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Initial Observations of Salt Sieving in Frozen Soil
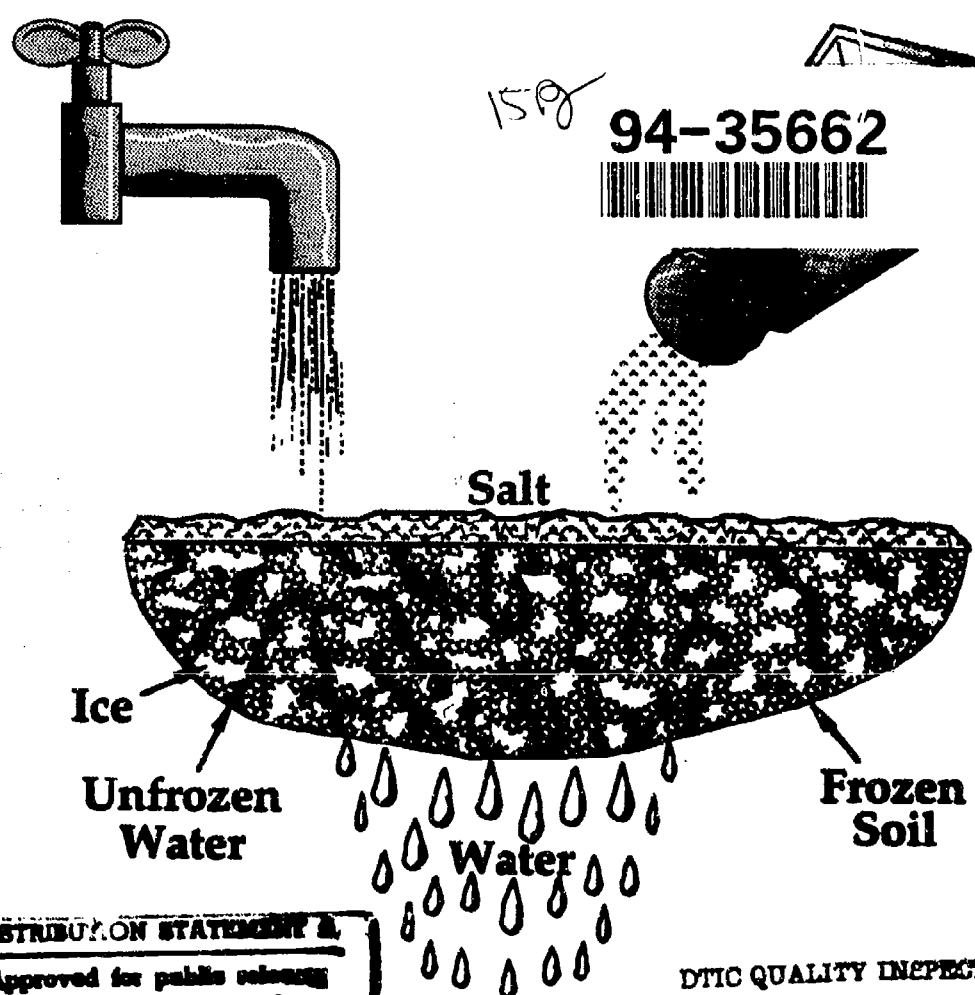
Patrick B. Black

August 1994

94-35662

Salt

Ice

Unfrozen
Water

Water

Frozen
Soil

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Abstract

The role of solutes in the transport of water through frozen porous media is more complicated and subtle than simply lowering the freezing point of the water. This report presents evidence that unfrozen water films in soil act as a semipermeable membrane selectively filtering solutes. The calculated film thickness at the test temperature (−0 05°C) indicates that all solute should pass. The additional influence of anion exclusion arising from a diffuse electrical double layer suggests that solute movement is restricted and a "soil-sieving" process results. Experimental observations are reported for a specially designed constant-volume ice-sandwich permeameter. Proposed research for a constant-stress ice-sandwich permeameter is presented as a means of overcoming experimental uncertainties of the present system.

CRREL Report 94-9

**US Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

Initial Observations of Salt Sieving in Frozen Soil

Patrick B. Black

August 1994

PREFACE

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Initial Observations of Salt Sieving in Frozen Soil

PATRICK B. BLACK

INTRODUCTION

Not all water freezes at a single temperature in a porous medium. Instead there is a general decrease in unfrozen water content as the temperature decreases. Furthermore, fine-grained soils that undergo freezing will withdraw water many times their saturation value from the surrounding environment and create layers of ice lenses. This strong affinity for liquid water in these freezing soils is a topic of much concern for all engineering endeavors in climates where freezing occurs. Strength, transport of water and contaminants, and viability of biological systems are all influenced by the behavior of the unfrozen water in these frozen porous media.

Chemical effects on ground freezing are usually considered simply as a freezing point depression of the soil water, as the effects of osmotic pressure grouped in a vague description of chemical potential. The freezing point depression and osmotic pressure are easily quantified using bulk solution thermodynamics, but the influence of dissolved solutes on bulk moisture movement is more subtle than the chemical potential calculated according to bulk solution chemical thermodynamics. In addition to the effect of lowering the chemical potential that solutes have on a solution as given by the classic Gibbs–Duhem equation, water in a porous medium also experiences a surface free energy (Everett 1961). This additional surface free energy explains why water remains liquid in small pores when it would otherwise freeze if in an unrestricted bulk solution. But there is still more to the porous media matrix and solution interaction.

The large surface area of the porous media greatly influences water. Short-range forces, such as van der Waals and electrostatic, lead to considerable cumulative effects because of the larger surface area.

For instance, it is the large specific surface area of a clay that results in a larger volume of unfrozen water than in an equal volume of silt at low temperatures.

These surface forces have two important consequences for the fate and transport of solutes through freezing soil. First, there is not an abrupt discontinuity in solute concentration across an advancing freezing front, as exists in the one-dimensional freezing of a bulk solution (Taylor 1989). Second, there is a selective flow of ions through the films of unfrozen water (Miller et al. 1975).

The initial goal of this project was to obtain experimental data on the transport of moisture through frozen soil resulting from the influence of physiochemical changes in the soil water. It is intended that as the experimental techniques are perfected, the resulting detailed measurements will allow the implementation of intricate mathematical models, which will eventually allow us to isolate the importance of the various parameters suspected of playing a major role in soil freezing.

BACKGROUND

It is suspected that the presence of even trace amounts of dissolved solutes can, under certain environmental conditions, dominate the movement of water through frozen soil (Kemper and Rollins 1966, Miller et al. 1975, Black and Miller 1990). Unfortunately, direct experimental observation of this effect has not yet been achieved; it is the intent of this research to obtain such data.

Kemper and his students performed a series of important experiments in the period from 1960 to 1970. They found that low-moisture clay pastes acted as a semipermeable membrane. When a hy-

draulic pressure gradient was applied across the paste, the soil would selectively pass ions, causing a concentration increase on the high-pressure side of the soil. This process was called "salt sieving," or reverse osmosis.

A qualitative explanation for this effect is obtained by modeling the movement of rigid spherical molecules through a membrane that exhibits a diffuse electrical double layer. This approach will closely follow that set up by Kemper and Evans (1963) and Kemper (1960). First the bulk behavior of a dilute solution in contact with a semipermeable membrane will be discussed. Then the movement of two sizes of rigid spheres through a cylindrical pore in a rigid membrane will be developed. The concept of exclusion efficiency will then be introduced by comparing the flow due to exclusion with a hydraulically induced flow. Finally the influence of a double layer emanating from the membrane on the exclusion efficiency of charged ions will be added.

Osmotic pressure

If a dilute ionic solution is hydraulically connected to pure water through a perfect semipermeable membrane, an osmotic pressure difference will result that causes a mass flux of water from the pure water side to the salt water side to minimize the pressure difference. This process is represented in Figure 1. Equilibrium is obtained when the height difference between the air–solution interfaces in the two vertical capillary tubes equals the osmotic pressure difference between the solution and the pure water. The osmotic pressure π is calculated with sufficient accuracy by the van't Hoffs equation (Castellan 1971):

$$\pi = cRT \tag{1}$$

where c = molar concentration of solute in solution
R = universal gas constant
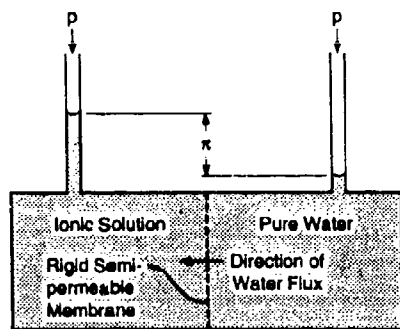T = absolute temperature.

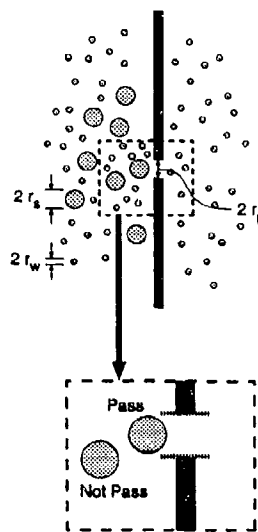Figure 1. Ideal semipermeable membrane.

Figure 2. Ideal pore-scale interaction between water and ion molecules with a rigid pore.

If the perfect semipermeable membrane is replaced by a soil–water–ice system, the height of the air–solution interface will most likely be less than that calculated by the van't Hoffs equation. This is because the soil does not consist of perfectly uniform pores that selectively pass the water but not the ions. Instead, it is considered a leaky semipermeable membrane whose efficiency depends on a number of factors.

At the pore scale of observation, the semipermeable membrane resembles a rigid membrane consisting of fixed pores and individual molecules of water and solute ions as depicted in Figure 2. In this figure, the radius of the water molecule is r_w, the radius of the solute ion is r_s, and the pore radius is r_p. The water and ions are all in constant motion due to their thermal energy. These random thermal motions result in a constant bombardment of, and momentum transfer to, the membrane and the water just inside the pore. This is equivalent to saying that the flux of water and solute molecules hitting the membrane and pore water exert a pressure on the membrane and pore.

Large solutes

First take the case that the solute ion is larger than the pore ($r_s > r_p$). On the right side in Figure 2, the water molecules are free to hit the membrane as well as the pore and thus exert equal pressure on both. On the left side, though, while the water molecules behave the same as on the right side, the solute ions occasionally block the pore, so that the water molecules have fewer opportunities to transfer their momentum to water molecules just inside the pore. The pressure on the water just inside the pore

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on the left side is therefore less than on the right side, and it is proportional to the amount of replacement of water molecules by the solute ions (i.e. the concentration of the solution). The resulting pressure gradient across the pore will cause a flow of water from the right side to the left side. In terms of Figure 1, the flow will persist until a corresponding counter-pressure gradient is created by the height of the air–solution interface.

Again in terms of Figure 1, the total external pressure on the system is p. This pressure is taken up by the pressures associated with the water p_w and the solute. Using the notation RS for the right side of the membrane and LS for the left side, the pressure balance is given by

$$p = (p_w)_{LS} + \pi = (p_w)_{RS}. \tag{2}$$

Thus the pressure due to the water component on the left side is less than on the right side by the amount due to the solute (i.e. the osmotic pressure). This is another way to explain the consequence of the larger solute ion not adding to the pressure inside the pore. Kemper and Evans expressed eq 2 in terms of the total pressure p and the osmotic pressure by using the identity $p_w = p - \pi$ to obtain

$$p = (p - \pi) + \pi. \tag{3}$$

In this model, all molecules are assumed to be rigid spheres. As such, only a collision in which the entire molecule is within the pore will transfer all the molecule's momentum to the water just inside the pore. Collisions at distances less than the molecular radius from the pore wall will impact the membrane, and the molecule is assumed to impart all of its momentum to the rigid membrane. As Kemper and Evans (1963) showed, the available area A_w for water molecule impact on water inside the pore of radius r_p is reduced from the total area of the pore A_p by

$$\frac{A_s}{A_p} = \frac{\pi(r_p - r_s)^2}{\pi r_p^2} = \frac{(r_p - r_s)^2}{r_p^2}. \tag{4}$$

Since the effective pressure on water just inside the pore is a function of the flux of molecular bombardment, it will likewise be reduced from the pressure in bulk solution by the factor $(r_p - r_w)^2 / r_p^2$.

Small solutes

In the second case, consider that the solute ion is smaller than the pore ($r_s < r_p$). In this model the solute ion is no longer completely blocked from enter-

ing the pore. The observed behavior will be the same as for the water molecule. The available area A_s for solute ion molecule impact on water inside the pore is reduced from the total area of the pore A_p by

$$\frac{A_s}{A_p} = \frac{\pi(r_p - r_s)^2}{\pi r_p^2} = \frac{(r_p - r_s)^2}{r_p^2} \tag{5}$$

and the effective pressure on water just inside the pore will likewise be reduced from the pressure in the bulk solution by the factor $(r_p - r_s)^2 / r_p^2$.

This results in a pressure drop δp_{pore} across the pore. Employing eq 2 and 3 gives this local pressure drop:

$$\delta p_{pore} = (p_w)_{RS} - \left[(p_w)_{LS} + \pi\right]$$

$$= p_{RS} - \left[(p_{LS} - \pi) + \pi\right]. \tag{6}$$

Including the restriction effects from eq 4 and 5 gives

$$\delta p_{pore} = (p_{RS} - p_{LS})\frac{(r_p - r_w)^2}{r_p^2}$$

$$- \pi \left(\frac{(r_p - r_w)^2 - (r_p - r_s)^2}{r_p^2} \right) \tag{7}$$

Osmotic efficiency

Kemper and Evans introduced the concept of efficiency or effectiveness of a membrane to create an osmotic pressure difference by a comparison to hydraulically induced pressure drops. A local pressure drop δp_{pore} resulting from a hydraulically induced gradient through the pore is

$$\delta p_{pore} = (p_{RS} - p_{LS})\frac{(r_p - r_w)^2}{r_p^2}. \tag{8}$$

They obtained an osmotic efficiency coefficient by taking the ratio of the osmotic pressure drop obtained from eq 7 when the external hydraulic gradient is zero to a purely hydraulic pressure drop from eq 8. This ratio is

$$\sigma = 1 - \frac{(r_p - r_s)^2}{(r_p - r_w)^2}. \tag{9}$$

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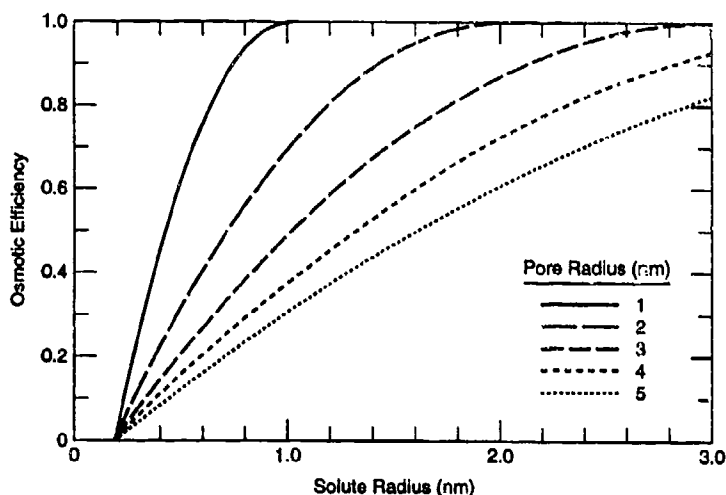*Figure 3. Osmotic efficiency predicted by eq 9.*

Figure 3 displays the osmotic efficiency coefficient as a function of solute size for several pore sizes. The osmotic efficiency coefficient is negligible for small (<1 nm) solutes such as Na^+. Based on the physical factors presented so far, soil-water systems would be very poor semipermeable membranes because of the large film thicknesses in most soils (>10 nm). Soils, though, tend to have a net surface charge that when surrounded by the solutes dissolved in the soil water creates a diffuse double layer. The addition of the double layer creates a smaller effective pore size, which increases the osmotic efficiency coefficient.

Double-layer model

In the double-layer model the surface of the soil particle has a net negative charge that is balanced by the ions in the soil-water solution. The spatial distribution of charges thus becomes both a fixed surface charge and a diffuse zone emanating from the surface as pictured in Figure 4. The cation concentration is highest next to the soil surface and decreases with distance to that of the bulk soil-water solution. Thus,

there is a diffuse region of net positive charge balancing the negative charge of the soil particle. Oppositely the anion concentration decreases closer to the soil surface.

If two soil particles are in close proximity, the resulting charge distribution will overlap, creating a thicker zone of high ion concentration when compared to the bulk solution, as sketched in Figure 5. The important conclusion to be drawn from this is that the passage of anions is seriously hampered

Distance from Particle A
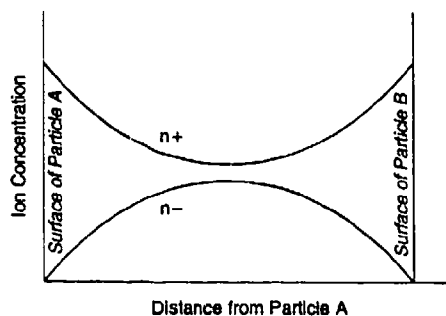
a. Slight overlap of charge distribution.

Distance from Particle A
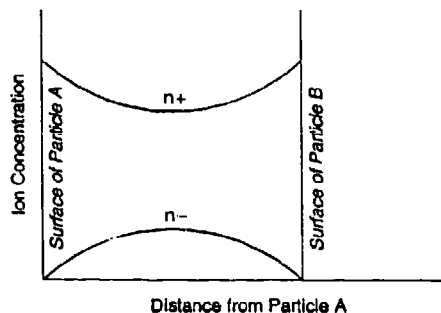
b. Greater overlap of charge distribution because particles are closer together.

Figure 5. Overlapping double layers.

Distance from Surface of Particle

Figure 4. Ion concentration in a double layer for negatively (n–) and positively (n+) charged ions.

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when the spacing between soil particles is small. Kemper and Maasland (1964) found that the double-layer model correctly predicted the observed influence of solute valence, concentration and hydraulic pressure gradient on the sieving process in low-moisture, ice-free clay pastes. While their work was of interest in understanding the dynamics of soil–water–solute systems, it had very little application in nature because of the lack of naturally occurring high pressure gradients in dry clays. The freezing process, however, generates tremendous pressure gradients in the thin unfrozen water films separating the soil from the ice (Black and Miller 1985). It seems reasonable, then, to suspect that salt sieving might become a significant driving mechanism of water through frozen soil.

EXPERIMENTAL DETAILS

A novel apparatus based on the Miller ice-sandwich permeameter (Miller 1970) was constructed. It consists of a brass cylinder containing a wafer of air-free frozen soil that is bounded by endcaps. The apparatus is connected to capillary tubes and immersed in a constant-temperature bath, as shown in Figure 6. The sample is 5 cm in diameter and 5 mm thick. The apparatus uses Millipore VCWP 04700 filter paper.

Preliminary preparations for the experiment consist of filling the sample chamber with a soil slurry made with deaired MilliQ water. The particle size distribution for this soil is presented in Figure 7. It is an Alaskan silt previously used by Black and Miller (1990). The apparatus is then assembled under water to prevent air contamination, and the
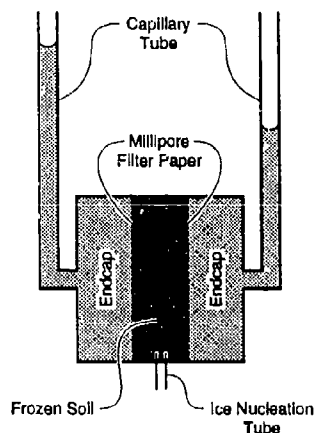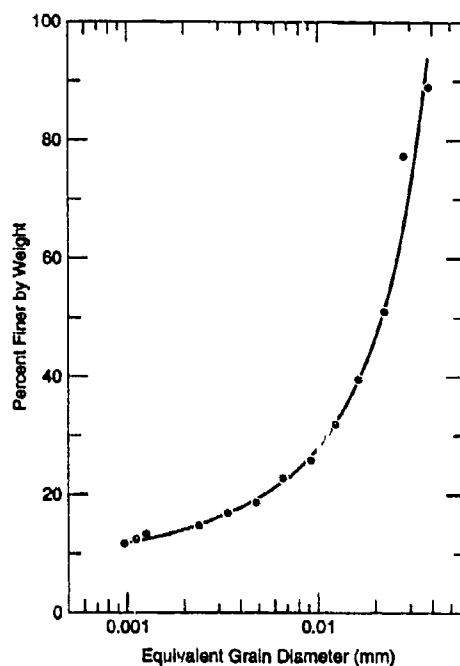

Figure 7. Soil particle size.

endcaps are flushed with additional deaired MilliQ water. The apparatus is then submerged in a constant-temperature bath and cooled to the operating temperature of –0.055°C (±0.004°C). The soil water is then seeded with an ice crystal by freezing the nucleation tube, and the meniscus levels on the vertical capillary tubes are monitored to determine if freezing is complete (Fig. 6). When the soil water is frozen, a small hydraulic pressure drop (~10 cm) is imposed across the frozen sample; that is, the air–water meniscus in one capillary tube is raised to a level 10 cm higher than in the other tube. Elevation change of the meniscus in each tube is monitored with time.

This capillary tube geometry is described as being a simultaneous falling and rising head permeameter. The defining equation for the change in distance between the two meniscuses ϕ with time t was derived to be

$$\ln\left(\frac{\phi_i}{\phi_n}\right) = \frac{K_w R^2}{2r^2 \ell}(t_n) \qquad (10)$$

where R = radius of the frozen soil wafer
     ℓ = thickness of the frozen soil wafer
     r = internal radius of the capillary tubes
     K_w = hydraulic conductivity.

The subscripts are i for the initial time and n for any

Figure 6. Experimental setup.

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other time. Eq 10 predicts that the hydraulic conductivity is the slope of a plot of $\ln(\phi_n/\phi_i)$ vs. t_n.

A run consists of monitoring changes of ϕ with time resulting from the initial imposed hydraulic gradient ϕ_i. Several runs were conducted to determine the behavior of water flow through the frozen sample. This by itself represents a major experimental undertaking. Figure 8 presents the results of one of the tests.

RESULTS AND DISCUSSION

Inspection of Figure 8 reveals an interesting trend: the curvature changes with time. Since the geometry was fixed, the only terms free to vary in eq 10 are ϕ and K_w. In an experiment of this type, some ice redistribution is expected during the initial time period when the head is imposed. This is a result of ice melting on the high-pressure side of the frozen wafer. This redistribution should be short lived because of the isothermal condition and the small initial head (Black and Miller 1990). The hydraulic conductivity then is assumed to reach a steady-state value after a time duration measured in minutes, not hours as in Figure 8. Therefore, ϕ_n must be changing with time.

According to our hypothesis, ϕ_n will change with time if there is a gradient in the solute concentration. The source of these solutes was the soil itself. The act of flushing high-purity water through the soil had the effect of "leaching out" solutes originally present in the soil. In the configuration used in this setup, the flushed solutes would be deposited in the endcap on the low-pressure side of the sample. This buildup of solutes would create a concurrent osmotic pressure *if* the frozen soil acted as a semi-permeable membrane. The osmotic pressure would
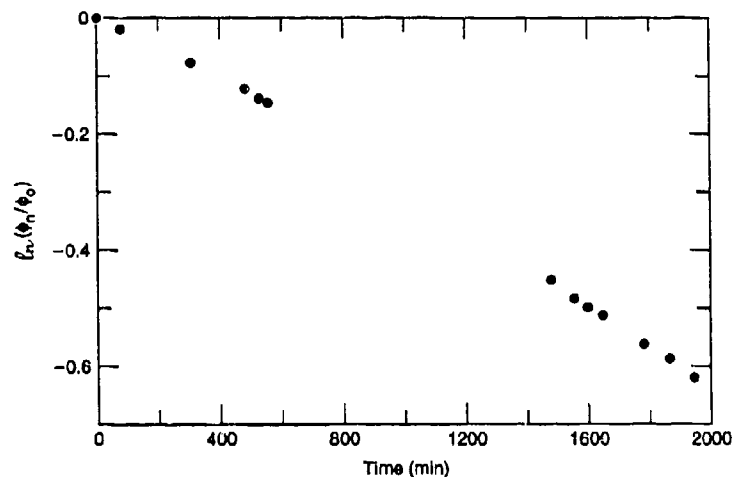

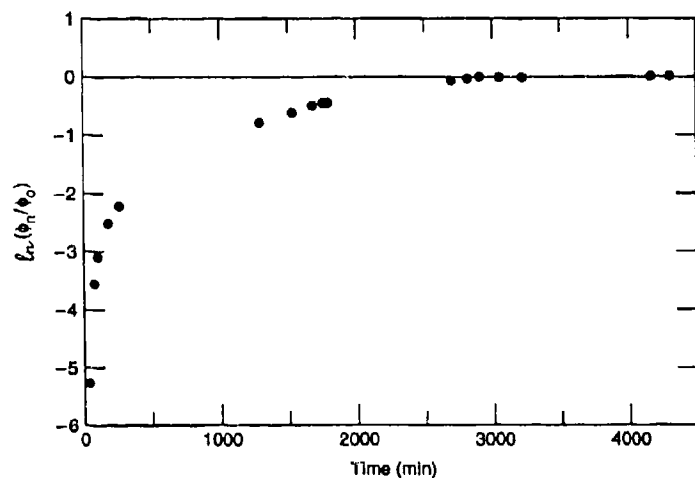*Figure 8. Experimental data for $\ln(\phi_n/\phi_o)$ vs. time (with a head; ϕ_i is initial).*

Figure 9. Experimental data for $\ln(\phi_n/\phi_f)$ vs. time (without a head; ϕ_i is final).

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manifest itself by increasing the flow rate of water with time through the sample as more solutes are flushed from the soil, as indicated in Figure 8.

Further support of the presence of flushed solutes and a demonstration of the salt-sieving property of this soil is presented in Figure 9. These data were obtained by continuing the experimental run presented in Figure 8, but the meniscuses started out at the same level so that there was no initial hydraulic gradient. The water went from the previously high-pressure side through the frozen soil to reach the previously low-pressure side. This behavior qualitatively agrees with the salt-sieving theory as explained below.

If solutes were flushed out of the soil into the low-pressure side during the forced flow of clean water during the test in Figure 8, and then the water flow was shut off, there would be a chemical imbalance between the two sides that could only be balanced if the solutes diffused from one side to the other. If the solutes were not allowed to diffuse through the frozen soil because of the diffuse double layer, then the clean water must have been "sucked" through the frozen soil to balance the osmotic pressure.

It was the original intent of these experiments to first measure the hydraulic conductivity and then to impose an osmotic gradient by spiking the MilliQ water on one side with a known NaCl concentration. Following this strategy, it was not necessary to monitor the solute concentration on both sides of the sample, so no provisions were made for easy access to the sample in the apparatus. The data presented in Figure 8 were expected to give a constant slope that would determine the hydraulic conductivity, from which the osmotic efficiency coefficient would be determined for a given osmotic pressure gradient. The nonlinear behavior of the data in Figure 8 did not allow the planned tests to continue. Instead, it is argued, the salt-sieving nature of this frozen soil was so prevalent that even these initial tests were dominated by the process.

Further analysis of these data are possible without the detailed history of solute concentration by drawing on past analyses of this soil (Black and Miller 1990) and the theoretical study of transport through a frozen permeameter (Miller et al. 1975). Three alternative approaches to data analysis are presented. In the first approach the possible existence of salt sieving is determined by calculating the osmotic efficiency coefficient from double-layer theory applied to ice–water–soil systems. With justification for the salt sieving in this frozen soil, the

source and magnitude of ions resulting in the observed time-dependent mass flow is then obtained with a simple leaching model. Finally the possible influence of ice lens formation on the observed flow is examined.

A measure of the osmotic efficiency is calculated using an unfrozen water film thickness and a measure of the distance of significant anion exclusion. Miller et al. (1975) presented a discussion of the double layer influence on the adsorbed film of unfrozen water. For a -0.05°C frozen soil containing a comparable solute concentration as predicted below in the analysis of eq 11, they predicted a film thickness of approximately 2 nm. This thickness is still to large to have a significant osmotic efficiency coefficient (eq 9). The predicted film thickness coupled with negative adsorption of anions will have the additional effect of reducing the apparent film thickness (Fig. 4). Actual calculation of anion exclusion, as with every calculation of the double layer, is difficult because of the complex boundary conditions in soil systems.

A rough measure of the thickness of the layer of anion exclusion is possible by calculating the Debeye length for a flat surface (Black 1992):

$$\lambda^2 = \frac{\varepsilon_0 kT}{2n_0 e^2 v_0^2} \tag{11}$$

where ε_0 = dielectric constant of water
  n_0 = concentration of the ions in the bulk soil-water solution (ions/volume)
  v_0 = valence of the ions in the bulk soil-water solution
  e = elementary charge
  k = Boltzman constant
  T = absolute temperature.

It is the distance at which there is a 1/e drop in ion concentration. Using a concentration of 10^{-4} M (see below), a value of 30 is obtained. For the purpose of these rough calculations, it is important to note that the Debeye length is of the same order of magnitude as the film thickness predicted by Miller et al. (1975). This would indicate a near-perfect osmotic efficiency ($r_p < r_s$ in eq 9) for this frozen soil.

Since it is justified to suspect that this soil acts as a semipermeable membrane, the observed time-dependent mass flow is therefore possible if there is a comparable time-dependent ion concentration on the discharge side of the sample. Leaching of solutes from the soil should result in the necessary time-dependent solute concentration. The osmotic pressure
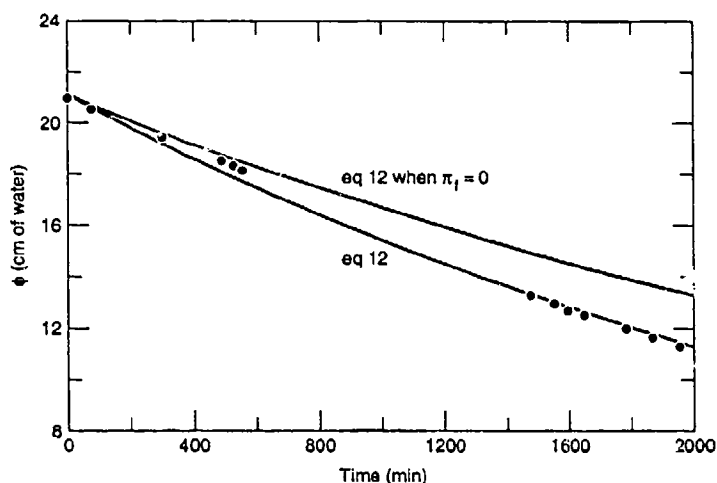
Figure 10. Experimental data for ϕ vs. time, with predictions from eq 12, both with and without an osmotic effect.

difference across the wafer should start at zero and asymptotically approach a maximum when the solute concentration in the low-pressure endcap equals the solute concentration within the soil wafer.

A first-order approximation is obtained by assuming an exponential cumulative flow dependence. The data presented in Figure 8 were modeled by assuming a constant hydraulic conductivity that was obtained by taking the slope of the data greater than 0 minutes and less than 100 minutes. Data in this time range are assumed to have undergone the initial redistribution of ice but still lack a measurable osmotic pressure. The remaining data are then modeled by the following variation of eq 10:

$$\phi_{n+1} = \phi_i \, e^{-\frac{K_w R^2}{2r^2 f}(t_n)} - \pi_f \left(1 - e^{-\frac{\phi_i - \phi_n}{2T1}}\right) \quad (12)$$

in which $T1$ is a characteristic time constant of the system and π_f is the maximum obtainable osmotic pressure gradient across the wafer.

A nonlinear optimization was performed on the data to determine the values of the unknown parameters in eq 12 using Mathcad 4.0 (Mathsoft Inc. 1993). Optimum values of $\pi_f = 5.47$ cm and $T1 = 10.64$ were obtained for $K_w = 5.7 \times 10^{-8}$ m/s. Figure 10 contains the data along with the predicted curve from eq 12 and another curve obtained from eq 12 by assuming that there is no osmotic effect ($\pi_f = 0$). The "best fit" prediction to the data is clearly obtained when the osmotic effect is included. This magnitude of osmotic pressure corresponds to a

concentration of 2.4×10^{-4} M, which is well within normal soil solute concentrations (Black and Miller 1990). The significance of $T1$ is not readily apparent. If detailed transport information such as the film thickness, viscosity and pressure profile were available, $T1$ might then be predictable from a breakthrough curve.

One final analysis of these data is obtained by a simple comparison of inflow and outflow data. Figure 11 shows a plot of corresponding changes in the meniscuses for the same data as in Figure 8. The figure shows that more water appears to be flowing into the frozen wafer than is flowing out. This behavior would be a direct result of leakage, but the data in Figure 9 appear to contradict this hypothesis. The latter data show that there is a discharge of water even if there is no hydraulic head. It is still possible that there is leakage and the osmotic pressure is driving water up the low-pressure tube, but it is difficult to determine if there is a leak. Another probable cause of the observed behavior is the formation of ice lenses.

The frozen wafer was contained within a constant-volume chamber. Under this condition, the soil is free to undergo consolidation if pressure is applied to the wafer. An ice lens could therefore form and consolidate the soil while the volume
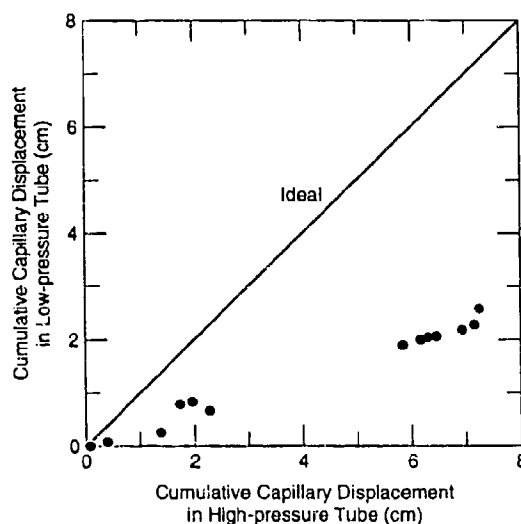

Figure 11. Inflow vs. outflow.

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for the system in the chamber remained constant. This process would result in an increase outflow of water due to the specific volume change upon freezing. The data do not appear to agree with this hypothesis, but it could still be possible, along with leakage. The only method of eliminating this experimental artifact is to maintain the sample under a constant stress to prohibit ice lens formation. The current apparatus is not capable of maintaining constant stress.

CONCLUSIONS AND RECOMMENDATIONS

Based on the experimental data and the analysis presented, the observed flow behavior of this frozen soil appears to result from an osmotic effect resulting from the in-situ soil solutes. If this is the case, higher solute concentration gradients would seriously influence overall moisture transport through this frozen soil.

This brief discussion of the results is not sufficient to quantitatively determine salt-sieving properties of this frozen soil. But it does seem evident from inspection of the data that the process is present. Therefore, if we are to attempt to even measure the hydraulic conductivity of frozen soil, the mechanisms responsible for the behavior of solutes in frozen soils must be understood.

Since this experiment was conducted, a new design for a constant-stress ice-sandwich permeameter was completed. This device, when constructed, will prevent ice lenses from forming, and it will monitor electrical conductivity changes resulting from ion concentration gradients. It is intended that the new apparatus will allow more detailed analyses to be performed. Future studies of the role of the double layer in frozen soil will lead to a better understanding of changes in film thickness of the unfrozen water (and the ensuing change in hydraulic conductivity), the role of the streaming potential in the movement of solutes and a possible model of solute redistribution, if any, in freezing soil.

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REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words)

The role of solutes in the transport of water through frozen porous media is more complicated and subtle than simply lowering the freezing point of the water. This report presents evidence that unfrozen water films in soil act as a semipermeable membrane selectively filtering solutes. The calculated film thickness at the test temperature ($-0.05°C$) indicates that all solute should pass. The additional influence of anion exclusion arising from a diffuse electrical double layer suggests that solute movement is restricted and a "salt-sieving" process results. Experimental observations are reported for a specially designed constant-volume ice-sandwich permeameter. Proposed research for a constant-stress ice-sandwich permeameter is presented as a means of overcoming experimental uncertainties of the present system.

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