

# PRESSURE EFFECTS ON CONDUCTANCE OF FROZEN MONTMORILLONITE SUSPENSIONS

*by*

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## ABSTRACT

THE influence of pressure on the conductance of frozen montmorillonite suspensions was measured in the temperature range from 0°C to -12°C on Na- and Ca-saturated samples. Pressures invariably increase the conductance of frozen suspensions. The change in conductance with pressure is postulated to be due to pressure melting of the ice in the frozen suspension. From swelling pressure data the increase in unfrozen water with pressure at constant temperature is calculated and shown to be consistent with the effect of pressure on conductance.

## INTRODUCTION

WHEN a one-component, two-phase system is subjected to pressure, the phase composition of the system will change so as to decrease the total volume. In a frozen clay-suspension one has a two-component (clay and water), three-phase system, namely, clay, unfrozen adsorbed water, and ice. Pressures would, hence, be expected to transform some ice to unfrozen water. A system of ice and water can be in equilibrium only at a specific temperature and pressure. In a frozen clay-suspension unfrozen adsorbed water can exist in equilibrium with ice over a large temperature range below freezing. The reason is that the thermodynamic properties of the adsorbed water phase vary with the thickness of the unfrozen film. In the frozen clay-suspension the adsorbed water freezes gradually as the temperature is lowered, decreasing the thickness of the unfrozen film. The ice phase at each temperature is in equilibrium with an unfrozen water layer whose properties are constantly changing as the temperature is lowered.

Thus, a frozen clay-suspension consists of mineral particles, ice, and thin films or unfrozen water on the mineral surfaces (Nersesova and Tsytoich, 1963; Anderson and Hoekstra, 1965). Current flow in response to an electrical gradient in a frozen soil occurs almost entirely through the unfrozen water films (Vershinin *et al.*, 1949). Conductance measurements on frozen clay can, therefore, be used to investigate the deposition of the unfrozen water, and are, in particular, useful as an indication of changes in the liquid-like films

caused by a variation of an external factor such as, for example, temperature (Hoekstra, 1965) or pressure.

The purpose of the research described herein was to measure the changes in conductance of frozen clay-suspensions caused by external pressures, and to deduce from the result how the quantity of unfrozen water might be affected by pressure. Martynov (1959) reports an increase in the unfrozen water in frozen montmorillonite mixtures of 4% if the pressure was raised 5 kg/cm<sup>2</sup> at a temperature of -5.8°C and larger increases at higher temperatures below 0°C. Unfortunately the experimental methods employed are not given.

### MATERIALS AND METHODS

The Wyoming montmorillonite used was first suspended in distilled water and allowed to settle until particles larger than 1 micron (equivalent Stokes' Law diameter) had settled out. The remaining suspension was passed through an Amberlite IR-120 cation exchange resin saturated with Na. The Ca-clay was prepared by mixing 500 ml suspension with 50 ml of 1 N CaCl<sub>2</sub> in a centrifuge tube. The suspension was spun down and the supernatant was poured off and 25 ml, 1 N CaCl<sub>2</sub> added and mixed with the clay suspension. This process was repeated four times. Subsequently the clay suspension was washed eight times with 250 ml aliquots of distilled water. The homoionic montmorillonite suspensions were concentrated to the water contents used in a pressure membrane apparatus.

Figure 1 shows a sketch of the high-pressure cell. The cell was made of steel. The sample was contained in a 1-in. cylindrical cavity. The sides of the cylinder walls and bottom were insulated by lacquer paints. The cell was closed by a bolted flanged cover. A cylindrical portion of the cover protrudes into the cavity bore and holds a radial O-seal. In the cover an inlet and outlet valve were inserted, the inlet connected to a nitrogen gas tank. Nitrogen pressures were read on a gauge. The electrodes used were Conax Electrode glands, type A. These electrodes provided pressure seals up to 2500 psi and electrical insulation for the copper electrodes. The two copper electrodes were  $\frac{1}{4}$  in. diameter and were spaced  $\frac{1}{4}$  in. in the cell. The electrodes were connected to a General Radio type 1650-A Impedance bridge and an external null detector. Resistance was measured at 1000 cps. The bridge provides an accuracy for absolute resistance measurements of 1% for the ranges used in this experiment. However, resistance changes could be detected to a higher degree of accuracy.

Through the bottom of the high pressure cell, coolant from a constant temperature bath was circulated. In this way temperature could be adjusted anywhere from +10°C to -20°C. Two-inch styrofoam was placed around the pressure cell to maintain uniform temperatures. A calibrated thermistor was taped to the pressure cell, and resistances measured with a Wheatstone bridge. Since steel is a relatively good heat conductor, the temperature read

closely corresponded to the sample temperature. As the cooling plate is at the bottom of the cell the sample was never at a temperature higher than the cell walls, which prevented evaporation of water. Oil-pumped nitrogen was used so that little water condensed on the sample. A 1-in. thick sample of clay at water contents ranging from 100–270% was compacted in the cell with the electrodes in place. Care was taken to eliminate macroscopic air

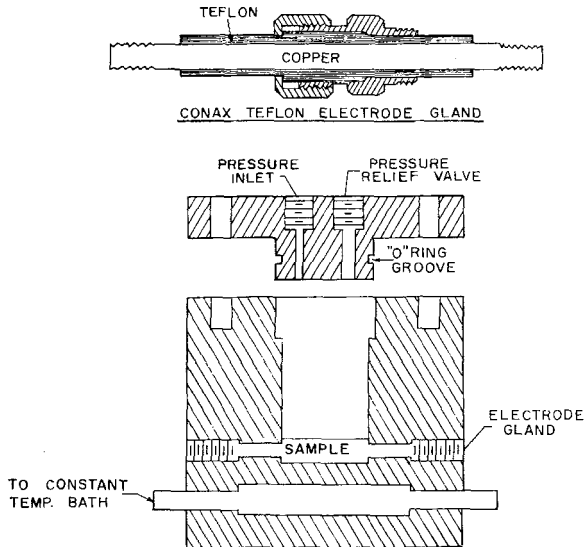


FIG. 1. Schematic diagram of electrode and high pressure cell.

pockets in the sample. Since the solubility of air in ice is less than that in water, one expects the formation of small air bubbles upon freezing. This, however, would not affect the saturation of the frozen soil since, as long as there is ice present, the unfrozen water will maintain a constant thickness at certain temperatures and pressures. Pressure could perhaps change the configuration of the air bubble and hence, the conductance of the soil. The close agreement (Fig. 2) between the compression and the pressure release cycle suggested that such effects, if present, were probably small.

During freezing of clay suspensions, water migration occurs. The water movement can seriously affect the reproducibility of the results. To minimize water movement the samples were frozen in less than 5 min at  $-20^{\circ}\text{C}$ . All measurements were taken during the warming cycle.

Particle rearrangement occurs during freezing and thawing of the montmorillonite suspension (Anderson and Hoekstra, 1965). The interlamellar water migrates to and from the pore spaces upon freezing and thawing and the  $d(001)$  spacing changes. Moreover, the unfrozen water content of a frozen soil apparently increases under pressure, and the particles perhaps

rearrange to accommodate the extra interlamellar water. Again the agreement between the compression and release cycle is perhaps the best indication that conductance changes due solely to mechanical effects of particle rearrangement caused by pressure was small. Resistance at a certain temperature was measured as a function of pressure up to 1500 psi, both during the compression and pressure release cycle. Before changing the pressure to a new level, resistances were allowed to stabilize. After each pressure change the resistance stabilized within 10 min.

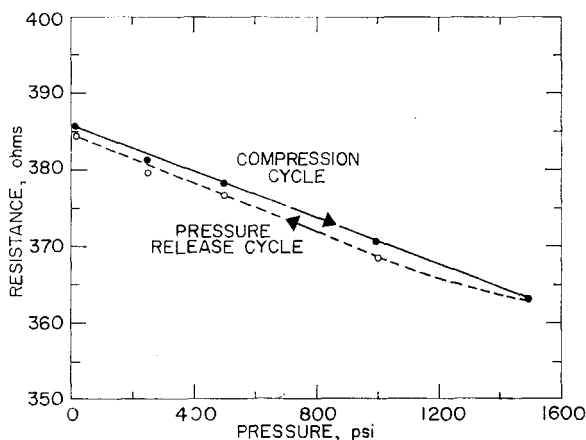


FIG. 2. A typical plot of resistance (ohms) versus pressure (psi) for Na-montmorillonite at constant temperature.

## RESULTS

The effect of pressure at constant temperature can be most conveniently represented by the relative resistance, which will be defined as the ratio of the resistance at a pressure  $p$ ,  $R_p$ , to the resistance at atmospheric pressure,  $R_0$ . Introduction of this parameter facilitates representation of the results on different samples and allows comparison of the two homo-ionic forms of the montmorillonite clay used. The ratio  $R_p/R_0$  has a different  $R_0$  for each temperature, since the resistance of a suspension decreases with increasing temperature. It was found that the ratio  $R_p/R_0$  is affected very little by the spacing of the electrodes. In Fig. 3a the relative resistance is given as a function of pressure at several temperatures for sodium Wyoming montmorillonite at a water content of 174%. Values of  $R_p/R_0$  less than 1.0 indicates that the resistance is decreased by pressure. In Fig. 3b, the same data are respectively given for a Ca sample at a water content of 165%. In Fig. 4a and b the relative resistance at 1500 psi is plotted as a function of temperature for Na- and Ca-samples. The value of  $(R_{1500})/R_0$  is a measure of the impact

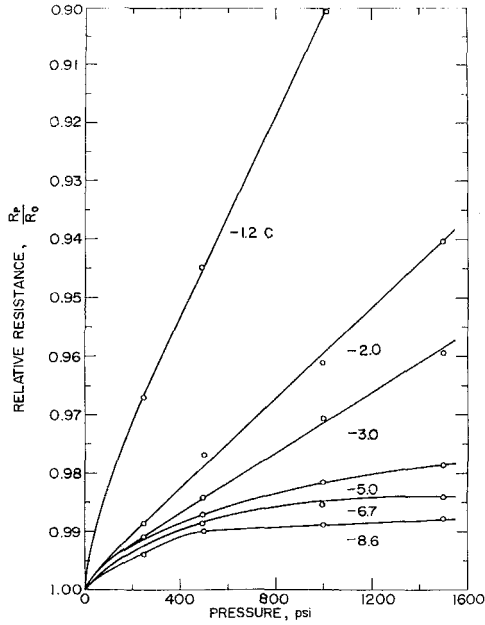


FIG. 3a. Relative resistance as a function of pressure for frozen Na-montmorillonite at a water content of 174% at several temperatures, °C.

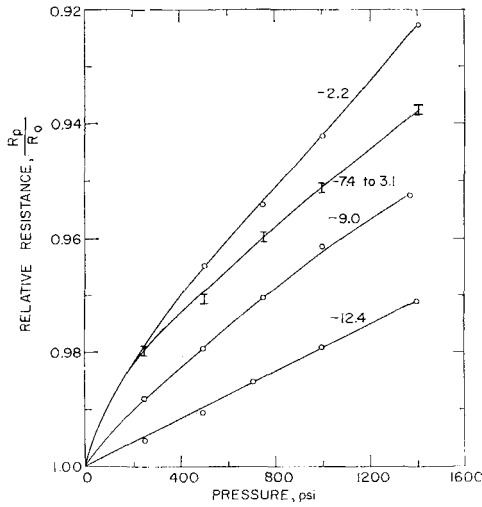


FIG. 3b. Relative resistance as a function of pressure for frozen Ca-montmorillonite at a water content of 165% at several temperatures, °C.

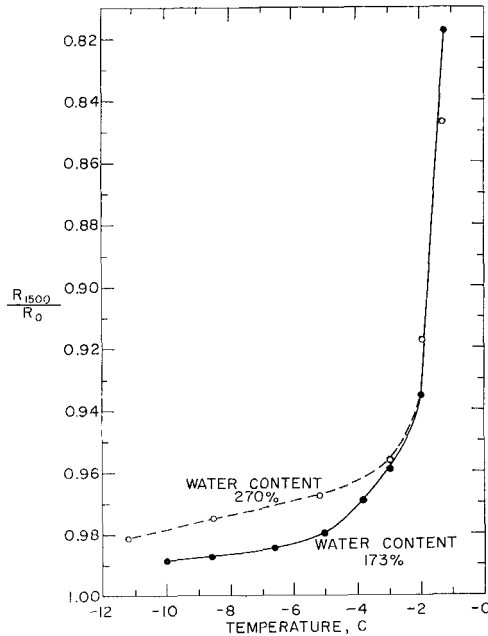


Fig. 4a. The relative resistance at 1500 psi for Na-montmorillonite samples as a function of temperature.

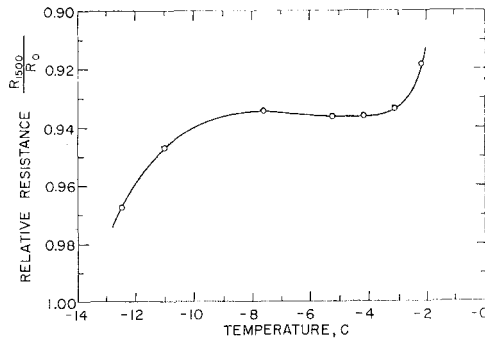


Fig. 4b. The relative resistance at 1500 psi for Ca-montmorillonite samples.

of pressure on the resistance of frozen montmorillonite suspensions. Water content does affect the relative resistance, as is shown in Fig. 4a. However, the results show the same behavior at 173% and 270% water. The difference in magnitude of the relative resistance versus pressure is probably due to the disposition of the ice phase.

DISCUSSION

When a montmorillonite water suspension is frozen, interlamellar water migrates to the pore spaces and the  $d(001)$  spacing collapses to a value between 20–16 Å determined by temperature and nature of the exchangeable ions (Anderson and Hoekstra, 1965). The exchangeable ions do not move with the water to the pore spaces, but remain between the clay lamella, preserving the electro-neutrality of the system (Hoekstra, 1965). The concentration of the ions between the lamella in the frozen clay can be calculated by dividing the surface charge density  $1.25 \times 10^{-7}$  me/cm<sup>2</sup> by the thickness of the film of unfrozen water (3–5 Å). Such a calculation yields a concentration of 4.1–2.5 equivalents of Na or Ca in the films of unfrozen water. In electrolytic solutions of such high concentrations, pressure increases the resistance slightly (Adams and Hall, 1931). The decrease in resistance due to pressure observed in the frozen clay probably cannot be attributed to the presence of electrolytes in the clay-adsorbed water. The decrease in resistance is most likely due to one of two factors; an increase in the amount of unfrozen water caused by pressure, or an alteration in the viscosity of the unfrozen water due to pressure. However, one does not reasonably expect the influence of pressure on the viscosity of the water to be as temperature dependent as indicated in Fig. 4a and b. For example, the pressure dependence of the conductivity of sea water was not measurably influenced by temperature over the range from 0.0° to 25°C (Horne and Frysinger, 1963) and part of the conductance increase with pressure in sea water is postulated to be due to the pressure dependence of the viscosity of the medium. Also, it is doubtful if the structure of the unfrozen water could significantly alter the conductance in a one- or two-layer complex. The changes in conductance probably should be attributed to changes in the amount of unfrozen water.

The effect of pressure on the amount of unfrozen water can be evaluated from thermodynamic arguments. In a frozen soil where ice and unfrozen adsorbed water are in equilibrium, the partial molar free energy of adsorbed water,  $\bar{F}_l$ , equals the molar free energy of ice,  $\bar{F}_s$ , provided ice freezes out as normal hexagonal ice. If bulk supercooled water is chosen as the standard state, then the difference between the partial molar free energy of unfrozen adsorbed water and the molar free energy,  $F^\circ_l$ , of the standard state in a frozen suspension is:

$$\Delta\bar{F}_l = \bar{F}_s - F^\circ_l = RT \ln (p^\square/p^\circ) \tag{1}$$

where  $p^\circ$  is the vapor pressure of supercooled water and  $p^\square$  is the vapor pressure of ice, which equals the vapor pressure of adsorbed water. Both  $p^\circ$  and  $p^\square$  can be obtained from Dorsey (1940, pp. 199, 462). Thus,  $\Delta\bar{F}_l$  can be obtained at any temperature below freezing as long as ice is present in the sample.

A plot of  $\Delta\bar{F}_l$  as a function of water content can be obtained from swelling pressure data available for both Na- and Ca-montmorillonite. Warkentin *et al.* (1957) and Koenigs (1961) determined swelling pressures as a function of water content. At constant water content swelling pressure,  $\Delta P$ , is related

to  $\Delta\bar{F}_l$  of the adsorbed water by:

$$\Delta\bar{F}_l = -\bar{V}_l \Delta P \tag{2}$$

where  $\bar{V}_l$  is the partial molal volume of adsorbed water. For several water contents the value of  $\Delta\bar{F}_l$  was computed from the corresponding swelling pressure. Swelling pressures are normally determined at room temperature and can be corrected to lower temperatures by (Lewis and Randall, 1961, p. 165).

$$\frac{d}{dT} \left( \frac{\Delta\bar{F}_l}{T} \right) = + \frac{H_l^0 - \bar{H}_l}{T^2} \tag{3}$$

where  $H_l^0$  is the molar heat content of pure liquid water (the standard state) and  $\bar{H}_l$  is the molar heat content of the water in the liquid phase in the soil.

At the relative high water contents of interest in this paper, larger than 0.35 g of water per g of clay,  $H_l^0 - \bar{H}_l$ , is very close to zero (Mooney *et al.*, 1952) and a temperature correction for  $\Delta\bar{F}_l$  is not required. In Fig. 5,  $\Delta\bar{F}_l$  is plotted as a function of water content for both Na- and Ca-montmorillonite samples. Unfrozen water contents at any temperature can be obtained from this curve, by calculating  $\bar{F}_l$  from equation (1). For example, at  $-5^\circ\text{C}$ ,  $p^\circ$  is 3.163 mm Hg and  $p^\square$  is 3.013 mm Hg, which results in  $\Delta\bar{F}_l = 25.89$  cal/mole. Referring this value to Fig. 5, where water content is plotted versus

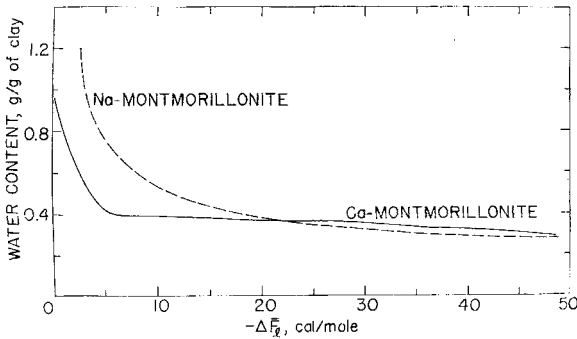


FIG. 5. Partial molar free energy of adsorbed water in cal/mole for Na- and Ca-montmorillonite valid in the temperature range from  $0^\circ\text{C}$  to  $-10^\circ\text{C}$ .

$\Delta\bar{F}_l$ ,  $-25.89$  cal/mole can be seen to correspond to 0.37 g of water in montmorillonite. Differentiating equation (1) with respect to pressure,  $P$  at constant temperature yields:

$$\frac{\delta}{\delta P} (\Delta\bar{F}_l) = \left( \frac{\delta F_s}{\delta P} \right)_T - \left( \frac{\delta F_l^0}{\delta P} \right)_T \tag{4}$$

and identifying the partial derivatives with respect to pressure as the molar volume of ice,  $V_s$ , and the molar volume of supercooled water respectively,  $V_l^0$ , one obtains after integration

$$(\Delta\bar{F}_l)_P = (V_s - V_l^0)(P - P_a) + (\Delta\bar{F}_l)_{P_a} \tag{5}$$



where  $P$  is any arbitrary pressure and  $P_a$  atmospheric pressure. At any one temperature all parameters in equation (5) are known,  $(\Delta\bar{F}_l)_{P=P_a}$  from the ratio of the vapor pressure of ice to supercooled water, and  $V_s$  and  $\bar{V}_l^0$  from handbook data. The value of  $(\Delta\bar{F}_l)_P$  at any temperature can be referred to Fig. 5 to obtain the unfrozen water content at pressure  $P$ . For example, at  $-5^\circ\text{C}$  and atmospheric pressure,  $\Delta\bar{F}_l$  is  $-25.89$  cal/mole, and at 1500 psi,  $\Delta\bar{F}_l$  was calculated from equation (5) to be  $-21.72$  cal/mole. The unfrozen water content is, thus, increased under 1500 psi at a temperature of  $-5.0^\circ\text{C}$  by  $0.03$  g per g of clay. In Fig. 6, the change in unfrozen water content caused

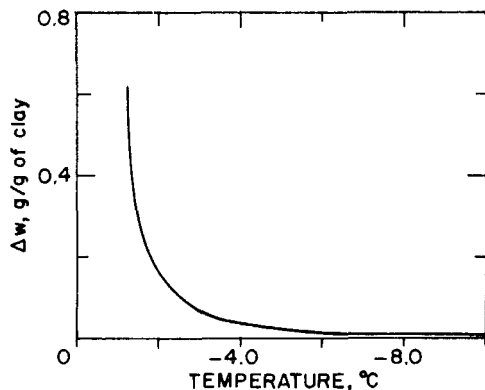


FIG. 6. Increase in unfrozen water in g per g of clay caused by a pressure of 1500 psi for Na-montmorillonite as a function of temperature below freezing.

TABLE 1.—INCREASE IN UNFROZEN WATER,  $\Delta W$ , CAUSED BY A PRESSURE INCREASE OF 1500 psi IN GRAM OF WATER PER GRAM OF CLAY FOR Ca-MONTMORILLONITE AT DIFFERENT TEMPERATURES BELOW FREEZING

Temperature, $^\circ\text{C}$	$\Delta W$ , g/g of clay
-1.0	0.295
-1.2	0.230
-1.4	0.145
-1.5	0.105
-2.0	0.010
-3.0	0.005
-4.0	0.005
-5.0	0.000
-6.0	0.010
-7.0	0.020
-8.0	0.015
-9.0	0.015
-10.0	0.020

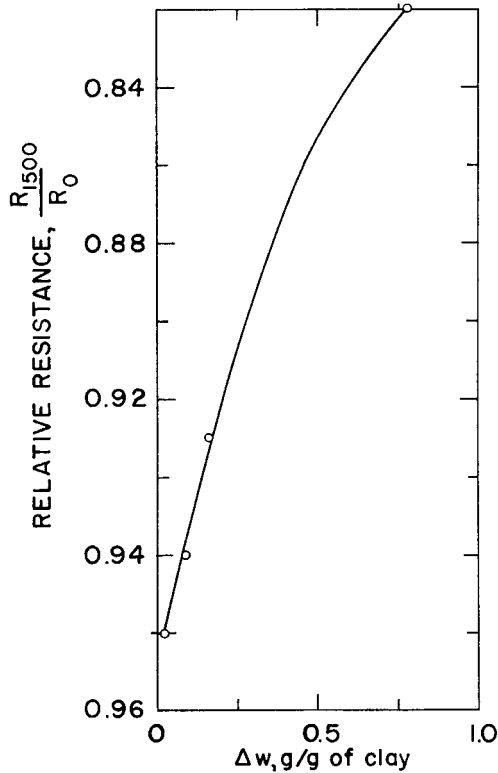


Fig. 7. Increase in unfrozen water caused by a pressure of 1500 psi as a function of relative resistance at 1500 psi.

by a pressure of 1500 psi is plotted as a function of temperature for Na-montmorillonite.

The conductance measurements provide only indirect evidence for the correctness of the procedures used in calculating the effect of pressure on the amount of unfrozen water in frozen suspensions. The value of  $(R_{1500})/R_0$  for Na-montmorillonite shows a continuous increase with increasing temperature below  $0^\circ\text{C}$ . The increase in the amount of unfrozen water caused by 1500 psi pressure shows the same general behavior. In Fig. 7 the increase in unfrozen water at 1500 psi pressure is plotted versus the corresponding value of  $(R_{1500})/R_0$ . It shows a consistent relation. For Ca-montmorillonite the plot of  $(R_{1500})/R_0$  shows a plateau ranging from a temperature of  $-7.5^\circ\text{C}$  to  $-3.0^\circ\text{C}$ . In Table 1 the effect of pressure on the amount of unfrozen water is given. There is essentially no effect of pressure on the amount of unfrozen water in the temperature range from  $-6.0$  to  $-3.0^\circ\text{C}$ . Also the increase in unfrozen water caused by pressure is considerably less for Ca-montmorillonite

than for Na-montmorillonite, which is also reflected in the values of  $(R_{1500})/R_0$ . The conductance data, thus, provide some confidence in the calculation used to determine the effect of pressure on the amount of unfrozen water.

The results reported here have a significant bearing on the theory of strength of frozen ground. Consider a stress applied to a local area of a frozen sample. The unfrozen water content in the vicinity of the stressed area will rise and a flow of unfrozen water could take place to areas of lower stress, much in the same way as flow of unfrozen water occurs under electrical and temperature gradients (Hoekstra and Chamberlain, 1964; Hoekstra, 1965). Tsytoovich (1959) postulated that even ice lenses could be transplanted by this mechanism in frozen soils. The films of unfrozen water will maintain a constant thickness determined by pressure and temperature and if the unfrozen water migrates through the unfrozen films, ice will melt to replenish the films of unfrozen water.

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