# Thermo-Osmotic and Thermoelectric Coupling in Saturated Soils

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Thermally induced flows of moisture and electricity in saturated clays were measured experimentally as the water content, exchange capacity, and pore-water electrolyte concentration were systematically varied. Prior work on thermoosmosis in soils is reviewed, and possible coupling mechanisms are discussed in the light of new experimental results.

The clay-water systems studied exhibited characteristic thermoelectric and thermo-osmotic effects. Measureable currents on the order of 1 to 10 microamperes per degC per cm were detected, with the warmer side having the more positive polarity. The thermoelectric current increased consistently with increasing water content, exchange capacity, or electrolyte concentration in the pore water.

Thermo-osmotic pressures on the order of a few tenths of a centimeter of water per degree Centigrade were measured with net flow occurring to either the warm or cold side. The peculiar temperature-dependence of activity coefficients of electrolytes in the pore water is suggested as a possible explanation for a given direction of moisture flow. Thermal contributions to moisture movement in saturated soils are minor compared to thermal moisture flow in partially saturated media.

•NORMALLY, we are accustomed to thinking strictly in terms of conjugate force-flux phenomena, i.e., a hydraulic gradient producing only a flow of water, an electric field producing only a flow of current, and so on. These conjugate force-flux relationships are described by well-known phenomenologic laws such as Darcy's, Ohm's, Fourier's, and Fick's. Coupling effects, on the other hand, arise when a driving force of one kind (e.g., a temperature gradient) produces a flow of another (e.g., an electruc current).

The present paper deals only with thermal coupling in clay-water systems. Results of electrokinetic studies and more general aspects of coupled flow phenomena in soils are described elsewhere by Gray and Mitchell (7), Gray (8) and Winterkorn (25).

Thermo-osmosis, a thermally induced flow of moisture in porous media, can occur under natural conditions. This phenomenon has attracted the attention of soil scientists because of its possible contribution to the net transfer of soil water and nutrients. To a lesser extent, thermo-osmosis has also been of interest to engineers because of its suspected role in problems dealing with frost heaving and moisture accumulation under pavements.

The engineering significance of thermoelectric coupling in soils is less apparent. It may be important in problems pertaining to corrosion of underground pipes carrying fluids at temperatures far above or below ground temperature. The existence of thermoelectric coupling in soils is yet another example of the extent of interaction that can occur between flows of moisture, heat, dissolved salts, and electric current in the ground.

The precise nature of thermo-osmotic flow is still not well understood. Several different transfer mechanisms have been proposed. Most of the research, both theoretical and experimental, has focused on inert, partly saturated systems where vapor phase transfer plays an important part. The nature of the thermo-osmotic process

becomes more complicated when the porous medium itself is charged or the permeant is an electrolyte. Thermal gradients then give rise to secondary electrical effects that should be taken into account.

The present paper presents results of thermo-osmosis tests with saturated, claywater systems in which the direction of flow was contrary to results usually reported in the literature. Various hypotheses that have been used to explain the nature of thermo-osmotic flow are briefly reviewed. A new hypothesis is tentatively advanced to explain the experimental results of the study.

#### **REVIEW OF PAST WORK**

#### Thermo-Osmosis

In reviewing both the past work on thermo-osmosis and the results of the present study it is essential to keep in mind some important distinctions. In the first place, it is necessary to consider whether the system is inert (i.e., uncharged) and whether only single-component flow of matter (e.g., pure water) occurs. Charged membranes or clayey soils saturated with electrolyte solution do not meet these criteria. In addition, it is necessary to distinguish between partially and fully saturated systems. In the former, thermo-osmotic flow may occur in both the vapor and liquid phase.

Thermo-osmosis across inert membranes has been investigated extensively by Haas and Steinert (10) and to a lesser extent by Rastogi et al (17) and Corey and Kemper (4). Cellophane, an inert membrane with a very small pore size (from 5 to 20 Å), was used in these studies. Significant thermo-osmotic flows from hot to cold were detected in cellophane membranes, the effect becoming more pronounced as the average pore size was reduced. Rastogi observed a linear relationship between temperature gradient and osmotic flow; however, the magnitude of this flow also varied with the mean temperature in the membrane.

Carr and Sollner (2) studied thermo-osmosis across charged membranes. They reported that the rate of thermo-osmotic flow varied in proportion to the temperature difference (as observed by other investigators), but in this case the proportionality factor depended strongly on the electrolyte concentration of the outer solution. A typical plot of thermally induced flow rate against the logarithm of the concentration gave a bell-shaped curve as shown in Figure 1. They concluded, therefore, that thermo-osmosis with electrolyte solutions is an electrochemical phenomenon and is related to electro-osmosis.

In 1965, Kobatake and Fujita gave a theoretical account of Carr and Sollner's earlier experimental findings. They likewise concluded that thermo-osmotic flow in a charged membrane-electrolyte system is caused by an electrical field set up in the membrane by the applied thermal gradient. Furthermore, they argued that the dependence\* of the electro-osmotic coefficient on the electrolyte concentration of the outer solution also explains the characteristic behavior of thermo-osmosis in charged membranes.

Thermo-osmosis has been studied extensively in partially saturated soils by Bouyoucos (1), Smith (18), Gowda et al (6), Gurr et al (5), Taylor et al (20, 22), and Philip and deVries (16). Although thermally induced flow of moisture in the vapor phase (from warmer to cooler areas) is widely believed to be the dominant transfer mechanism, film flow in the liquid phase cannot be ruled out (Winterkorn, 23).

Vapor phase transport is believed to result mainly from a molecular diffusion process. Convection also plays a minor role as shown by Taylor and Cavazza (20). Moisture tends to evaporate at the warmer side and condense at the colder side, thus maintaining a vapor pressure gradient.

<sup>\*</sup>The electro-osmotic transport coefficient (i.e., the amount of water transferred per unit charge) also depends on the fixed membrane charge as described by Gray (8).





Figure 1. Typical dependence of thermo-osmotic flow on concentration of external electrolyte in a negatively charged, acidic membrane (after Carr and Sollner, 2).

Figure 2. Thermo-osmotic pressure as a function of temperature gradient for various mean temperatures, Orly silt (after Habib and Soeiro, 9).

Transport in the liquid phase, either in thin films or small capillaries, is more complex. Cary (3) has suggested four possible mechanisms:

1. Thermally induced surface tension gradients or differences in soil moisture suction;

2. Differences between specific heat content of adsorbed water on solid surfaces and the bulk liquid in the pores;

3. Random kinetic energy changes associated with hydrogen bond distributions that develop in thermal gradients; and

4. Thermally induced osmotic or electro-osmotic gradients.

Thermo-osmosis in saturated soils has received only limited attention. The transfer mechanism in this case is poorly understood. Vapor phase transport must be ruled out, and, since there are no air-water interfaces, surface tension gradients can also be eliminated as a possible transfer mechanism.

Taylor and Cary (21) investigated thermo-osmosis in a saturated Millville silt loam, and Habib and Soeiro (9) in a saturated Orly silt. The results of the latter investigation are shown in Figure 2. Both studies report a flow of water from the higher toward the lower temperature. Habib and Soeiro reported that water movement was greatly amplified when electrolytes were mixed with the soil. Haas and Steinert (10) also reported a large increase in thermo-osmosis when a charged membrane was inserted adjacent to and in series with an inert cellophane membrane.

Cary (3) tabulated available data on the magnitude of thermally induced moisture flow in porous media. His summary included both artificial membranes and soils in various states of saturation. He was able to compare the effects of various parameters such as mean temperature, hydraulic conductivity, and initial moisture content. Cary's summary is reproduced in Table 1. All thermal moisture flows reported in Table 1 were from warm to cool.

The data in Table 1 show that thermal moisture flow is far greater in partially saturated as opposed to fully saturated soils. In unsaturated soils the relative importance of thermally induced flow rises rapidly as the moisture content decreases. Compared with moisture flow under hydraulic gradient, thermal moisture flow becomes relatively more important as the hydraulic conductivity decreases. In saturated media the thermo-osmotic pressure tends to increase with increasing mean temperature.

Type of Porous Material	Moisture Content or Suction, bars	Thermal Flow, mm H <sub>2</sub> O/day/ °C/cm	cm H₂O Head Equiv. to 1 C Gradient	Mean Temper- ature	Type of Solution Flowing	Phase of Flow
Sintered glass 10 <sup>4</sup> Å						· · · ·
mean nore diameter	Saturated	0	0	25	Distilled water	Liquid
Du Pont 600 cellophane	Saturated	0. 1	-	40	Double-distilled	Liquid
Cellulose acetate, 27 Å					water	
mean pore diameter	Saturated	- ·	7.0	20	Distilled water	Linuid
Millipore filter, 100 Å						
mean pore diameter	Saturated	-	0.09	20	Distilled water	Liquid
Wyoming bentonite						
paste, 18 percent	Saturated	0.1	4.0	35	0.1 N NaCl	Liquid
Yolo loam soil, $B = 1.4$	0.06	2.0	5.5	35	0.01 N CaSO4	Liquid + vapor
Houston black clay	0.66	0.7	-	38	Distilled water	Liquid + vapor
Houston black clay	1.4	0.8	-	37	Distilled water	Liquid + vapor
Millville silt loam,						
B = 1.5	Saturated	_	0.07	25	Water	Liquid
Millville silt loam	2.2	-	$1.4 \times 10^3$	25	Water	Vapor + liquid
Millville silt loam	126	_	8.3 × 10 <sup>4</sup>	25	Water	Vapor
Columbia loam, B = 1.2	0.07	1.8	3	19	Distilled water	20 percent vapor,
Columbia loam, B = 1.2	0.24	0.9	13	8	Distilled water	33 percent vapor, 67 percent liquid
Columbia loam, B = 1.2	0.24	2.0	14	33	Distilled water	55 percent liquid 55 percent vapor, 45 percent liquid
Columbia loam. B = 1.2	0.45	1.6	250	25	Distilled water	Vanor + liquid
Stable air	100 percent porosity	0. 4	8 × 10 <sup>4</sup>	27	Distilled water	vapor

<sup>a</sup>From Cary (3).

# Thermoelectric Coupling

Electrical effects associated with thermal osmosis—particularly in charged membranes containing electrolytes—have probably not been fully appreciated. In unsaturated soils the electrical influence on thermo-osmosis can perhaps be disregarded because of the dominant role of vapor phase transfer. In saturated media, on the other hand, electrical effects become important in characterizing thermo-osmosis. Even Aubert in his early work concluded that thermo-osmosis was electrical in its origin and was related to electro-osmosis.

Thermoelectric membrane potentials are difficult to isolate because the measured emf's include electrode potentials that must be evaluated and taken into account. Nevertheless, thermoelectric potentials on the order of 0.05 mv/deg C have been reported by Ikeda (12) for dilute KCl solutions and a cation selective collodion membrane. The warmer side had the more positive potential. Thermoelectric potentials with a typical value of 0.3 mv/deg C for sandstones and shales have been reported by Madden and Marshall (15). They did not give the polarity of the potentials.

Simultaneous measurement of induced electrical current during thermo-osmosis has been carried out by Gowda et al (6) in clay soils and by Taylor and Cary (21) and Habib and Soeiro (9) in a silt loam. They detected small currents (generally decreasing with time) on the order of 1 to 5 microamps. Taylor reported a current flow from cold to warm; however, there was considerable fluctuation in the induced electrical current and potential indicating instability in the electrodes (brass screens) and the electrical properties of the system. Habib and Soeiro do not give the polarity of their measured currents; they furthermore dismiss the electric current as an electrode phenomenon. Neither of these latter investigators made provisions for the use of reversible electrodes nor were the test conditions well-suited for the detection and evaluation of electrical effects.

# APPLICATION OF IRREVERSIBLE THERMODYNAMICS TO THERMAL COUPLING

As Winterkorn pointed out (25), the theory of irreversible or non-equilibrium thermodynamics is a convenient means of analyzing the simultaneous flows of water, heat, salts, and electric current in porous media. A detailed account illustrating practical applications of the theory has been given by Katchalsky (13) and Taylor (19).

Taylor and Cary (22) outlined a theoretical analysis based on the thermodynamics of irreversible processes for evaluating coupled flows of heat and water in continuous soil systems. Taylor (19) also derived the following phenomenologic equation for describing the simultaneous transfer of water and heat across a discontinuous system, viz., an inert membrane or porous soil plug:

$$J_{w} = \frac{L_{ww} v_{w}}{T} \Delta P + L_{wq} \frac{\Delta T}{T^{2}}$$
(1)

$$J_{q} = L_{qw}v_{w} \Delta P + L_{qq} \frac{\Delta T}{T^{2}}$$
(2)

where

 $J_w \prime J_a$  = the net fluxes of water and heat respectively;

 $\Delta P$  = hydraulic pressure drop across the porous plug;

T =the absolute temperature;

 $L_{ww'}$   $L_{qq}$  = direct transfer coefficients, e.g., the hydraulic and Fourier heat conduction coefficients respectively; and

 $L_{wq}$ ,  $L_{qw}$  = coupled transfer coefficients.

The following assumptions were made in the derivation of these equations:

- 1. There is only single-component flow of matter, viz., pure water.
- 2. The system is inert and no chemical reactions occur within it.

3. External force fields are absent or cancel out.

4. The system is never too far from equilibrium, i.e.,  $\Delta \mu_W << RT$  and  $\Delta T << T$ .

5. Linearity exists between forces and fluxes.

The derived equations are in finite difference form, i.e., they have been integrated over the thickness of the membrane or porous soil plug. This is not as rigorous a formulation as it is when the phenomenologic equations are left in differential form. In this latter case, the driving forces are usually expressed as gradients and the flows are defined only locally at a point within the system (Taylor and Cary, 22). The finite difference form is probably more useful for experimental purposes. It assumes, however, that suitable "averages" can be found for the coefficients,  $L_{ik}$ , and the temperature, T, within the temperature interval,  $\Delta T$ , of interest.

Equation 1 states that the net flux of water is the sum of two transfer processes that can occur simultaneously. The first is the flow of water that is controlled by the pressure difference,  $\Delta P$ , and the hydraulic conductivity of the soil; the second is the flow of water that is induced by a temperature difference,  $\Delta T$ .

These equations are in fact specific cases of a general relationship in irreversible thermodynamics, viz., the allowable superposition of contributions to a given flux from both conjugated and non-conjugated driving forces alike. The principle of linear superposition and the force-flux relationships are expressed in mathematical shorthand by

$$J_{i} = \sum_{k=1}^{n} L_{ik} X_{k} \quad (i, k = 1, 2, 3, ... n)$$
(3)

where the  $J_i$  and  $X_k$  are generalized fluxes and forces respectively and the  $L_{ik}$  are the phenomenologic transport coefficients previously defined.

When an external temperature gradient is applied across a soil plug the system eventually tends toward a steady-state condition. If a counter osmotic pressure is allowed to build up in response to a thermally induced flow of water, the net flux of water will vanish at the steady state, i.e.,  $J_w = 0$ . Under these boundary conditions Eq. 1 may be written as

$$\left(\frac{\Delta \mathbf{P}}{\Delta \mathbf{T}}\right)_{\mathbf{J}_{\mathbf{W}}=\mathbf{0}} = \frac{-\mathbf{L}_{\mathbf{W}\mathbf{Q}}}{\mathbf{L}_{\mathbf{W}\mathbf{W}}\mathbf{V}_{\mathbf{W}}\mathbf{T}} = \frac{-\mathbf{Q}^{*}}{\mathbf{V}_{\mathbf{W}}\mathbf{T}}$$
(4)

where Q\* is the so-called heat of transfer. Equation 4 indicates that the excess of pressure (the thermo-osmotic pressure) that will build up on the hot (or cold) side of a system in response to a unit temperature difference,  $\Delta P/\Delta T$ , depends on the heat of transfer, Q\*, the specific volume of water, V<sub>w</sub>, and the average temperature of the system, T. The heat of transfer in turn is a function of the physical properties of a membrane or porous plug. In general, Q\* increases with decreasing pore size and increasing temperature.

At present there are no a priori grounds for predicting the sign of  $Q^*$  in saturated systems, i.e., which direction the thermally induced flow of water will take. The exact mechanism of coupling between matter and heat flows is not well understood. In unsaturated systems a net flow of water to the cold side has always been observed. This is understandable because of the dominant role of vapor phase transport that occurs towards the cold side. In experiments with saturated systems using cellophane (Haas and Steinert, 10), silty soils (Taylor and Cary, 21, and Habib and Soeiro, 9), and charged membranes (Carr and Sollner, 2), a flow of water to the cold side has always been reported.

One of the purposes of the present study was to determine not only the magnitude of thermo-osmotic coupling in saturated clay-water-electrolyte systems but also the direction. A clay-water system is much more complex because one is no longer dealing with an inert, single-component system (an assumption contained in Eqs. 1, 2, and 4). Applied thermal gradients will now give rise to thermoelectric and secondary electro-osmotic effects. The possibility of thermally induced osmotic gradients deserves careful consideration.

In this regard it is useful to keep in mind that temperature affects the activity coefficients of dissolved salts or ions in the pore water, and this in turn affects the chemical potential of water. The standard expression for the chemical potential of a species, "i", in terms of its activity is given by

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

and the relationship between chemical potential of a dissolved solute,  $\mu_{\rm S}$ , and that of its solvent (water),  $\mu_{\rm W}$ , is given by a form of the Gibbs-Duhem equation,

$$d\mu_{W} = -\frac{n_{S}}{n_{W}} d\mu_{S}$$

where  $\mu_i$  = chemical potential of species i,

 $a_i = activity potential of species i,$ 

 $n_i$  = number of moles of species i,

 $\bar{\mathbf{R}}$  = molar gas constant, and

T = absolute temperature.

Assuming the number of moles of solute and solvent are fixed, their chemical potentials are exactly inversely related. Thus, an increase in solute activity due to temperature will produce an increase in solute chemical potential and a corresponding decrease in solvent (water) chemical potential. The dependence of solute activity on

(5)

· (6)



Figure 3. Mean activity coefficient of sodium chloride in 0.1 to 4.0 molal solutions as a function of temperature (after Harned and Owen, 11).

temperature (and concentration) has been measured by Harned and Owen (11). Typical response curves for sodium chloride are shown in Figure 3.

# EXPERIMENTAL PROCEDURE

Thermal coupling experiments were run in conjunction with electrokinetic experiments; the latter are described elsewhere (Gray and Mitchell, 7). The effects of a systematic variation in water content, exchange capacity, and external electrolyte concentration on thermal coupling were investigated. Other variables, such as the type of counterion and the degree of saturation, were held constant by restricting the investigation to fully saturated, sodium clays. A detailed account of the experimental procedure has been given (8); salient features are summarized in the following.

#### Materials and Apparatus

Experimental data were obtained on three types of material: a pure kaolinite (Hydrite UF), an illitic clay (Grundite), and an artificial silty-clay comprised of equal parts by weight of kaolinite and silica flour.

The clays were made as nearly homoionic to sodium ion as possible by washing batches of clay in concentrated solutions of sodium chloride. The excess salt was then removed by leaching the clays with distilled water. The clays were subsequently dried in an oven at 230 F, lightly pulverized, and stored in sealed jars for further use. Weighed amounts of each clay were later mixed with the desired electrolyte solution into thick slurries prior to their introduction into a specially constructed flow cell.

The flow cell itself was designed so that known thermal, electrical, and hydraulic

pressure gradients could be applied across the clay samples. Provisions were made to monitor the flows of electricity and water (or solution) that resulted from the application of any one of these gradients. The flow cell was bounded at two ends with retractable pistons, each with a recessed porous stone and electrode in its face. By placing the flow cell assembly in a loading frame it was possible to reduce the water content to any predetermined level. A schematic diagram of the flow cell and test layout is shown in Figure 4.

## Thermo-Osmotic and Thermoelectric Tests

Internal heating and cooling coils were installed in the piston heads in order to establish a temperature gradient across the clay sample for thermal coupling tests. The heating and cooling coils in turn were connected to external constant temperature circulators. Temperatures were monitored with thermistor probes and a digital thermometer. The flow cell and test equipment were kept in a constant-temperature room maintained at 20 C.



Figure 4. Schematic diagram of flow cell and test layout.

Thermo-osmotic pressures were measured in lieu of osmotic flow rates; this procedure was adopted for experimental convenience. The standard procedure was to apply a temperature gradient across a clay sample and observe the buildup in pressure as indicated by the rise or drop of water level in standpipes on either side. The ends of the clay plug were electrically short-circuited through an ammeter and the induced thermoelectric current recorded concurrently with the thermo-osmotic pressure. Reversible silver-silver chloride electrodes were used to measure the current; chloride solutions were used as the permeant in all tests.

Upon applying a temperature gradient, the water level quickly rose in the standpipes because of an initial thermometric expansion, but the two levels equalized because the standpipes were connected by an open bypass valve. Periodic temperature readings were taken to determine how quickly the system approached a steady-state distribution. Five hours proved to be an adequate time interval for temperature stabilization.

At the end of five hours, the bypass valve was closed and a temperature-induced pressure difference could develop across the clay plug. The pressure difference was directly proportional to the difference in water level in the two standpipes. The levels were read with the aid of a cathetometer. Periodic readings of the pressure difference were taken until an equilibrium pressure was reached. This was taken as the steady-state condition at which the volume flow vanishes,  $J_v = 0$ . The pressure difference at this point was the thermo-osmotic pressure of interest.

Simultaneous readings of the thermoelectric current were also taken. A continuous and characteristic plot of current vs time for each clay-water system was obtained in this manner.

#### RESULTS

A typical thermo-osmotic pressure buildup curve for kaolinite is shown in Figure 5. A gradient of approximately 1 C/cm and a mean temperature of about 26 C were common to all tests. Steady-state thermo-osmotic pressures are shown plotted vs water content in Figure 6 for the various clay-water-electrolyte systems. Except in two instances, the pressure rise always occurred at the hot side.

Typical thermoelectric behavior of the clay-water systems is shown in Figures 7 and 8. The induced thermoelectric current is shown plotted as a function of time for



Figure 5. Thermo-osmotic pressure buildup in kaolinite.



Figure 6. Thermo-osmotic pressure vs water content in clay-water-electrolyte systems.

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Figure 7. Thermoelectric current vs time in kaolinite for various water contents and normality of saturating solution. Average temperature gradient is 1 C/cm.



Figure 8. Comparison of thermoelectric curve envelopes for three clays.

various water contents and pore-water electrolyte concentrations in Figure 7. The electric current flow was always from hot to cold, i.e., the hot side had the more positive polarity. The current tended to increase as either the salinity of the saturating solution or the water content was increased. A comparison of the thermoelectric behavior of the three clay systems is shown by a plot of thermoelectric curve envelopes in Figure 8. For a given saturating solution and temperature gradient, the thermoelectric current increased with increasing exchange capacity of the clay.

The initial buildup in current shown in Figures 7 and 8, which reached a peak after one or two hours, is partly a streaming current effect caused by thermometric expansion and expulsion of water from the voids. This could be verified by noting an almost identical response (but with opposite polarity) when the sample was allowed to return to thermal equilibrium.

#### DISCUSSION AND CONCLUSIONS

Thermo-osmotic flow in saturated, clay-water systems is comparable in magnitude but opposite in direction to results reported by other investigators (see Table 1).

The polarity of the thermoelectric current in a clay-water system agrees with that observed by Ikeda (12) for a negatively charged, collodion membrane. While electrode potentials may have contributed to the induced current in the former, they cannot explain the systematic variation in thermoelectric current with exchange capacity, water content, and concentration of external electrolyte as shown in Figures 7 and 8.

A possible explanation for the direction of thermo-osmotic flow as reported herein may lie with the peculiar dependence of activity coefficients on both temperature and concentration shown in Figure 3. A difference in activity coefficient of solvent (or solute) between the warm and cold sides of a porous medium produces a difference in chemical potential. This means that a flow of solvent or salt must then occur to equalize this imbalance. The results in Figure 3 are for bulk electrolyte solutions; to test out the hypothesis further it would be necessary to determine activity coefficients for soil water electrolytes over a range of concentrations and temperatures. The concentrations shown in Figure 3 lie within the range of counterion concentrations one might expect in the interstitial water of a charged, porous medium such as a clay soil.

The preceding explanation assumes that thermally induced osmotic gradients are the dominant transfer mechanism in saturated, charged membrane systems. If secondary electro-osmotic effects are the cause, then a positive polarity is required at the cold side to produce a flow to the hot; however, the reverse was observed in the present study. Thus, an electro-osmotic explanation is apparently ruled out.

The results of this study confirm earlier investigations in suggesting that the relative magnitudes of thermally induced moisture flows are not particularly significant in saturated soils. The same is not true, it should be emphasized, in the case of partially saturated soils.

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