THE WATER–ICE PHASE COMPOSITION OF CLAY/WATER SYSTEMS

1. The Kaolinite/Water System

Duwayne M. Anderson, Allen R. Tice and Amos Banin

June 1974

PREPARED FOR
DIRECTORATE OF MILITARY ENGINEERING AND TOPOGRAPHY
OFFICE, CHIEF OF ENGINEERS
DA PROJECT 4A061102B52E
BY
CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.
This report was prepared by Dr. Duwayne M. Anderson, Research Soil Scientist; Allen R. Tice, Engineering Technician; and Dr. Amos Banin, Visiting Research Soil Scientist. Dr. Anderson is Chief of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Mr. Tice is a member of the Earth Sciences Branch. Dr. Banin is a Professor in the Department of Soil and Water Science, The Hebrew University, Rehovot, Israel.

Technical review of the report was performed by Lawrence F. Gatto of the Earth Sciences Branch.

The report was prepared under DA Project 4A061102B52E, Research in Military Engineering and Construction, Task 02, Research in Snow, Ice and Frozen Soil, Work Unit 001, Physics and Chemistry of Earth Materials.

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

Manuscript received 13 March 1973
CONTENTS

Introduction .............................................................. 1
Experimental procedure .................................................. 1
Results ................................................................. 4
Discussion ............................................................ 7
Literature cited .......................................................... 7

ILLUSTRATIONS

Figure
1. Schematic diagram of the isothermal calorimeter ............... 3
2. Unfrozen water vs temperature plot of the kaolinite/water system .... 4
3. Double freezing exotherms and their shift with time during freeze-thaw cycling of NaCa/montmorillonite/water mixture .............. 5
4. Low temperature differential thermal analysis curves for the kaolinite/water system ........................................ 6

TABLE

Table
1. Equations providing the best fit for segmented portions of the kaolinite/water system ........................................ 5
THE WATER-ICE PHASE COMPOSITION OF CLAY/WATER SYSTEMS
I. THE KAOLINITE/WATER SYSTEM

by

D.M. Anderson, A.R. Tice and A. Banin

Introduction

Evidence that a continuous, unfrozen water phase separates ice from the mineral or organic matrix in frozen soils has come from many sources and the existence of such a phase is now a widely accepted fact.1-3 12-15 17-19 Questions regarding the nature of the unfrozen interfacial water and ice phases, at least in qualitative terms, have been answered. The unfrozen interfacial water behaves as a two-dimensional liquid; water molecules and solutes are freely mobile in this zone down to about \(-30^\circ\text{C}\).4 Although it has been claimed that anomalous ice phases exist in frozen soil, these reports have not been confirmed and in all instances where detailed investigations have been made the ice formed is normal hexagonal ice I. The principal factors determining the water-ice phase composition of frozen clays and soils are specific surface area and temperature.7 12 11 Pressure is a less important, but significant, factor; an increase in pressure at constant temperatures increases the unfrozen water content.3 14 19 The effect of solutes in the interfacial zone is to increase the unfrozen water content in accord with that predicted from the freezing point depression.4 11 In addition, the geometrical arrangement of individual particles, the manner in which freezing is accomplished, and the history of freeze-thaw cycling are known to be important.10

During the past decade various methods of obtaining phase composition curves (unfrozen water contents as a function of temperature) have been developed.2 5 6 10 18 19 These methods yield roughly comparable values provided that sample histories are the same. In an earlier paper7 we reported water-ice phase composition data determined by the isothermal calorimeter method for a number of soils and clays. When these water-ice phase composition curves were normalized to unit surface area, the unfrozen water content values at given temperatures for the kaolinite/water system appeared to be higher than those of other clay/water and soil/water systems. Since those data were obtained the design of the calorimeter has been improved to reduce the transfer of the latent heat of freezing between adjacent cells when the samples are successively nucleated. In this paper we describe the improved calorimeter and report additional data obtained for the kaolinite/water system for comparison with the data obtained earlier.

Experimental procedure

The clay used was kaolinite No. 7, from the Dixie Rubber Pit, Bath, South Carolina, obtained from Ward’s Natural Science Establishment. The clay was crushed and sieved through a No. 50 sieve (0.29 mm) but was otherwise in its natural form.

Polyox (polyethylene oxide, a product of Union Carbide Co.) was added to one set of samples of the dry powdered clay in a concentration of 0.008 g/g clay. This was accomplished by first adding appropriate amounts of a 2% water-Polyox solution, then adding distilled water to bring the water/clay ratio to the desired values. The resulting paste was then mixed until it was homogeneous.
The calorimeter consists of two subsystems: the body and coolant circulating system and the sample holder and sensor system (Fig. 1a). The bottom portion was constructed of an aluminum body 23 cm OD and 3.2 cm high with a 5.7-cm-ID hole at the center. A channel 5 cm wide × 2.2 cm high was cut on a radius of 3.8-cm-ID to provide a circulation path for the coolant that bathes the sample holders and to provide an opening for the reference thermocouples of the top portion when they are lowered into place. Two 1.3-cm nipples screwed into the body connect the body to the coolant supply and return reservoirs. A baffle blocks the channel between the two nipples to insure unidirectional flow. O rings seal the coolant body and cover. The cover plate was fabricated from aluminum 1.3 cm thick. It contains a milled groove 1.3 cm wide by 1 cm deep with 15 holes on a radius of 7.6 cm to accommodate the sample cups, allowing them to be bathed by the circulating cooling fluid. Provisions were made for O ring seals around each cup. Adjacent to each sample cup are 15 tapped holes, each containing a septum seal, nylon washer and a threaded plug with a 3.2-mm hole drilled through the center to accommodate reference thermocouple thermometers. Surrounding the base is a 1.3-cm insulating jacket of Synthane. A 1.3-cm-thick Synthane insulating plate (not shown) is attached to the bottom.

The upper part of the calorimeter was machined to mate perfectly with the base and was designed for easy removal without the necessity of disconnecting the electrical connections. Figure 1b shows one of the 15 cells with the O ring seal that prevents the loss or gain of moisture by the sample during the determinations. Two thermocouples connected in opposition are provided for 14 of the 15 cells. The copper leads of each thermocouple pair are connected in parallel to a 16-position thermocouple switch (to observe the nucleation process for any given sample) and a strip connector which is connected to an automatic scanner, digital voltmeter and printer for continuous recording. An insulated, stainless steel sheath protects each thermocouple. The dummy 15th cell contains a thermistor for continuous temperature monitoring.

The calorimeter was operated in the following manner: soil samples were brought to successively different water contents ranging from dry to wet. In the case of silts, water content increments of about 0.02 g H₂O/g soil were found to be about optimum whereas for heavy clays increments of about 0.06 g H₂O/g soil were required. These sets of samples were put aside for two days and allowed to equilibrate at room temperature. After the sample cups were filled each cup was attached to the Synthane sample holder with three machine screws. The top plate was then secured with six flathead screws and the nucleating plugs were tightened. The coolant body and sample holder assembly were joined by six threaded rods and wing nuts.

The samples were cooled to the desired temperature by engaging the external circulating pump submersed in a constant (± 0.003°C) temperature bath containing 20 liters of coolant. A constant temperature was attained within the samples and apparatus in about 25 minutes. The data acquisition devices (either strip chart recorders for manual operation or an automatic scanner — digital voltmeter-printer) were started and the electrical signals from each differential thermocouple were sequentially monitored. Freezing was then initiated by touching the top of each sample in sequence with the tip of a 24-gauge needle cooled to liquid nitrogen temperature. As each sample froze, an electrical signal proportional to the heat released within the sample was recorded. When all the heat had dissipated from the samples and the temperature had returned to its original value, the circulating coolant was stopped. The samples were thawed by removing the sample holder assembly and placing it on a preheated, mating aluminum block designed to accept the sample cups and reference thermocouples. The external bath was readjusted to a new temperature, samples cooled to this temperature by reengaging the external circulating pump, and the whole procedure was repeated until the data for the phase composition curve were collected.

The data analysis was performed as follows. At each temperature, when the water content range of the samples had been properly selected, not all the samples nucleated and froze. A plot of
Figure 1. Schematic diagram of the isothermal calorimeter.
**The Water-Ice Phase Composition of Clay/Water Systems**

The water-ice phase composition of clay/water systems can be determined through the measurement of exotherm intensity $I$ (for the samples that did nucleate and freeze) vs water content yielded, by extrapolation, the minimum water content at which ice exists at this given temperature. This value was taken to be the unfrozen water content $W_u$ at a particular temperature and is also the freezing point depression at the extrapolated water content. In practice the plots were seldom made; instead, the extrapolation was done numerically by least squares regression. A plot of the unfrozen water content vs temperature then gave the ice-water phase composition of the particular clay.

**Results**

Phase composition data from -0.15°C to -5°C for the kaolinite/water system obtained with the new calorimeter, together with the earlier data, are presented in Figure 2. In addition, a complete set of data for a kaolinite/water/Polyox system is shown. Polyox is believed to be strongly adsorbed by kaolinite as evidenced by its ability to induce flocculation in dilute water suspensions. It was of interest to see which segment of the log-log plot would be affected.

Agreement between the data obtained with the two calorimeters is good; the two sets of data are virtually identical within possible experimental error. For most of the soil/water systems we have investigated, the experimentally obtained data are well represented by a simple power curve, $W_u = a\theta^\beta$, where $W_u$ is the unfrozen water content expressed in g H$_2$O/g soil, $\theta$ is temperature in degrees below freezing, and $a$ and $\beta$ are empirical constants. The clay/water systems so far investigated, however, are in fact more complex. Segments of two power curves are required for a good fit. For the data shown in Figure 2 the regression equations providing the best fit are given in Table I.
I. THE KAOLINITE/WATER SYSTEM

The significance of the discontinuities at $-1.5^\circ\text{C}$ shown in Figure 2 is suggested by an earlier observation, indicating that some clay/water systems contain at least two domains having different water contents and therefore different nucleating temperatures. The existence of two domains in a mixed sodium-calcium montmorillonite/water system is shown in the DTA data of Figure 3.\(^5\) The heteroionic clay/water mixture was prepared and allowed to equilibrate for 24 hours. Immediately prior to analysis, a small increment of water was added. Two exotherms were observed in the first run ($t_0$), one at $-12^\circ\text{C}$ and one at $-16^\circ\text{C}$. The samples were then melted and time was allowed for the redistribution of water within the system. After 43 minutes, a second run was made ($t_1$). Again two exotherms were observed, but with intensities reversed and noticeably shifted toward higher nucleation temperatures. The two exotherms merged into one ($t_2$ to $t_5$) when only short intervals were permitted between successive determinations.

It was shown earlier that each freeze-thaw cycle results in significant particle reorientation due to the redistribution of water.\(^1\) During freezing, water migrates to and is added to growing ice crystals. As the ice crystals enlarge they displace the soil particles and cause a rearrangement of the soil matrix. On warming, a progressive melting of the ice releases water that is then free to permeate the matrix. This is consistent with the idea that within the matrix, domains of differing nucleation temperatures exist.

Figure 4 shows the low temperature differential thermal analysis curves for kaolinite/water mixtures at different water contents obtained in a previous investigation.\(^4\) Considering only the primary exotherm, the peak heights diminish and shift to lower temperatures as the water content is reduced.

![Figure 3. Double freezing exotherms and their shift with time during freeze-thaw cycling of NaCa/montmorillonite/water mixture.](image)

**Table I. Equations providing the best fit for segmented portions of the kaolinite/water system.**

<table>
<thead>
<tr>
<th></th>
<th>$0 &lt; \theta &lt; 1.5$</th>
<th>$\theta &gt; 1.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite 1</td>
<td>$w_u = 27.93 \theta^{-0.12}$</td>
<td>$w_u = 36.91 \theta^{-0.78}$</td>
</tr>
<tr>
<td>Kaolinite 2</td>
<td>$w_u = 25.30 \theta^{-0.13}$</td>
<td>$w_u = 30.61 \theta^{-0.68}$</td>
</tr>
<tr>
<td>Kaolinite 1 and 2</td>
<td>combined</td>
<td></td>
</tr>
<tr>
<td>combined</td>
<td>$w_u = 26.25 \theta^{-0.14}$</td>
<td>$w_u = 32.92 \theta^{-0.71}$</td>
</tr>
<tr>
<td>Kaolinite with Polyox</td>
<td>(polyethylene oxide)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$w_u = 25.52 \theta^{-0.16}$</td>
<td>$w_u = 38.06 \theta^{-0.97}$</td>
</tr>
</tbody>
</table>
A plot of peak intensity vs water content extrapolates to a water content of 0.024 g H₂O/g clay at zero intensity. From Figure 4, it appears that zero intensity of the primary peak is reached at a freezing temperature of -36°C. Thus the extrapolated water content corresponds to the unfrozen water content at -36°C. The appearance of the low temperature exotherm at about -40°C is believed to be related to the nucleation of this residual water and to be an indication of a third domain in this clay/water system. Combining the data of Figure 2 and regressing samples 1 and 2 against \( \theta \) yields:

\[
W_u = 26.25 \theta^{-0.14}
\]

for \( \theta < 1.5°C \) and

\[
W_u = 32.92 \theta^{-0.71}
\]

for \( \theta > 1.5°C \).

Utilizing the latter and taking \( \theta = 36°C \) the corresponding value of \( W_u \) is 0.026 g H₂O/g clay, which is in excellent agreement with the value deduced from the DTA data.

Polyox (polyethylene oxide) is a high molecular weight polyether soluble in water; however, the mechanism of interaction between the polyethylene oxide molecule and water had not yet been established. When added to clay suspensions it is strongly adsorbed and induces flocculation. Figure 2 shows that when polyethylene oxide is added to the kaolinite/water system no effect is apparent in the first segment of the curve, but below \(-1.5°C\) the added polyethylene oxide significantly lowers the unfrozen water content. The water that freezes below \(-1.5°C\) can be attributed to an internal domain where the effect of adding polyethylene oxide leads to a reduction in volume of this domain due to flocculation. The volume of water in the outer domain does not change as it is associated with external surfaces which are much less affected by flocculation.
I. THE KAOLINITE/WATER SYSTEM

Discussion

Since the unfrozen water content data obtained earlier were confirmed by the determinations reported here, the earlier conclusion still stands: kaolinite retains more unfrozen water per unit of total surface area than does montmorillonite. The most important distinction between these two clay mineral types is that nearly all the surface area of kaolinite is exposed on external surfaces, whereas in the case of montmorillonite 80 to 90% is exposed in interlamellar regions (internal) and only 10 to 20% consists of external surfaces. One concludes, therefore, that the unfrozen water interface is thicker at a given temperature on external surfaces than on internal surfaces. This, however, should not be interpreted to mean that the water on the surfaces of kaolinite is held more tenaciously than on montmorillonite. It is possible to show that the results obtained in this study can be accounted for by assuming that the same general law of surface interaction governs the freezing of the water on the surface of both minerals but that it is modified by the fact that water layers of different thicknesses exist in various domains in the two clay/water systems.

The data presented here indicate three distinctly different domains within the kaolinite/water system insofar as nucleation and freezing are concerned. Two are indicated by the two segments of the log-log plot of \( W_u \) vs \( \theta \) shown in Figure 2, and a third is indicated by the low-temperature exotherms in the DTA curves of Figure 4. The isothermal calorimetric technique as employed to date is limited to values of \( \theta < 10 \). Consequently the data of Figure 2 could not be extended to search for a second point of inflection that would correspond to the third domain. An effort to extend the technique is being made and a theoretical investigation analyzing the implications of these results is in progress.

Literature cited

THE WATER-ICE PHASE COMPOSITION OF CLAY/WATER SYSTEMS

Literature cited (Cont'd)


THE WATER-ICE PHASE COMPOSITION OF CLAY/WATER SYSTEMS

I. THE KAOLINITE/WATER SYSTEM

Previous studies indicated that when water-ice phase composition curves are normalized to unit surface area, the unfrozen water content values at given temperatures for the kaolinite/water system are higher than those of other soils and soil constituents. The water-ice phase composition curve for this system has been redetermined using an improved isothermal calorimeter and the earlier curve confirmed. For most soils, water-ice phase composition curves are well represented by a simple power curve, \( W_u = a \theta^b \), where \( W_u \) is the unfrozen water content in g per g soil, \( \theta \) is the temperature in degrees below freezing and \( a \) and \( b \) are empirical constants. In contrast, the layer-lattice silicate/water systems so far investigated behave differently; segments of two power curves are required to fit the data. For kaolinite the equations yielding the best fit are \( W_u = 26.25 \theta^{-0.14} \) for \( 0 \leq \theta \leq 1.5 \) and \( W_u = 32.92 \theta^{-0.71} \) for \( \theta > 1.5 \). Addition of Polyox (polyethylene oxide) to the kaolinite/water system had little effect on \( W_u \) in the range of \( 0 < \theta < 1.7 \) but diminished \( W_u \) significantly at values of \( \theta > 1.7 \). Values of \( W_u \) per unit surface area (determined by ethylene glycol adsorption) for the kaolinite/water systems are more than twice as large as those for the two representative montmorillonite/water systems investigated.

D.M. Anderson, A.R. Tice and A. Banin

Approved for public release; distribution unlimited.

Office, Chief of Engineers
Washington, D.C.
<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th></th>
<th>LINK B</th>
<th></th>
<th>LINK C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Clays</td>
<td>ROLE</td>
<td>WT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay minerals</td>
<td>ROLE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay soils</td>
<td>ROLE</td>
<td>WT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calorimeters</td>
<td>ROLE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>ROLE</td>
<td>WT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>