EFFECT OF THERMAL GRADIENT ON IONIC DIFFUSION IN FROZEN EARTH MATERIALS

I: EXPERIMENTAL

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PREFACE

This report was prepared by Dr. Richard P. Murrmann (Research Chemist, Earth Sciences Branch) and Dr. Pieter Hoekstra (Research Physicist, Physical Sciences Branch). The authors are members of the Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

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by

Richard P. Murrmann and Pieter Hoekstra

INTRODUCTION

Ions diffuse in frozen earth materials through continuous films of interfacial water located at mineral/mineral and ice/mineral boundaries[9] [10]. Although both ionic and thermal gradients exist in frozen soil[2] [3], little is known of how temperature gradients affect the distribution of ions. The temperature dependence of the diffusion coefficient of sodium ions in frozen bentonite clay[10] and frozen silt soils[9] is shown in Figures 1 and 2, respectively. The value of the diffusion coefficient decreases rapidly with decreasing temperature but is remarkably high relative to that for solid state diffusion even at temperatures as low as -15°C. This decrease in ionic mobility is due, in part, to a decrease in thermal energy of the ions but results primarily from a concurrent reduction in film thickness of the interfacial water through which the ions diffuse. In view of this knowledge alone, one would predict, in the presence of a thermal gradient, a higher rate of movement of ions toward higher temperature since ionic mobility increases in this direction. However, water in the interfacial layer is also mobile[1] and it moves towards the cold side[6] [7]. Although the water moves by a diffusive process and should not exert a viscous drag on the ions moving in the opposite direction there is a possibility of interaction between water diffusion and ionic diffusion. Thus, it is difficult to even qualitatively anticipate the effect of a thermal gradient on ionic distribution.

The objective of this investigation is to resolve this uncertainty by determining the degree of perturbation of both ionic concentration and moisture content profiles by thermal gradients in samples where the concentration profile can be predicted in the absence of a thermal gradient.

MATERIALS AND METHODS

Selection and preparation of earth material

Wyoming bentonite No. 25 (Ward's Natural Science Establishment) was selected for this study because the temperature dependence of the diffusion coefficient of sodium ions[10] as well as that of many other properties such as unfrozen water content[8] [12], interfacial film thickness[1], and electrical conductivity[5] [11] of the frozen, sodium-saturated mineral are known over a wide temperature range. The $<2\mu$ fraction of Wyoming bentonite was obtained by gravity sedimentation. This fraction was sodium-saturated by successive extraction with 1N NaCl solution. The salt content of the clay paste was reduced by successive extraction with distilled water until the clay dispersed,
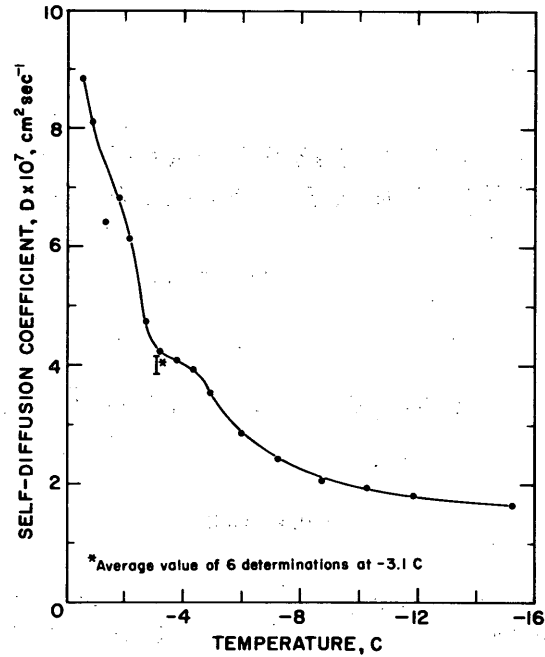
Figure 1. *Apparent self-diffusion coefficient of Na ions in frozen bentonite-water paste as a function of temperature.*
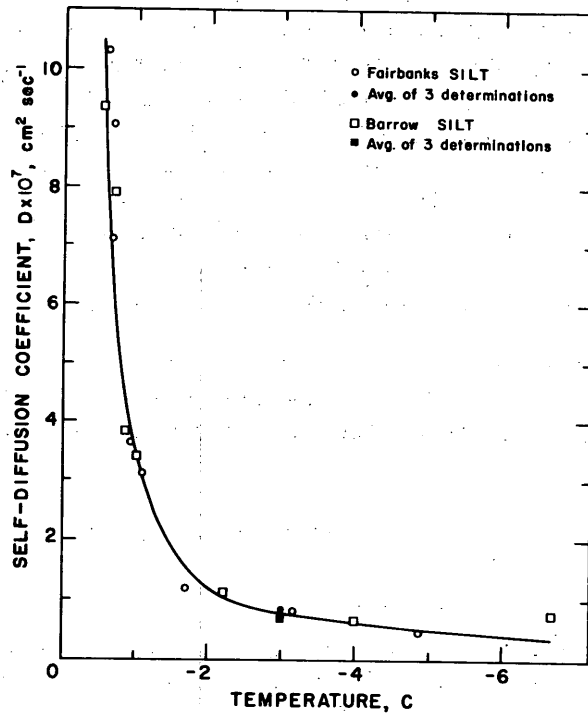

Figure 2. *Apparent diffusion coefficient of Na ions in frozen Fairbanks and Barrow silt as a function of temperature.*

and, subsequently, by removal of solution using a pressure membrane cell. The final NaCl concentration in the extract was 10^{-4}N. The clay contained 0.96 meq of exchangeable Na ions per gram of clay.

Experimental apparatus

The apparatus for determination of the effect of thermal gradient on diffusion of sodium ions in frozen Na-bentonite paste was constructed in a way that made it possible to simultaneously maintain the same temperature gradient across 12 different samples with each sample in a different temperature range. A portion of this apparatus is shown in Figure 3. It consisted of a rectangular aluminum bar (A), 2 cm deep x 12 cm wide x 42 cm long, with provision at each end (not shown) for circulation of cooling solution. A linear temperature gradient could be established across the
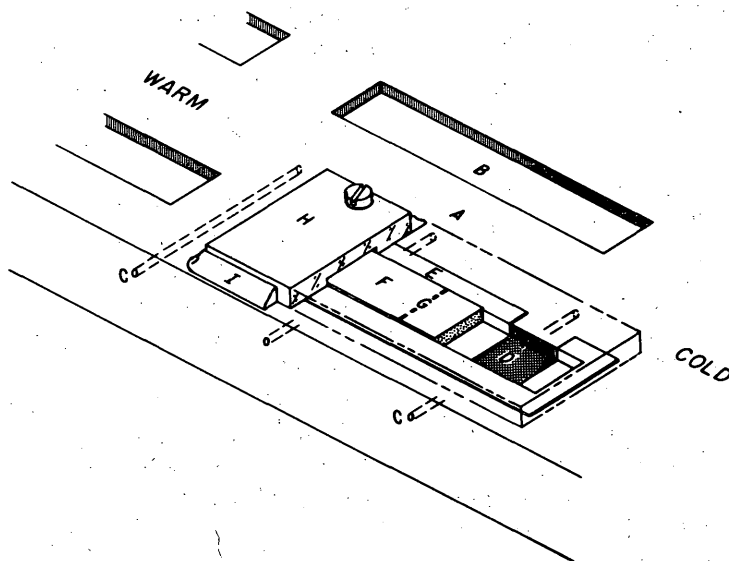

Figure 3. Diagram of apparatus used for diffusion study. A) aluminum sample bar, B) milled groove for clay sample, C) thermocouple position, D) silicone grease, E) aluminum foil tray, F) clay paste, G) place of application of ^{22}Na, H) Lucite sample cover, I) sealing compound.

aluminum bar by maintaining the ends of the bar at two different constant temperatures. Twelve sample grooves (B), 0.16 cm deep x 0.64 cm wide x 10 cm long, were milled in the bar to accommodate clay samples (F). The position of the sample was such that the direction of diffusion along the long axis of the sample was parallel to the temperature gradient across the aluminum bar. Thermocouples (C) were placed at intervals in the aluminum bar. It was verified that sample temperature was the same as that of the aluminum block in a position directly below the sample by placing thermocouples in the clay during preliminary tests. During the experiment, clay was not placed in direct contact with the aluminum bar but instead it was placed in small trays (E) fabricated by pressing aluminum foil into the grooves in the bar using a suitable die. Silicone grease (D) insured good thermal contact between the bottom of the aluminum foil tray and the aluminum bar. The trays facilitated sample handling during the experiment.

Experimental procedure

In preparing clay samples, the aluminum foil trays on the aluminum bar were carefully filled with clay paste using a spatula. An attempt was made to orient the clay particles parallel to the direction of sodium ion diffusion by smoothing the clay along the long axis of the sample with the

flat side of the spatula. The weight of clay paste added to each sample was determined in order to maintain uniformity between samples. It required about 2.2 g of clay paste containing 1.44 g water/ g clay to fill each sample tray. Two microliters of carrier-free ^{22}Na as NaCl having a total activity of about 0.1 μc was carefully added across the center width of each clay sample (G) using a 10-μl liquid syringe. It was possible to add the ^{22}Na to the sample in a band about 1 mm wide. A Lucite cover (H) to prevent moisture loss was then tightly screwed across the top of each sample. A groove having the same dimensions as the clay sample was milled on the underside of the Lucite cover to prevent contact with the clay paste. A sealing compound (I) was placed around the edge of the cover at the point of contact with the aluminum bar as a precaution against moisture loss.

As soon as all samples were prepared, the clay paste was frozen by placing dry ice in contact with the aluminum bar and circulating cooling solutions at -25°C at the ends of the bar. It required about 15 minutes to freeze all the samples, which was fast enough to prevent migration of moisture to the freezing front[5]. The time that elapsed between addition of ^{22}Na solution to the first sample and freezing of the last sample was about 2 hours. By assuming a value of 1.5 x 10^{-6} cm^2 sec^{-1} for the apparent diffusion coefficient of sodium ions in unfrozen clay at 25°C[13], it was calculated that no significant diffusion should have occurred in the unfrozen clay paste during this period.

After all samples were frozen, the temperatures of the cooling solutions at the ends of the aluminum block were adjusted to 0°C and -13°C in order to establish the desired temperature gradient. The entire apparatus was then insulated with 2-in. Styrofoam. It required several hours for thermal equilibrium to be established but this time was short compared to the 3-to 7-week duration of the experiment. The temperatures at the thermocouple positions in the aluminum bar were measured frequently during the diffusion period. A clay sample was not removed from the apparatus until ^{22}Na had diffused almost to the ends of the sample. The samples at the warm end of the aluminum bar were analyzed first, the samples in the coldest temperature range requiring the longest diffusion time. After an aluminum foil tray containing frozen clay paste was removed from the aluminum bar, it was cut into 11 sections of equal length. By using a specially constructed cutting block with 10 cutting blades, it was possible to reproducibly section each of the samples. The activity of ^{22}Na in each sample section was then measured using a gamma ray scintillation detector in conjunction with a timer-scaler. The weights of dry clay and water in each sample section were also determined.

RESULTS AND DISCUSSION

The results for the 12 samples included in this investigation are shown in Figure 4 which includes moisture content, temperature, experimental ^{22}Na activity, and ^{22}Na activity expected in the absence of a temperature gradient, each variable plotted with respect to distance from the plane of application of ^{22}Na to each sample. The temperature data were obtained from Figure 5 which indicates temperature as a function of both sample position and distance along the aluminum sample bar. The ^{22}Na activity is expressed as the relative ^{22}Na activity (A/M), the ratio of the ^{22}Na activity in each sample section (A) to that in the entire sample (M) determined by summing the values of the ^{22}Na activity in each of the 11 sample sections. The distance corresponding to the relative ^{22}Na activity and also the moisture content of a sample section was taken to be the distance from the plane of ^{22}Na application to the center of the sample section. In the absence of a temperature gradient, the conditions of this experiment would correspond to one-dimensional diffusion in an infinite medium from an instantaneous planar source. The solution of Fick's Law for these conditions is given by Crank[4] as
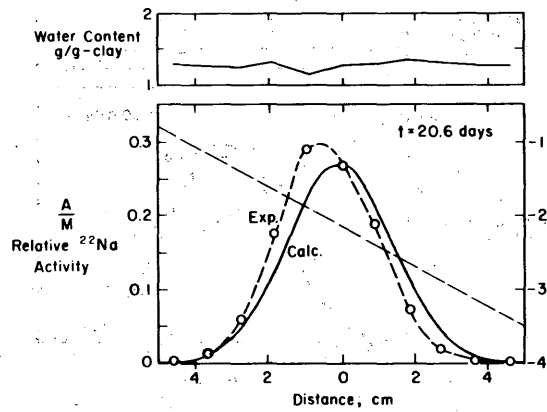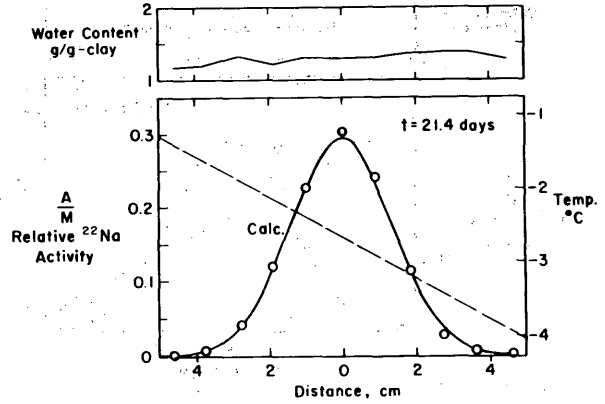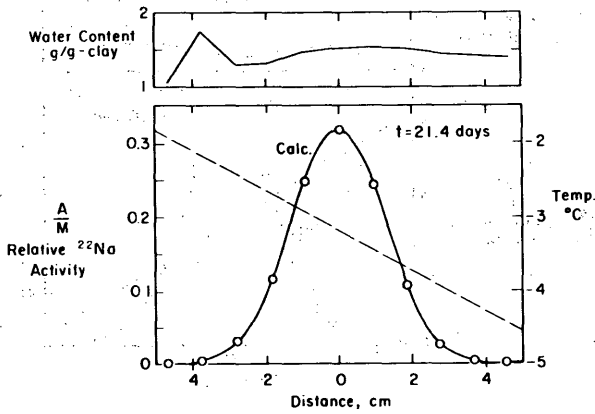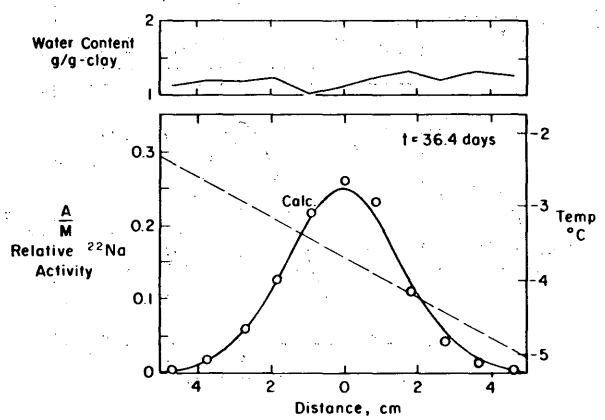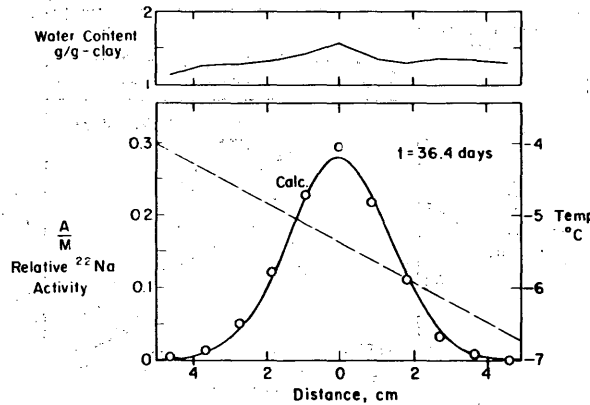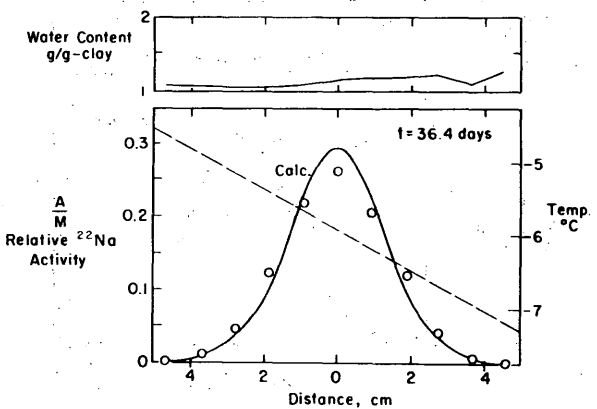
Figure 4. Experimental ^{22}Na activity, calculated ^{22}Na activity, temperature, and water content with distance from plane of ^{22}Na application at time of sampling.
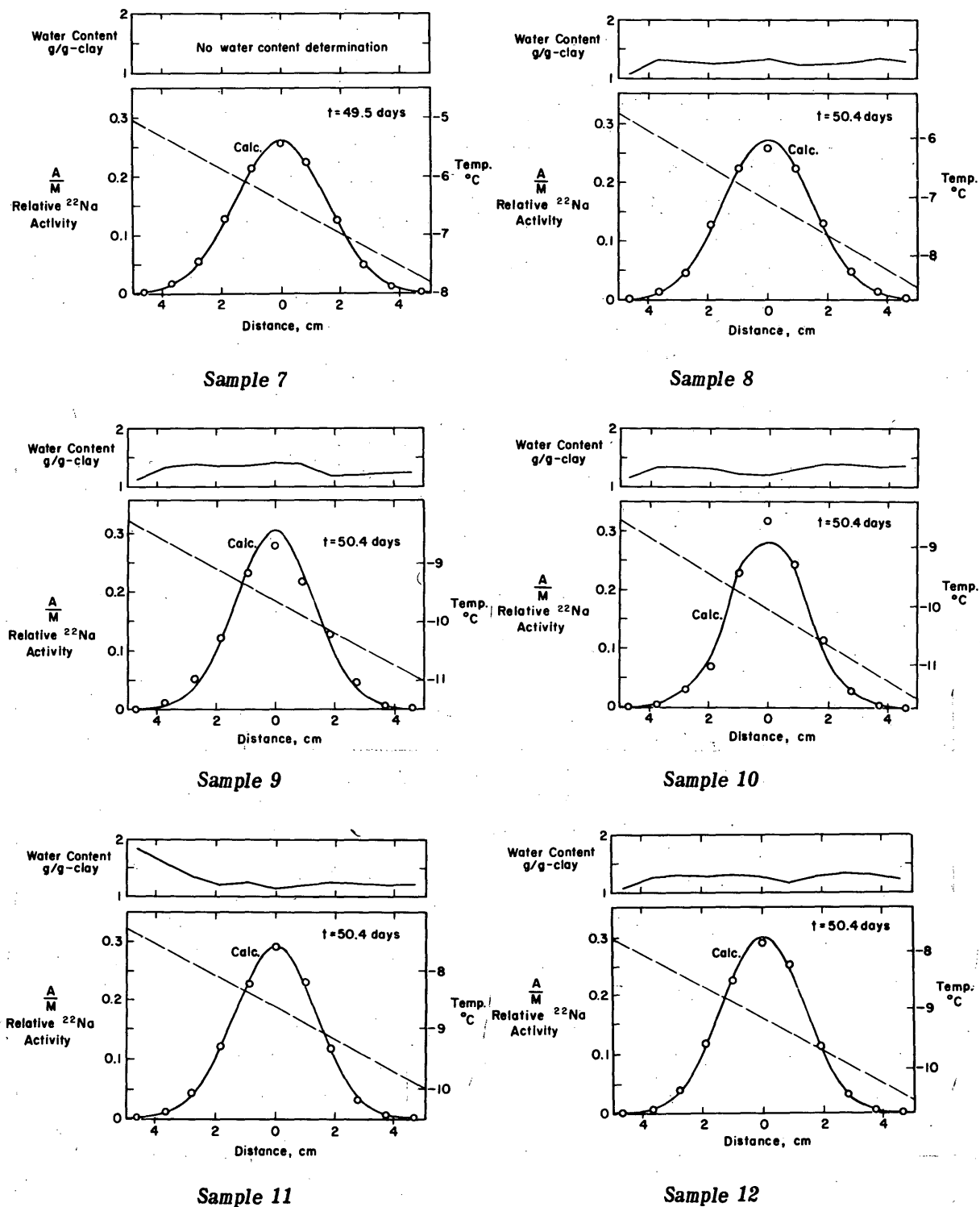
Figure 4. Experimental ^{22}*Na activity, calculated* ^{22}*Na activity, temperature, and water content with distance from plane of* ^{22}*Na application at time of sampling.*
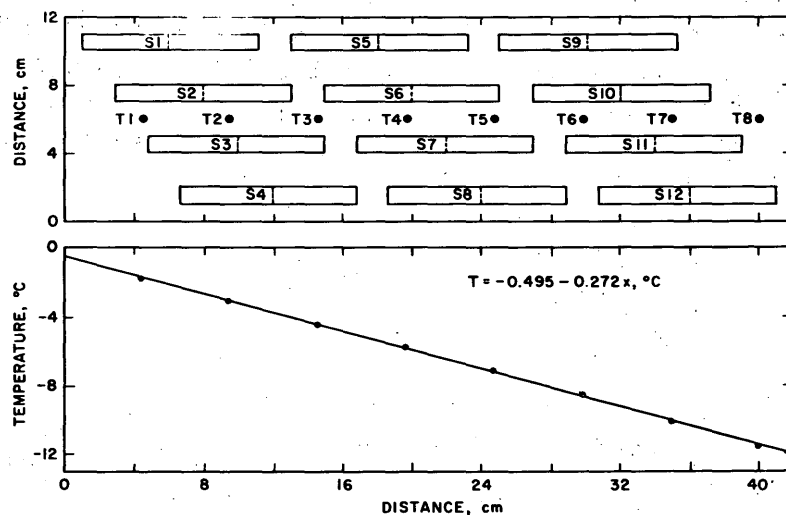
Figure 5. Temperature as a function of sample position and distance
along the aluminum bar. Above: top view of aluminum sample holder.
S and T indicate sample and thermocouple. Below: temperature with
respect to sample position and distance along bar.

$$\frac{A}{M} = \frac{(\pi Dt)^{-\frac{1}{2}}}{2} \exp\left(\frac{-X^2}{4Dt}\right)$$ (1)

where D is the apparent diffusion coefficient in cm^2 sec^{-1}, t is the time in seconds, and X is the
distance from the plane of application ($X = 0$) in centimeters. Equation 1 was used in calculating
the relative ^{22}Na activity profile expected in the absence of a temperature gradient. The value of
D for the temperature at the plane of application of ^{22}Na to each sample was obtained from Figure
1, and the time used was the same as that shown in Figure 4 for each sample for diffusion of ^{22}Na
under the influence of a temperature gradient. The temperature gradient across each sample was
0.27°C cm^{-1}, but the temperature range of each sample varied from 0.7°C to 3.5°C, and 8.5° C to
11.6°C.

The moisture content of the samples was less than 1.44 g water per g clay, the moisture con-
tent at the beginning of the experiment. However, this loss of moisture from the samples should
have had no effect on the experimental results since the value of the diffusion coefficient in frozen
bentonite is independent of water content in the range from 1 to 10 g of water per g clay[11]. The
moisture content varied slightly with distance in each sample and between different samples but
there was no net accumulation of water at the cold end of the sample, showing that neither vapor
transport nor mass flow or diffusion of water in this direction occurred preferentially as expected.
This result indicates that migration of ions was unaffected by migration of water in interfacial
films towards the cold end of the sample.

Although the ^{22}Na distribution profile for sample No. 1 where diffusion is most likely to be
influenced by a temperature gradient shows a net accumulation of ions towards the warm side of
the sample in the direction of increased ionic mobility, the ^{22}Na distribution profile in all other
samples was remarkably similar to that predicted for diffusion in the absence of a temperature
gradient, indicating that the thermal gradient had little effect on ionic diffusion in the frozen

bentonite. Thus, the results of this experiment show that thermal gradients of $0.3°C$ cm^{-1} or less have little effect on the redistribution of ions or on the migration of water in frozen earth materials.

Using the data provided in this report, it should be possible to predict the conditions, if any, under which ionic distribution in frozen soil would be significantly influenced by thermal gradients. This prediction would require a solution of Fick's Law for the boundary conditions previously described but with diffusion coefficient distance-dependent.

$$\left(\frac{\partial C}{\partial t}\right) = \frac{\partial \left[D(X) \left(\frac{\partial C}{\partial X}\right)\right]}{\partial X}. \tag{2}$$

From Figure 1, the functional relationship between D and T can be deduced. The relationship between T and X is expressed in Figure 5. Thus, one can construct a relationship between D and X for use in solution of eq 2, since

$$\frac{\partial D}{\partial X} = \frac{\partial D}{\partial T}, \frac{\partial T}{\partial X}. \tag{3}$$

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13. ABSTRACT

Ionic concentration and water content profiles in frozen bentonite samples subject to a thermal gradient of $0.3°C \, cm^{-1}$ but different temperature intervals were obtained in the temperature range from 0°C to -12°C in order to determine the extent to which thermal gradients influence the movement of ions in thin films of interfacial water. The moisture content distribution was found to remain virtually unchanged after times ranging from 20 to 54 days, indicating that ionic movement was not affected by mass flow of mobile water in thin films. The ionic distribution profiles were essentially as expected in the absence of a temperature gradient. These observations support the conclusion that thermal gradients have little influence on redistribution of ions in frozen earth materials.

14. KEYWORDS

Bentonite
Frozen soils
Ionic diffusion
Soil water

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