion of the soil water is unfrozen. At a given negative temperature the amount of unfrozen water present varies considerably with the type of soil, being greater with finer-grained soils. It also depends on whether the soil is freezing or thawing, and in the latter case further depends on the lowest temperature reached during freezing.

In certain field problems the application of the specific heats and unfrozen water contents determined by the calorimetric observations requires consideration of the effects of overburden pressures and moisture supply.

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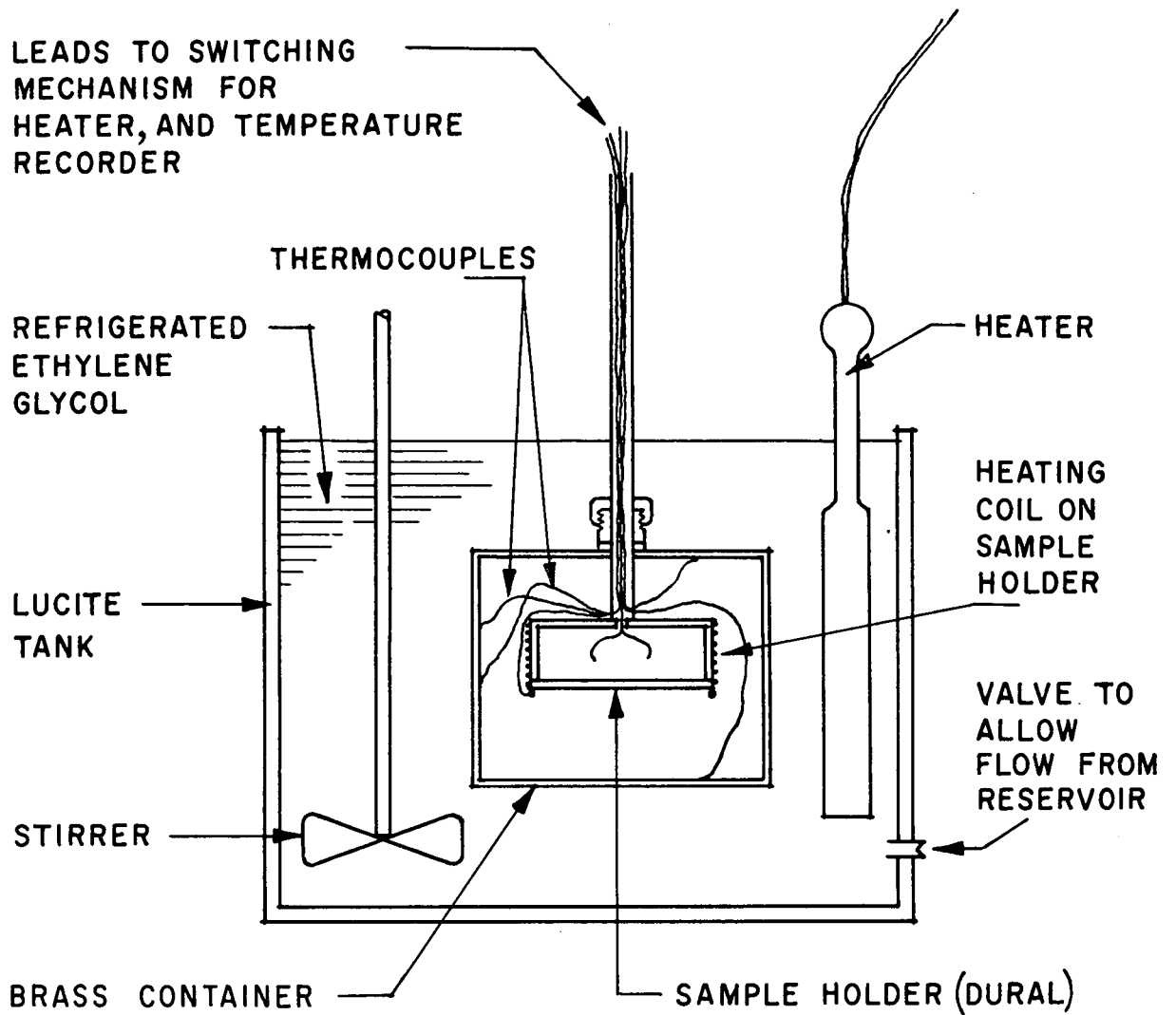
Discussion

R. Yong asked, with reference to the unfrozen moisture contents of samples with different total moisture contents, whether the density of such samples differs initially, to which the author replied

that it would differ initially. Yong enquired further what mechanisms were considered responsible for the presence of unfrozen water. The author stated his belief that capillarity is responsible at least for the first 1° - 2° C below 0° C. Yong's first question might be answered better by saying that although the initial density was changed by changing the initial moisture content, the question was whether the magnitude of the change was significant. Furthermore, as freezing progresses, the unfrozen water content becomes lower and lower, and it is this (decreasing) quantity of water which determines the degree of packing of the particles.

A. E. Corte requested information on the possibility of expressing the results as time/temperature curves for the soils. The author replied that in fact such curves were observed directly with the calorimeter. They were not very meaningful, however, unless the size of the sample was taken into account. Corte said he was interested in more details on supercooling. The author answered that this was shown clearly, the temperature falling slowly to somewhat below 0° C and then rising suddenly to just below 0° C. After that a much slower cooling takes place. Supercooling varied with soil type and with different samples of the same soil. Although hardly statistically significant, it is felt that results of the repeated freezing of the same sample showed less variation than that between freezings of different samples of the same soil.

N. W. Radforth wanted further information as to the "suction properties of the water" which were suggested as the cause of the unfrozen water. The author clarified the question by stating that it would be more precise to say "suction properties of the soil" because the water is regarded as being largely just ordinary water. The suction properties were those often referred to as "moisture potential" or "pF" of the soil. Radforth then asked if the moisture is distributed evenly throughout the sample. The author replied that even in those tests carried out most slowly, the unfrozen moisture content was similar to that found in the other tests. Therefore a state of equilibrium could be assumed to have been reached in the sample. As far as the unfrozen water is concerned, this means the suction properties, or pF, would be uniform throughout (the water having no tendency to migrate). Because each sample is quite uniform, it can be assumed that the unfrozen moisture content was uniformly distributed.



THE CALORIMETER

FIGURE I

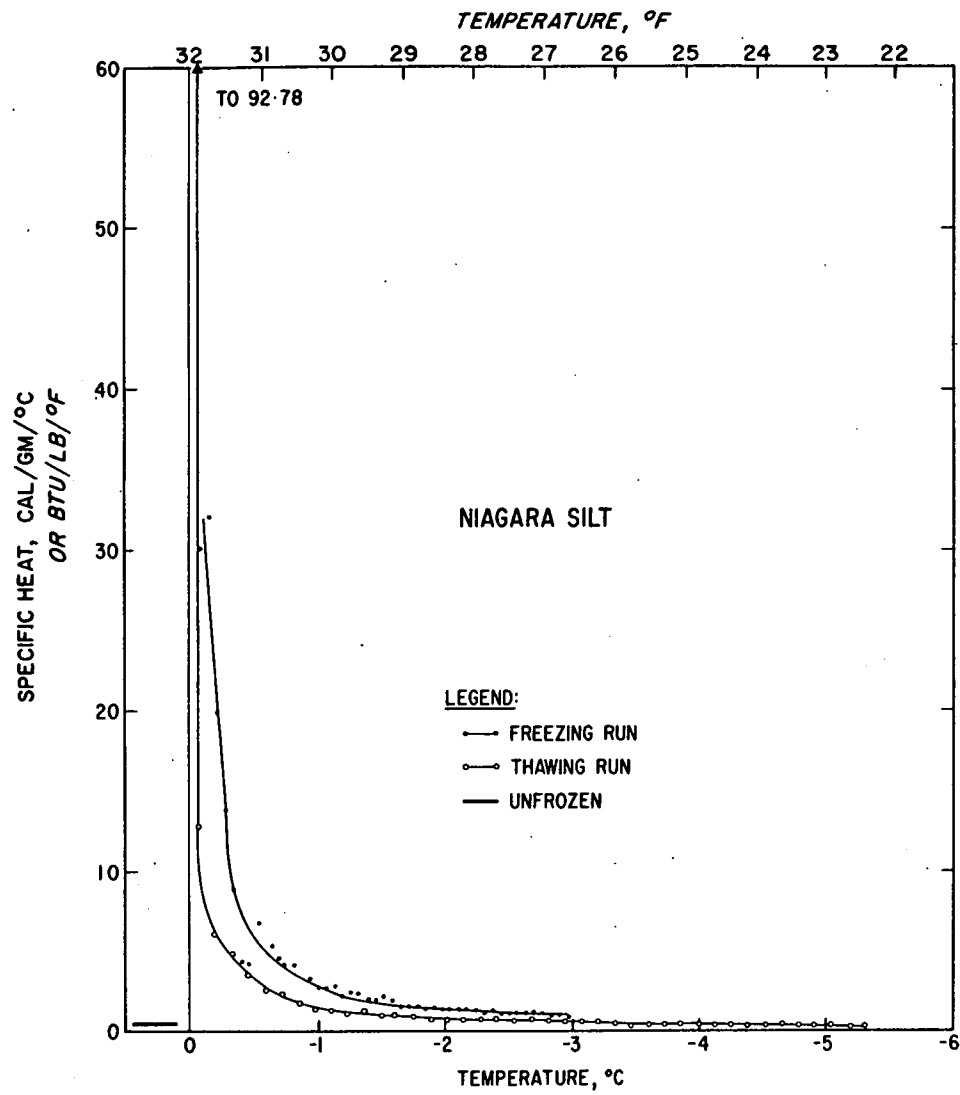


FIGURE 2

SPECIFIC HEAT OF NIAGARA SILT DURING FREEZING AND THAWING.

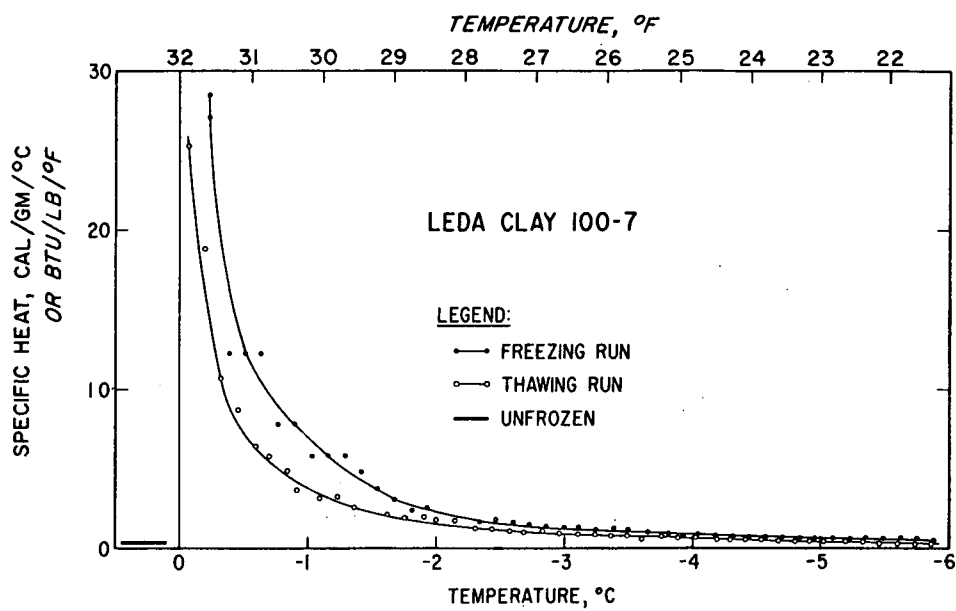


FIGURE 3

SPECIFIC HEAT OF LEDA CLAY 100-7

DURING FREEZING AND THAWING.

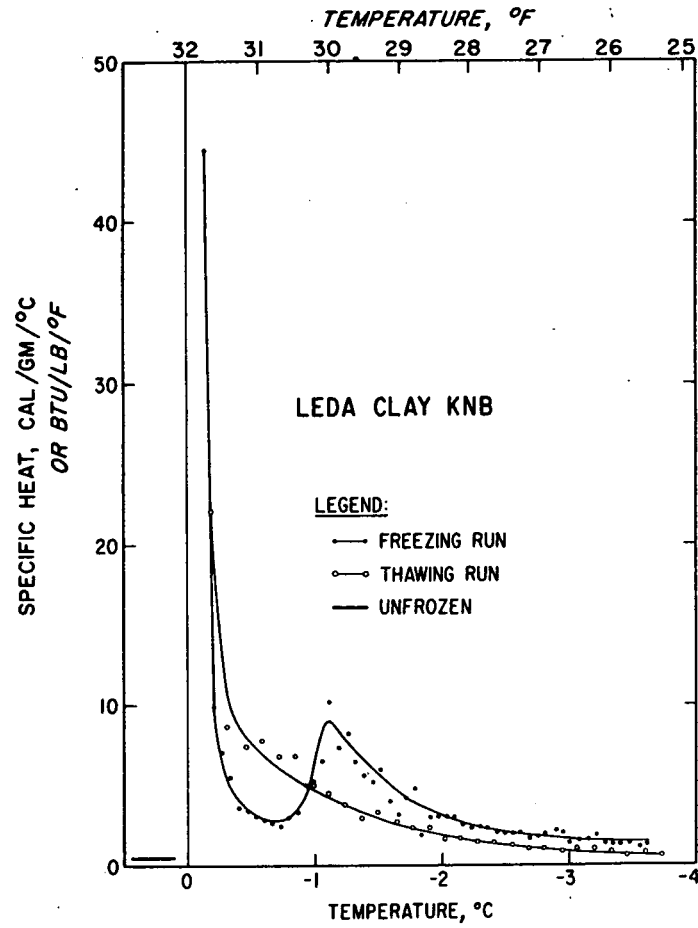


FIGURE 4

SPECIFIC HEAT OF LEDA CLAY KNB DURING FREEZING AND THAWING.

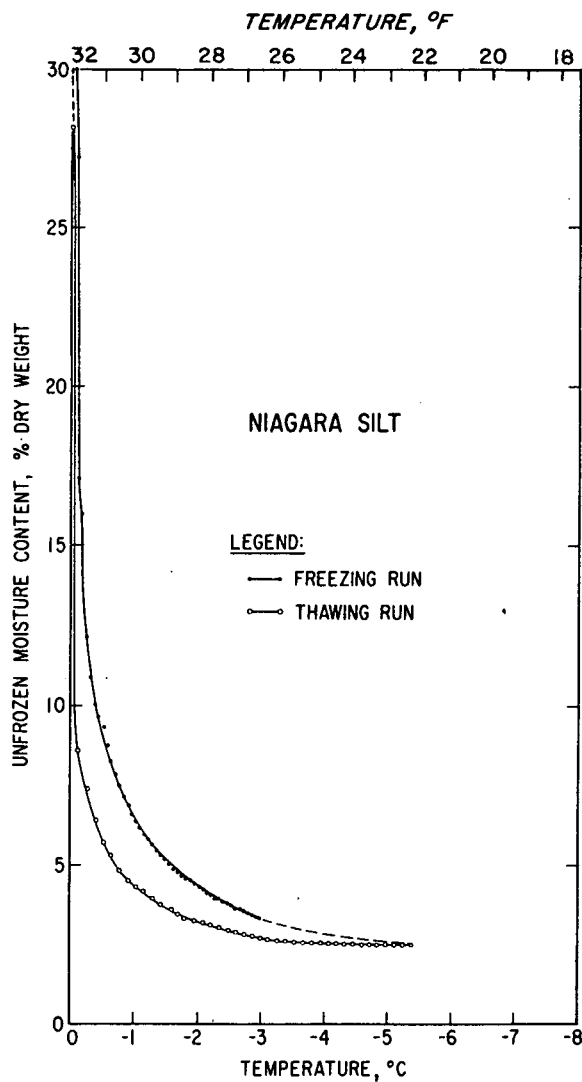


FIGURE 5

UNFROZEN WATER CONTENT OF NIAGARA SILT DURING FREEZING AND THAWING

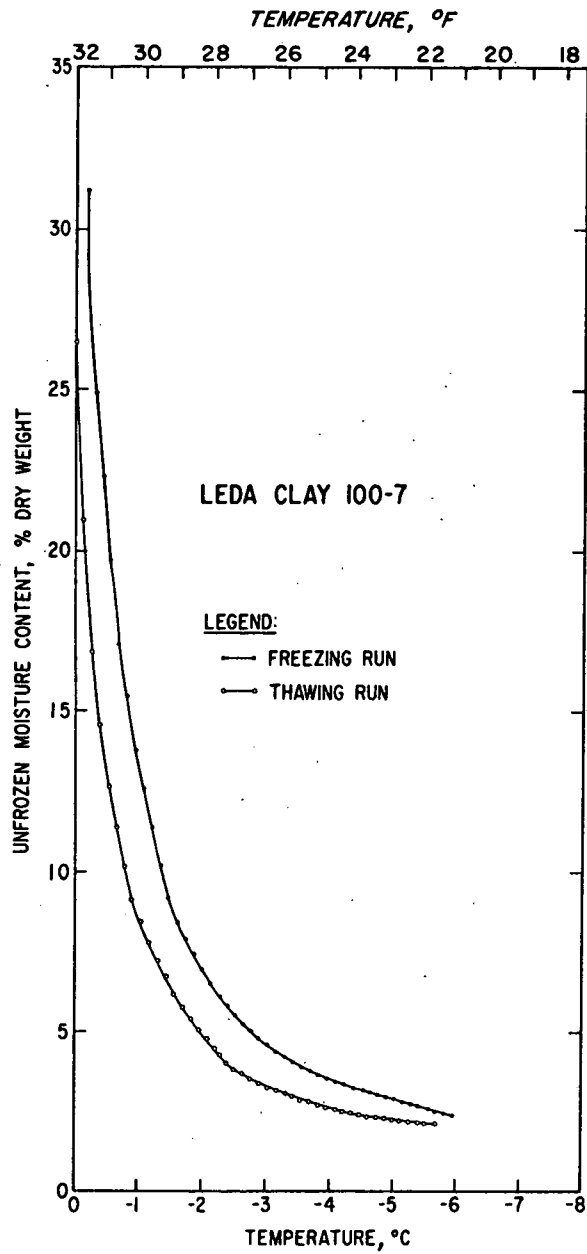


FIGURE 6

UNFROZEN WATER CONTENT OF LEDA CLAY 100-7
DURING FREEZING AND THAWING.

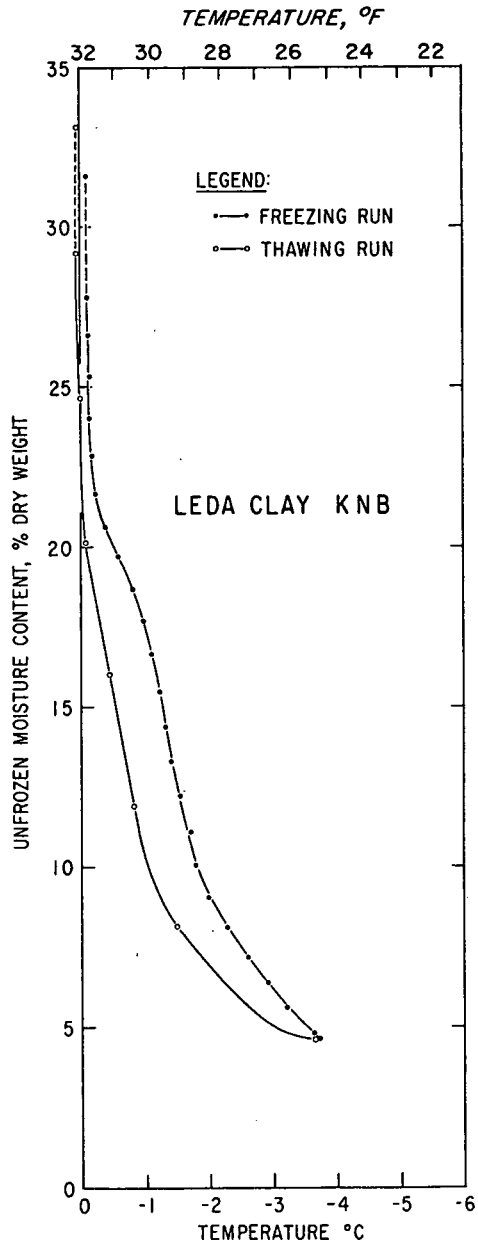


FIGURE 7

UNFROZEN WATER CONTENT OF LEDA CLAY KNB DURING FREEZING AND THAWING.

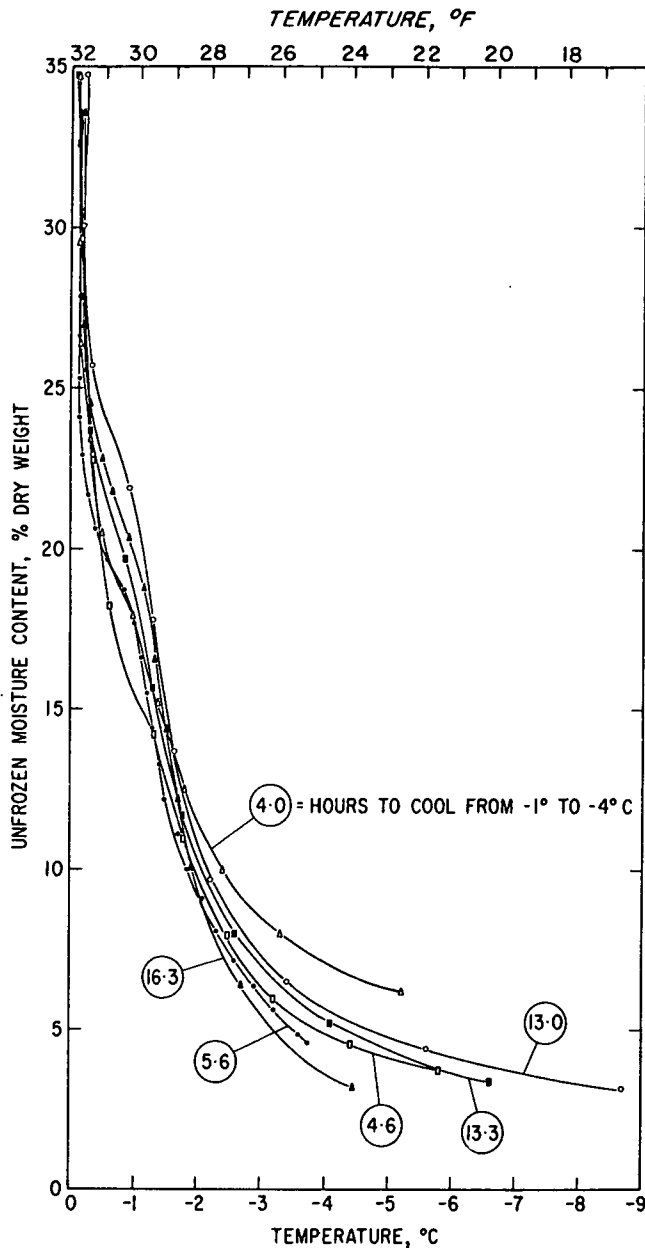


FIGURE 8

THE UNFROZEN WATER CONTENT OF LEDA CLAY KNB APPEARS INDEPENDENT OF THE RATES OF FREEZING SHOWN.

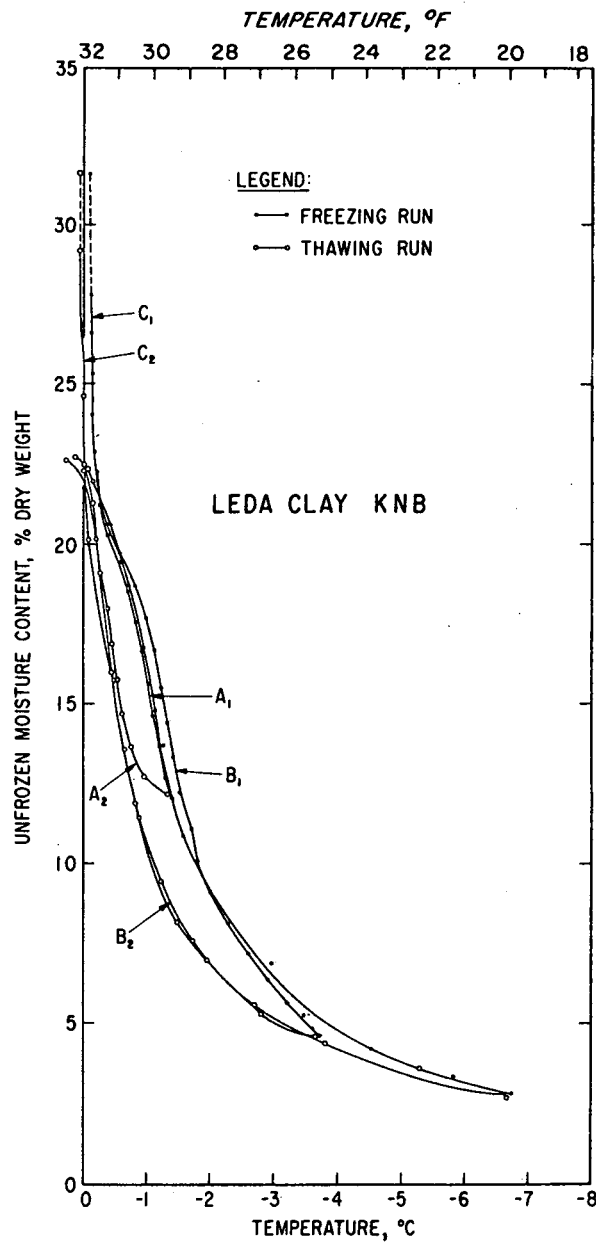


FIGURE 9

UNFROZEN WATER CONTENTS OF SAMPLES OF LEDA CLAY, OF 32 PER CENT MOISTURE CONTENT (CURVES C₁, C₂), AND 22 PER CENT MOISTURE CONTENT, (CURVES A₁, A₂ AND B₁, B₂).

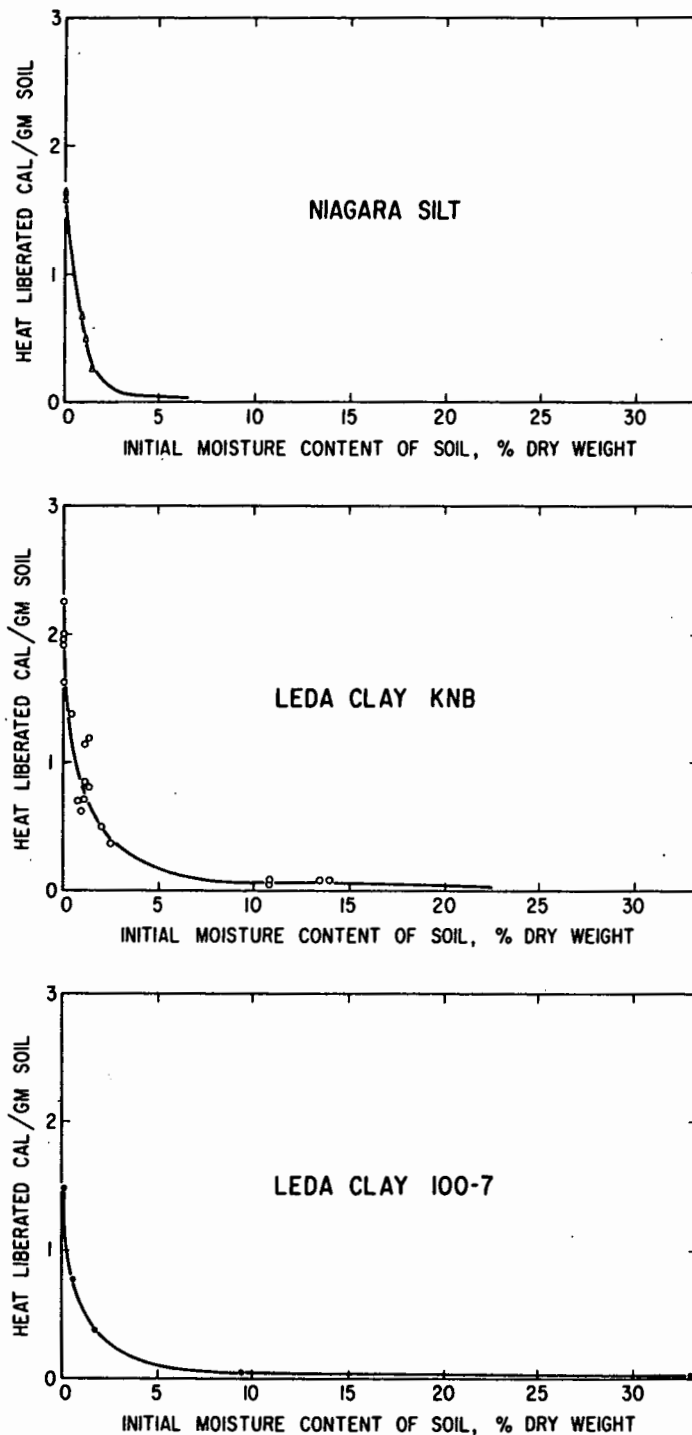


FIGURE 10

HEAT OF WETTING OF SOIL SAMPLES OF VARIOUS INITIAL MOISTURE CONTENTS. IT IS APPARENT THAT THE ADDITION OF WATER AT MOISTURE CONTENTS ABOVE ABOUT 4 PER CENT DRY WT. IS NOT ASSOCIATED WITH LIBERATION OF HEAT.