

Phase Composition Measurements on Soils at Very High Water Contents by the Pulsed Nuclear Magnetic Resonance Technique

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A simple, rapid method of determining the unfrozen water content of frozen soils is described in detail. The method uses the first pulse amplitude of a pulsed nuclear magnetic resonance analyzer. Phase composition curves were obtained for four soils at very high total water contents. Three of the soils (Manchester fine sand, Fairbanks silt, and Goodrich clay) had been previously examined by another method (isothermal calorimeter). The fourth (Kotzebue silt) is a naturally saline soil found in low-lying coastal regions of Alaska. This soil was tested both in its natural state and with the soluble salts removed. The phase composition curves obtained by the nuclear magnetic resonance method are consistent with those obtained by using the isothermal calorimeter, but the nuclear magnetic resonance method saved time, requiring only 48 h. It also provides a high degree of reproducibility and can be used over a wide range of temperatures. As expected, the unfrozen water content of the saline soil was much higher in its natural state than after removal of the soluble salts. In addition, the unfrozen water content of all four soils appears to increase somewhat as the total water content of the sample is increased.

The most commonly used device to determine the amount of unfrozen water in frozen soils has been the adiabatic calorimeter. Successful results have been reported by Nersesova (1), Nersesova and Tsytoich (2), Lovell (3), Kolaian and Low (4), and Williams (5, 6). The major disadvantage in using the adiabatic calorimeter is that the heat capacities of all the soil components must be known. Recently, Anderson and Tice (7) used low-temperature differential thermal analysis and reported determinations for several homoionic derivatives of Wyoming bentonite, kaolinite, and halloysite. As a result of this success, an isothermal calorimeter was developed and phase composition curves for a group of soils encompassing a wide range of surface areas have been reported (8, 9). Although each technique involves a different set of assumptions, the final results are remarkably consistent. One major disadvantage in using the isothermal calorimeter is that the temperature range is restricted to a lower limit of about -7°C , the maximum degree to which the soil-water can be easily undercooled. It is also difficult to initiate freezing at temperatures much above -0.5°C .

Recent construction developments (e.g., the Alaskan pipeline and related facilities) in arctic and subarctic regions have made it necessary to be able to obtain information on the amounts of unfrozen water in frozen soil. Prediction equations of sufficient accuracy for general engineering use have been developed (10, 11) whereby phase composition curves can be calculated from a knowledge of the specific surface areas or the liquid limits of the soils in question. The surface area equation has been used in designing foundations for drilling platforms and vertical support members (VSMs) for the Alaska pipeline.

There are many instances, however, when these prediction equations are not applicable. In cases where large ice lensing occurs, for example, the existing methods and equations take into consideration the water associated with the mineral constituents only; the unfrozen water that is associated with ice grain boundaries and that caused by the presence

of solutes may not adequately be accounted for. This study reports phase composition data for four soils at very high water contents (above the saturated paste water content) and for one soil (Kotzebue silt) that contained a high concentration of soluble salt. (The Kotzebue silt was taken from a proposed building construction site located at Kotzebue, Alaska.) The net effect of the salts is that the freezing temperature of the soils in this area is lowered to such a point that the supporting members might require refrigerating to prevent settlement. For effective design of the thermopiles, phase composition data at various water contents and densities for each soil must be known.

The use of nuclear magnetic resonance (NMR) in direct measurements of water content in both frozen and unfrozen soil-water mixtures has been demonstrated by Ducros and Dupont (12), Graham and others (13), Wu (14), Hecht and others (15), Touillaux and others (16), Woessner and Snowden (17), Prebble and Curries (18), Pearson and Derbyshire (19), Woessner (20), and Tice and others (21). The phase composition data reported by Tice and others (21) were determined by means of a pulsed NMR analyzer. This promising new method circumvents the limitations of the adiabatic and isothermal calorimetric techniques and extends the range of temperatures and water contents to include both very high and very low values. This technique also makes it possible to explore the effect of hysteresis.

METHODS AND MATERIALS

The four soils selected for this investigation can be considered typical of many soils found in permafrost regions. Two came from Alaska and cover extensive areas: The Fairbanks silt is a wind-deposited, non-saline silt that covers much of the interior of Alaska; the Kotzebue silt is similar in texture to the Fairbanks silt except that it contains large concentrations of soluble salts typical of soils found in low-lying coastal regions. The remaining two soils—Manchester fine sand and Goodrich clay—were selected as being representative of sand and clay found in river valleys and deltas throughout much of Alaska.

The soils were sieved through a $300\text{-}\mu\text{m}$ sieve to remove the coarser materials. A portion of the Kotzebue silt was washed six times with distilled water to remove the soluble salts and thus to determine the effect of salt in the naturally occurring soil on the phase composition curve. Titration of the supernatant material with silver nitrate revealed no trace of salt. All the soils were deaired for 24 h before being placed in 19-mm outside diameter test tubes. Distilled, deaired water was then added to four samples of each soil type in progressively larger amounts, above saturation. A copper-constantan thermocouple was embedded in the center of each sample to allow accurate temperature determinations. The test tubes were sealed with rubber stoppers to prevent loss of moisture during the measurements. After thorough shaking, each sample was quickly frozen by immersion in liquid nitrogen and was then allowed to thaw. The samples were refrozen and brought to temperature in a bath of

Figure 1. Unfrozen water content versus temperature for three soils.

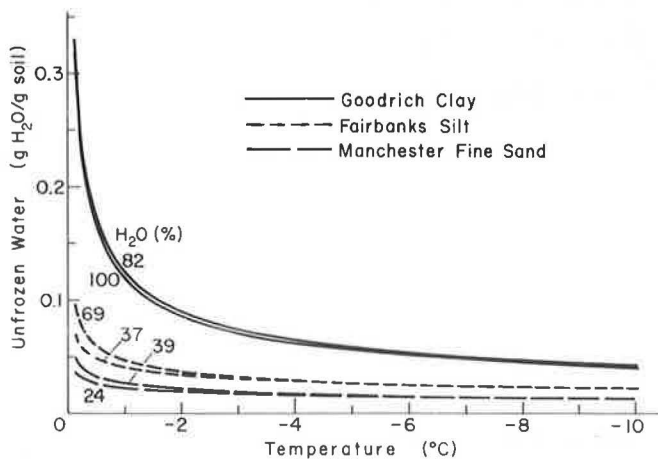
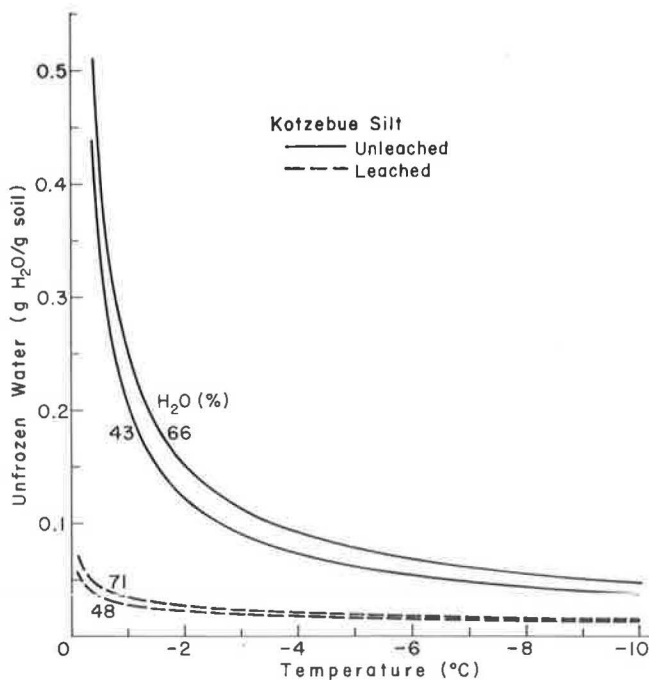


Figure 2. Unfrozen water content versus temperature for a leached and an unleached soil.



an ethylene glycol-water mixture. The temperature of the bath was regulated by a precision Bayley proportional temperature controller to within $\pm 0.03^\circ\text{C}$ throughout its range. The bath was vigorously stirred by circulating air delivered by a small pump. The frozen samples completely surrounded by the coolant were allowed to remain overnight for temperature equilibration.

A Praxis model PR-103 pulsed NMR analyzer was operated in the 90° mode, with a 0.1-s clock, and at a fast scan speed. The first-pulse amplitude was measured for each sample at various temperatures and water contents. The test tubes were sequentially removed from the bath, wiped dry, and inserted in the NMR analyzer probe. First-pulse amplitudes and temperature were recorded, and each sample was returned to the bath. Determinations took about 4 s each. After all the samples were analyzed at a given temperature, the bath temperature was changed. About 1 h was allowed for the samples to equilibrate at the new temperature. After the last determination, the samples were removed from the bath and brought to room temperature. After shaking, first-pulse amplitudes were recorded for each specimen at room temperature. Four such readings were taken and averaged to obtain a reference value for each specimen. Water contents were determined gravimetrically, and a ratio of the gravimetric water content to first-pulse amplitudes was formed for each. Unfrozen water contents were calculated by multiplying first-pulse amplitudes by their respective ratios to obtain a value for each temperature (21).

RESULTS AND DISCUSSION

The test results are shown in Figures 1 and 2 and given in Tables 1-5. Only the highest and lowest water contents are shown in Figures 1 and 2. In general, one concludes that the unfrozen water content increases somewhat as the sample water content is increased. The data all conform to the familiar power law found earlier by Anderson and Tice (8). As expected, higher values were found in the saline soils. The effect of solutes in increasing the unfrozen water content was approximately equal to that predicted from considerations of the ionic strength of the soil solution (22). The data also agree well with the isothermal calorimeter data of Anderson and Tice (8) for Fairbanks silt and unpublished data for Manchester fine sand and Goodrich clay determined by the same technique.

Complete phase composition data for those four soils were obtained in about 48 h. To obtain these data by isothermal calorimeter or other methods used

Table 1. Unfrozen water content versus temperature at various percentages of sample water content for Fairbanks silt.

37.5		41.3		51.1		58.1		69.5	
Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)
-0.2	6.1	-0.2	4.8	-0.3	6.6	-0.2	8.3	-0.2	7.7
-0.4	5.0	-0.4	3.7	-0.4	5.4	-0.4	6.5	-0.4	6.3
-0.6	4.5	-0.5	3.3	-0.4	5.0	-0.6	5.5	-0.5	5.5
-0.7	4.4	-0.8	3.4	-0.9	5.0	-0.8	5.4	-0.8	5.3
-1.0	4.3	-0.9	3.2	-0.9	4.4	-0.9	4.8	-1.0	5.1
-1.1	3.8	-1.0	3.2	-1.0	4.6	-1.1	4.6	-1.2	4.5
-2.0	3.5	-2.0	2.8	-2.1	3.5	-2.0	4.0	-2.1	4.1
-2.9	3.1	-2.8	2.4	-3.9	3.3	-3.0	3.5	-3.0	3.4
-4.2	2.8	-4.1	2.1	-4.1	2.9	-4.2	3.0	-4.0	2.8
-5.2	2.6	-5.3	2.2	-5.2	2.7	-5.2	3.0	-5.2	2.8
-6.5	2.3	-6.6	1.9	-6.5	2.4	-6.6	2.6	-6.4	2.3
-7.0	2.3	-6.9	1.9	-6.9	2.4	-7.1	2.6	-7.1	2.2
-8.3	2.2	-8.3	2.0	-8.3	2.4	-8.2	2.2	-8.4	2.3
-9.9	2.4	-9.7	1.9	-9.8	2.2	-9.8	2.2	-9.8	2.2

Table 2. Unfrozen water content versus temperature at various percentages of sample water content for Goodrich clay.

81.7		89.2		99.7	
Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)
-0.2	19.4	-0.2	20.1	-0.2	20.9
-0.5	19.0	-0.5	16.8	-0.4	16.9
-0.8	15.8	-0.7	14.6	-0.8	14.6
-0.8	13.9	-0.9	13.0	-1.0	13.8
-1.1	13.5	-1.1	12.5	-1.0	12.7
-1.3	11.4	-1.3	10.8	-1.2	11.4
-2.2	9.6	-2.2	8.9	-2.2	8.9
-3.1	8.3	-3.1	7.6	-3.1	7.6
-4.2	6.2	-4.3	6.3	-4.3	6.5
-5.2	5.7	-5.2	5.4	-5.2	5.7
-6.6	4.6	-6.6	4.4	-6.7	4.4
-7.3	4.6	-7.2	4.3	-7.2	4.4
-8.4	4.3	-8.6	4.1	-8.5	4.1
-9.9	3.8	-9.9	3.6	-9.9	3.7

Table 3. Unfrozen water content versus temperature at various percentages of sample water content for Kotzebue silt (unleached).

43.3		48.5		60.2		66.2	
Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)
-0.3	32.6	-0.5	42.4	-0.4	47.6	-0.4	49.8
-0.7	28.2	-0.7	32.0	-0.6	37.4	-0.7	38.6
-1.1	21.9	-1.0	22.9	-0.9	27.5	-0.9	27.6
-1.3	19.1	-1.2	20.3	-1.1	23.7	-1.0	24.9
-1.4	16.7	-1.4	17.2	-1.2	20.1	-1.1	21.1
-1.7	14.2	-1.6	15.0	-1.4	17.6	-1.4	18.1
-2.6	9.9	-2.6	10.0	-2.5	12.3	-2.5	12.9
-3.7	8.1	-3.6	7.8	-3.4	10.2	-3.2	10.6
-4.6	6.0	-4.4	6.5	-4.4	3.1	-4.0	8.7
-5.8	5.6	-5.5	6.0	-5.3	7.2	-5.0	7.6
-7.2	4.8	-6.9	5.4	-6.8	6.2	-6.9	6.4
-7.5	4.4	-7.4	4.9	-7.4	5.8	-8.2	5.9
-8.7	4.1	-8.6	4.7	-8.7	5.6	-9.8	4.7
-9.9	2.5	-10.1	3.9	-10.0	4.6		

Table 4. Unfrozen water content versus temperature at various percentages of sample water content for Kotzebue silt (leached).

44.3		47.8		61.4		71.4	
Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)
-0.2	4.7	-0.2	4.4	-0.2	4.4	-0.2	5.2
-0.4	3.7	-0.4	3.5	-0.4	3.8	-0.4	4.4
-0.5	3.4	-0.6	3.3	-0.6	3.7	-0.6	4.1
-0.8	3.3	-0.8	3.2	-0.8	3.7	-0.8	4.0
-1.2	3.5	-1.0	3.2	-1.0	3.3	-1.1	4.0
-1.2	3.0	-1.2	2.7	-1.2	3.1	-1.2	3.8
-2.1	2.4	-2.1	2.3	-2.1	2.4	-2.1	2.7
-2.8	2.1	-3.0	2.0	-2.9	2.1	-2.9	2.6
-4.0	1.9	-4.9	1.7	-4.1	1.8	-4.0	2.1
-5.2	1.8	-5.1	1.6	-5.0	1.7	-5.2	1.8
-6.4	1.5	-6.4	1.4	-6.4	1.5	-6.3	1.7
-6.7	1.5	-6.9	1.4	-7.1	1.4	-7.1	1.6
-8.3	1.4	-8.2	1.3	-8.3	1.4	-8.3	1.4
-9.9	1.4	-9.9	1.2	-9.8	1.2	-9.8	1.6

Table 5. Unfrozen water content versus temperature at various percentages of sample water content for Manchester fine sand.

24.3		28.0		29.0		38.6	
Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)	Temperature (°C)	Unfrozen Water Content (%)
-0.3	3.1	-0.3	3.5	-0.3	3.6	-0.3	3.8
-0.4	2.5	-0.5	2.9	-0.3	3.0	-0.4	3.2
-0.6	2.4	-0.7	2.4	-0.7	2.8	-0.7	2.8
-0.7	2.5	-0.9	2.6	-0.8	2.8	-0.9	2.9
-0.9	2.3	-1.0	2.4	-1.0	2.4	-1.0	2.8
-1.2	2.2	-1.3	2.4	-1.2	2.3	-1.2	2.9
-2.0	1.9	-2.1	2.1	-2.2	1.9	-2.1	2.2
-2.9	2.0	-2.9	1.9	-3.0	1.8	-3.0	1.9
-4.4	1.6	-4.3	1.6	-4.3	1.6	-4.3	1.7
-5.1	1.5	-5.3	1.6	-5.2	1.5	-5.2	1.5
-6.6	1.3	-6.5	1.3	-6.5	1.5	-6.6	1.4
-7.1	1.3	-7.2	1.4	-7.2	1.3	-7.1	1.3
-8.9	1.3	-8.2	1.6	-8.4	1.4	-8.4	1.6
-9.0	1.3	-9.9	1.4	-9.7	1.3	-9.9	1.2

earlier would have required several months. This is one of the most important values of the NMR method. In addition to a savings in the time required to obtain phase composition data, the high degree of reproducibility of data obtained by this method makes it possible to investigate hysteresis and other second-order effects. The method also appears to be readily adaptable to use in the field where rapid measurements are required. Further work toward this end is now in progress.

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