# FUNDAMENTAL SIMILARITIES BETWEEN ELECTRO-OSMOTIC AND THERMO-OSMOTIC PHENOMENA

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#### SYNOPSIS

The general theory of electro-osmosis in soils is presented, analysed on the basis of old and new experimental evidence and reduced to a form which can be easily employed for engineering purposes. Data on electro-osmosis in homoionic soils demonstrate the yield reducing effect of ionic conductance, and the importance of physico-chemical soil factors.

A new theory is presented for thermo-osmotic flow in soils, which is based on the original film flow concept of Bouyoucos, and on the experimentally observed fact that the water-affinity of soil decreases with increasing temperature. This theory is also reduced to a form which is directly useful in the hand of the engineer.

Evidence is presented that there exists a close fundamental relationship between electro- and thermo-osmotic phenomena and that thermal waves penetrating into the soil are accompanied by electrical waves. The general importance of this phenomenon is indicated.

Within recent years electro-osmotic phenomena have been applied to practical soil drainage and to soil stabilization problems  $(3, 4, 5, 7)^1$  while thermo-osmosis has been recognized as an important factor with respect to accumulation of water or desiccation underneath pavements. There exist indications that thermo-osmosis may also be utilized in engineering practice in a way similar to the presently evolving use of electro-osmosis. Best possible utilization of either phenomenon must, obviously, be based on an understanding of the fundamental mechanisms involved.

### BASIC THEORY OF ELECTRO-OSMOSIS

The phenomenon of water-movement in a capillary system resulting from application of an electric potential appears to have been first described by Reuss in 1808 (11). Major subsequent experimental contributions were made by Wiedemann (14) and by Guincke (10). Theoretical development is due mainly to Helmholtz who introduced the electric double-layer concept and formulated the still accepted theory of electro-osmosis. Gouy contributed the diffuse double-layer concept (16), which was developed further by Debye and his co-workers.

The systems in which electro-osmosis occurs, may be single capillaries, bundles of

<sup>1</sup> Italicized figures in parentheses refer to list of references at the end of the paper.

capillaries, or porous materials (diaphragms), of natural or artificial origin, such as porous ceramics, soils et alia. The liquids may be water, or any other liquid substance, possessing low, or best, no electric conductivities. The greater the electric conductivity of the liquid, the lower is the efficiency of electroosmotic water movement.

For easy demonstration of the theory, a capillary filled with water is employed. It has been found empirically that the water in such a capillary moves under an electric potential. For this reason it must be assumed from the laws of electricity that the cylindrical surface of the liquid carries a charge which must be equal and opposite to one carried by the capillary wall. The charge carried per cm. length of the surface of the liquid cylinder shall be called e, and the electric potential of the applied field shall be called E. The electric force acting on this cylinder section as a result of the applied potential is then:

$$F_e = eE \tag{1}$$

This liquid-sclid system represents a cylindrical condenser with a capacity:

$$C = \frac{DS}{4\pi d}$$
 in which

D = dielectric constant of water

- S =surface area of the condenser
- d = distance between center of charges on solid cylinder wall and on surface of moving liquid cylinder, respectfully.

If the capillary possesses a circular cross section and a radius r, then S becomes numerically equal to  $2r\pi$  and:

$$C = \frac{2r\pi D}{4\pi d} = \frac{Dr}{2d}$$

In such a condenser, an electric potential  $\varphi$  is established between the adjoining charged surfaces. This interfacial potential is equal to the quotient of charge over capacity, or:

$$\varphi = \frac{e}{C} = \frac{e^2 d}{Dr}$$

Consequently the charge e can also be expressed as a function of the interfacial potential  $\varphi$ , viz:

$$e = \frac{\varphi D \eta}{2 d}$$

The electric force  $F_{e}$  acting on the interface per unit length, in the direction of the applied potential E is then:

$$F_e = eE = \frac{\varphi DrE}{2d} \tag{2}$$

This force which tends to move the liquid water is resisted by the internal friction or viscosity of the latter. This resisting force  $F_r$  depends on the viscosity  $\eta$  of the liquid and can be expressed as:

$$F_r = S_\eta \frac{\Delta v}{\Delta r}$$
, in which (3)

S = surface of the liquid cylinder of 1-cm. length, =  $2\pi r$ ;

 $\frac{\Delta v}{\Delta r}$  = rate of velocity change with increasing

distance from the capillary wall.

Assuming that  $\frac{\Delta v}{\Delta r}$  is constant and, therefore, equal to  $\frac{v}{d}$ , we obtain for steady flow condition, where the moving and resisting force are equal to each other:

$$F_{e} = F_{r}$$
, or  $\frac{Dr\varphi E}{2d} = \frac{2\pi r\eta v}{d}$ ; (4)

and for the velocity of flow v:

$$v = \frac{D\varphi E}{4\pi\eta} \tag{5}$$

The volume V of liquid transported through the capillary in unit time is equal to the product of velocity and cross section of the capillary or:

$$V = \pi r^2 v = \frac{\phi \pi r^2 DE}{4\pi \eta} = \frac{r^2 D\varphi E}{4\eta} \qquad (6)$$

This equation demonstrates that:

1. The amount of water flowing through a capillary under the action of an electric field is directly proportional to the square of its radius, to the applied potential, and to the factor  $\frac{D\varphi}{4\eta}$ 

2. Keeping in mind that the interfacial potential  $\varphi$  is directly proportional to the charge e located on the surface of the moving liquid cylinder of 1-cm. length, it becomes clear that the amount of liquid moved by electroosmosis is directly proportional to the amount of electricity conducted by the same phenomenon. This relationship is known as Wiedemann's law.

Consideration of  $\varphi$ , D, and n—The values found in the literature for the dielectric constant D and the coefficient of internal friction  $\eta$  are statistical averages; this means, they have been obtained by measurements involving large numbers of molecules. These statistical values for D and  $\eta$  are constant for a certain temperature. On the other hand, interfacial phenomena involve only a limited number of molecules, and the statistical values hold only rarely, if at all, in such cases. It is well known that the dielectric constant D for water decreases quite considerably in the vicinity of electrically charged ions and surfaces. Also, a great deal of evidence exists to indicate that the viscosity  $\eta$  of water increases with decreasing distance from a surface of strong adsorption character. The interfacial potential  $\varphi$  can not be determined by itself, but is always associated with D and  $\eta$ . For this reason, the numerical values given for interfacial potentials in the literature (these potentials are usually called  $\varphi$ -potentials if calculated from electro-osmotic measurements and  $\zeta$ -potentials if calculated from electrokinetic measurements) depend on the choice of the values for the employed dielectric constant and coefficient of internal friction, respectively. Under these conditions, it is

more scientific and certainly more practical not to attempt to separate the factor  $\frac{D\varphi}{4\eta}$ but to use it as a whole, and to express it more simply as  $k_* = \frac{D\varphi}{4\eta}$ . This  $k_*$  is a characteristic constant for a specific solid-liquid interfacial system, and is a function of temperature. It must be determined experimentally for each soil-water system (and of course for any solidliquid system) under consideration (10).

It is possible now to write the formula expressing the volume V of liquid transported in unit time through the capillary of unit length under a potential E (volt per cm.) as follows:

$$V = r^2 k_s E \tag{7}$$

In engineering usage, flow through porous systems is normally expressed as the volume (or a linear dimension of the volume—cm. as employed by Darcy) which flows through a cross section of 1 sq. cm. of the system.

If 1-sq. cm. cross section of a capillary system contains a number  $n_{c}$  of capillaries, then the respective volume of flow is:

$$Vn_{e} = r^{2}k_{e} En_{e} \tag{8}$$

Since the product of the cross section of a single capillary and the number of capillaries per unit area is a two dimensional expression of the porosity of the capillary system; i.e. since the porosity n of the system can be expressed as:

$$n = r^2 \pi n_c$$
, we can write  
 $Vn_c = \frac{k_c n}{\pi} E;$ 

introducing  $V_p$  for  $Vn_e$  and

k for 
$$\frac{k_{\theta}}{\pi}$$

we can write:

$$V_p = nkE; \text{ or for } nk = k_0 \tag{9}$$
  
$$V_p = k_0E \tag{9a}$$

This equation states that the volume of liquid moved in unit time through a unit cross section of a porous system is directly proportional to the applied potential E, to the porosity n, and to a material constant k, the

latter being an expression of the electric, dielectric, and viscosity interrelationship at the solid-liquid interphase.

It is extremely important that this volume of flow is *not* a function of the individual pore size, but rather of the porosity n of the system. In other words, for the same surface-chemical character of the solid, the same liquid, and the same temperature, the amount of liquid moved per unit time and unit cross section under the same potential should be thesame for sands, silts, and clays, as long as their porosity is the same.

It should be noted that the simplified formula (9a) for electro-osmotic flow, is of the same form as that developed by Darcy for flow under a hydrostatic head. This being the case, the great amount of theoretical and practical knowledge assimilated by the engineering profession concerning flow through porous systems under a hydrostatic head, (flow nets for all types of conditions, theory and practice of well-points and injections, et al.) can be utilized "mutatis mutandis" for the problem of electro-osmotic drainage. On the other hand, the same problems which still are unsolved in the flow of liquids in unsaturated systems, also exist and are practically untouched in the field of electro-osmotic drainage.

Interfacial Relationships—It has been brought out above that in a saturated capillary system electro-osmotic permeability is a function only of the porosity and of the physicochemical interrelationship between solid surface and liquid. Attention must, therefore, be paid to the latter. Accepting Gouy's concept of the diffuse double layer and the experimental evidence that the viscosity of water increases with increase in strength of an electrostatic adsorption field, it follows that the shear plane in the liquid cylinder will be located at a distance from the solid surface where the electric moving force per sq. cm. equals the shear resistance per sq. cm. of the water. This distance, of course, varies with the electric surface structure of the solid wall and with the liquid employed. However, at this significant distance, the force and resistance picture should be very much the same for different natural soils. Consequently, as long as the water content of such systems is relatively large, and the "natural" shear-film

thickness small as compared with the pore dimensions, the electro-osmotic conductivity of soil-mineral systems should be to the greatest extent a function of the capillary pore space. This seems to be borne out by practical results obtained in engineering field and laboratory work with natural soils at moisture contents above the plastic limit, and employing low voltages per cm. This application is named electric drainage; it appears that for this use, the simple Helmholtz theory gives a reasonably representative picture.

The presented simple theory is, however, no longer applicable, when the moisture contents are sufficiently low that the shearing surfaces must pass through water layers which are within the electrostatic attraction field of the solid surface. Experimental evidence for this statement was provided by Quincke (10) almost 90 years ago. Among numerous electro-osmotic transference experiments, this author compared the water yield obtained with a capillary in which a glass rod was introduced to make a ringlike cross section for the moving liquid (I), with the yield obtained in a capillary with normal circular cross section (II). The dimensions of the two capillary systems were as follows:

	I	п
Radius of capillary in cm	0.0438	0.0264
Radius of rod in cm	0.0364	
Cross section of capillary in sq. cm	0.00604	0.00219
Cross section of rod in sq. cm.	0.00416	
Available cross section in sq cm	0.00188	0.00219
Perimeter/cross section in cm <sup>-1</sup>	268	76
Ratio of cross sections I/II	0.86	

Water transfer for the same electric conditions was 30 times greater for System I than for System II. According to the Helmholtz theory which localizes the moving force, and consequently the prime moving layer, in close vicinity to the perimeter, the respective ratio should be 268/76 or 3.5.

Quincke (loc. cit.) also observed in all his work with capillaries that the central part of the meniscus moved first upon application of the electric potential, a fact which hardly agrees with the Helmholtz assumption that the moving force is located in immediate vicinity of the wetted perimeter.

The cited evidence indicates that:

1. The electrifying influence of the charged solid surface extends to an appreciable distance into the liquid.

2. The applied electric potential acts on all molecules (and ions) within the sphere of in-

fluence of the electric field originating from the solid perimeter area, and that these molecules move as a direct consequence of their electric state and the applied potential rather than as an indirect consequence through transmission of momentum from a moving layer vicinal to the wetted perimeter.

3. There exists at low moisture contents a minimum applied potential—a type of electric yield value—which must be applied to obtain observable electro-osmotic flow.

4. There exists an optimum moisture content resulting in maximum water yield for a certain applied electric potential.

To these conclusions we may add one derived from molecular-theoretical considerations viz. that below the above named "yield" potential, electro-osmotic flow will not stop entirely, but that very slow flow will take place which may properly be called electro-osmotic creep.

So far, we have been dealing with pure electric-osmotic flow, i.e. one in which the electricity is carried solely by the molecules of the liquid dielectric. Such pure electroosmosis does not exist in normal soils possessing exchangeable cations and dissolved electrolytes. These ions, participate in the electric conductance and in water transfer, the water yield becoming less with increasing electric conductance of the soil moisture. The exchangeable ions are carried away in the process and are replaced by hydrogen ions.

At characteristic potential levels the clay minerals themselves are attacked with a consequent change in their adsorptive properties. Considering the physico-chemical activity of the internal surface, it follows that by choosing proper metal anodes it is possible to introduce desired cations into the system which can be fixed by the internal soil surface. Another possible development which renders desirable understanding of the actual surface-chemical mechanism involved in electro-osmosis is the potential use of hollow perforated anodes for the purpose of introducing liquid dielectrics other than water in order to replace the moving water and to assure continued removal of the water without having to resort to extremely high voltages as is normally required when the system dries out in the vicinity of the anode.

Very little is known concerning the practical possibilities of these variations, and there exists, therefore, a great and promising field of research along these lines, accompanied by a definite need for more fundamental experimental data on which a satisfactory and practically useful theory might be based.

Experimental Work on Electro-Osmosis—As a contribution in this direction, an experimental investigation was undertaken at our laboratory by Jose L. Escobar, employing a New Jersey Hagerstown clay and seven homoionic modifications. The composition and properties of the natural soil are given in Table 1.

TABLE 1 PROPERTIES OF THE NATURAL N. J. HAGERSTOWN SOIL

Separate	Size	Percentage found		
		Bouyoucos	ASTM	
	mm.			
sand silt clay colloids	1.00-0 05 0 05-0 005 <0.005 <0.002	10.5 51 5 38.0 20.0	$     \begin{array}{r}       12.2 \\       74 2 \\       13 6 \\       6.7 \\     \end{array} $	

Base exchange capacity of natural soil: 9.6 milliequivalents per 100 g.

			Moisture Density Relationships			
Liquid Lımıt	Plastic Index	age Lum.t	Proctor		Modified AASHC	
		Water	Density	Water	Density	
			%	lb. per cu. fl.	%	lb per cu fl.
29.5	7.7	20.5	18.8	103	16.5	113

The H-, Fe-, and Al-modifications were prepared by leaching the natural soil with dilute hydrochloric acid and with solutions of FeCl<sub>3</sub> and AlCl<sub>3</sub>, respectively, followed by washing with distilled water until no traces of Cl could be detected in the spent washing water. The Na-, K-, Mg-, and Ca-modifications were prepared by reaction of the H-soil with the calculated amounts of the respective hydroxides. Sufficient time was allowed to ensure complete reaction with the hydroxides of low solubility. The natural and homoionic soils were dried at 70 F. and crushed to pass a No. 10 sieve.

# Apparatus and Test Procedure—The following items of equipment were employed:

1. power supply unit, D.C., from 20 to 500 volt;

2. volt meter multitester (Radio City);

3. Weston 150 mA-meter;

4. 1300 ohm slide-wire;

5. cylindrical glass cells 4 in. long, 2-in. diameter;

6. small graduates for water collection and measurement;

7. aluminum electrodes.

Samples representing 200 g. of dry soil were mixed with an amount of distilled water approximately equaling the liquid limit of the respective soils and compacted into the glass cylinders. The aluminum electrode plates were placed in contact with the soil and clamped tightly by means of an appropriate device made of aluminum tubes, glass-rods, and rubber bands. It was attempted to hold the current at a constant intensity of 30 mA. However, this intensity had to be reduced when the resistance of the sample became so large that the power supply was insufficient to maintain it. This was the case for the Al- and H-soils.

Test Results—The test results are presented in three ways complementary to each other:

1. Description of reaction picture for the different soil modifications

2. Graphical presentation of relationship between released water and employed coulombs, volts, and watt hours, respectively (Fig. 1)

3. Graphical presentation of calculated coefficients of electro-osmotic permeability as a function of moisture content and electric potential, respectively (Figs. 2 and 3).

## 1. Description of the Reaction Picture

Natural soil: Test started with intensity of 30 mA requiring 66 Volt. Almost constant water flow observed for 94.5 min. during which time voltage rose to 132. Despite rapidly increased voltage, water flow diminished greatly. A summary of the data is given in Table 2.

Ca-soil: Very slow flow of water containing a high percentage of suspended colloids.

Na-soil: Very slow flow of water containing a high percentage of suspended colloids.

K-soil: Very slow flow of water containing a high percentage of suspended colloids. Mg-soil: Regular flow of clear water up to 72 min. at reasonable consumption of electricity, subsequent slow irregular flow.

*H-soil:* During the first 30 min. 13.4 cc. of clear water were drained in constant flow. From this point on the flow decreased despite rapid increase in applied voltage.



Figure 1. Electro-Osmotic Yield of Natural and Homoionic Hagerstown Soils

After 44 min. the voltage had become so high that it was necessary to cut the intensity to 20 mA. Notwithstanding this change, considerable heating took place in the sample, a phenomenon, which had not occurred with the other soil-modifications, and it became necessary to stop the experiment.

*Fe-soil:* Regular flow of clear water up to 55 min.

Al-soil: Flow of water started instantaneously with application of potential. Soon thereafter, many bubbles were observed at the cathode. The resistance increased to such an extent that the current had to be reduced to 10 mA. The flow of water remained constant. A new phenomenon was observed, viz., the moisture content at the anode appeared to be approximately the same small amounts flowed to both, the cathode and the anode.

## 2. and 3. See Figures 1-3.

Conclusions from Electro-Osmotic Experiments Inspection of the test-results leads to the following specific conclusions:

1. Application of an electric potential to a moist soil specimen leads to a combination of ionic and electro-osmotic conductance, the relative proportion of each depending upon the amount and type of exchangeable ions in the system and also on the amount and type of electrolytes dissolved in the soil-moisture.

2. From an energy point of view, the greater the proportion of electric conductance due to true electro-osmosis the greater is the economic yield. In other words, water yield per

448

as at the cathode, after 43 min. of treatment. The soil at the cathode appeared to be quite solid.

In some supplementary experiments, AlCl<sub>s</sub> solutions instead of distilled water were mixed with K- and Na-soils, respectively. After application, of an electric potential, water in

electric energy unit increases with increasing electric resistance of the liquid phase. This had already been stated by Quincke.

3. Of the soils tested, the Ca-, K-, and Namodifications gave lowest, the natural and Mg-modifications intermediate, and the H-, Fe-, and Al-modifications highest economic vields.

4. The electro-osmotic permeability of a soil is not a constant but varies with the moisture content and the applied potential. The lower the moisture content the greater is the importance of the character of the ionosphere surrounding the solid soil particles.

5. Further experiments on well defined clay-



Figure 2. Electro-Osmotic Permeability in sec. per volt. as a Function of Moisture Content

mineral systems employing, in addition to water, other liquid dielectrics are indicated.

6. The experimental data appear to justify the inferences drawn from the fundamental experiments and observations of Quincke (6).

## THERMO-OSMOTIC PHENOMENA

The term thermo-osmosis applies to moisture movement in soils caused by the existence of a temperature gradient. Considering the daily and seasonal temperature fluctuations on pavement surfaces, and the transmission of the resulting temperature waves through the pavement-base-soil systems (16) the importance of thermo-osmosis to the highway engineer is at once evident. Depending upon



Figure 3. Electro-Osmotic Permeability in sec.per volt. as a Function of Electrical Potential

the type of pavement, base, and subgrade soil, on the availability of moisture, and upon the amplitude of daily and seasonal temperature fluctuations, desiccation or water accumulation may take place in the base or subgrade soil. Water-accumulation, of course, means decrease or even loss of bearing capacity, and may thus lead to the failure of the road itself (16).

Every worker who has measured thermal

conductivity of moist soils has encountered thermo-osmotic phenomena. Patten (9) was probably the first to deal with this subject in American soil literature, in connection with his investigations on heat transference in soils; for him it was an annoyance rather than a subject for study. The first real study was made by Bouyoucos (2) in an outstanding piece of research. He found that:

1. Moisture moves from locations of high temperature to locations of low temperature.

TABLE	2
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	Water %	Voltage	W ter %	Voltage	
	N.t. soil			Ca-soil	
Initial	30.2	66	22.5	108	
cathode anode middle	26.4 15 0 22.2	235 (145 min.)	18.6 6.2 15.3	207 (120 min.)	
	Na-soil		K-soil		
Initial	25.2	16	25.6	40	
cathode anode middle	23.6 12.5 20.0	150 (140 min.)	22 7 12 2 19.5	175 (150 min.)	
	Mg soil		H-soil		
Initial	31.4	50	25	140	
cathode anode middle	$25.4 \\ 16 8 \\ 22.3$	220 (100 min.)	22.6 7.5 17.5	340 (50 min.)	
Fe soil	Fe soil	Al-soil			
Initial	28.8	100	27.8	300	
cathode	28 8	390	21.4	500	
middle	49.0	(60 min.)	17.2	(43 min.)	

2. There exists for each soil an optimum moisture content at which a maximum amount of moisture is moved under a certain temperature gradient.

3. This optimum moisture content falls in the vicinity of the plastic limit.

4. The moisture movement can only in part be ascribed to vapor phase movement.

In addition, Bouyoucos' work brought out a number of other important points which, unfortunately, cannot all be discussed at this place. The observed phenomena were explained by Bouyoucos by postulation of a variation in water affinity (or capillary potential) with variation in soil temperature.

W. O. Smith (12) checked the work of Bouyoucos with improved experimental arrangement and confirmed the experimental findings. However, he attributed the moisture movement to a special type of mass transfer of water vapor by convection; agreeing with Bouyoucos that vapor diffusion alone could not explain the magnitude of transfer, but not being ready to accept the explanation of Bouyoucos. Trejo (13) working with soil specimens compacted at the optimum moisture content for maximum water movementwhich, incidentally, is practically identical with the Proctor optimum moisture content for maximum density obtained by a specific amount of compaction energy-obtained the same general experimental picture as the previous workers. He also made experiments with partly open systems and found that the classical picture of the phenomenon occurred only in closed systems. Recently, Maclean and Gwatkin (8) made an excellent experimental study of thermo-osmosis in soils. Their data are probably the best and most useful in existence. As far as the theory is concerned, these authors accept the explanation of Smith, rather than that of Bouyoucos.

Theoretical Concepts—Theoretically, there exist four main concepts which may be applied to moisture movement through porous solid systems subjected to a thermic potential or to a water-vapor concentration potential (which for Case 1 and 2 does not necessarily have to be of thermal origin). These are:

1. Diffusion of water vapor through the pore space under a concentration or partialpressure potential.

2. Diffusion of water in solid solution, as observed for hydrophilic membranes separating chambers of different water-vapor pressure.

3. Movement as capillary water due to the difference in surface tension at different temperatures.

4. Flow of moisture in the film phase along the internal surface of the porous system due to change in water affinity with change in temperature.

In the case of soils, Concepts 2 and 4 are practically identical, except where the soil contains large amounts of hydrophilic organic matter. As a matter of principle, it must be stated that nature usually employs all means available and that the question is: how much do the different possible ways contribute to the total water transfer, or which of them is quantitatively the most important? The authors cited have proven with sufficient theoretical and experimental evidence, that movement by vapor diffusion and capillary movement caused by difference in surface tension can contribute only a small part of the observed conductance. Bouyoucos therefore postulated Concept 4, while Smith contributed the new concept of mass vapor transfer. It severely taxes the imagination to picture a mass vapor transfer in a soil system compacted at the optimum moisture content to maximum density, as was the case in Trejo's experimental work. There remains, then only the postulate of Bouyoucos which corresponds to Concept 4, and also theoretically to Concept 2. These concepts have been employed with great success to the water vapor permeability of membranes; they should be applicable to soils if they possess greater affinity for water at low than at high temperatures. That this is the case, was demonstrated by Baver and Winterkorn (1).

Accepting the experimental demonstration that the water-affinity of soil material decreases with increasing temperature, and assuming as most logical that the water moves in the film phase, a theory can be developed in very close analogy with the theory of electro-osmosis. This is done in the following employing the experimental data obtained by Bayer and Winterkorn.

It should be kept in mind that the moisture contents employed in this derivation were considerably below those giving optimum thermo-osmotic flow for the material under consideration. However, they are entirely sufficient for the intended purpose of demonstrating the theory.

Energy Considerations—It had been found that one gram of Putnam clay was able at 30 deg. C., to adsorb 25.8 percent of water from an atmosphere held at 30 mm. water vapor pressure, while at 40 C., it could adsorb only 10.8 percent of water from an atmosphere held at 30 mm. water vapor pressure. The work involved in these adsorption processes is respectively:

$$W_{20^{\circ}} = Pv_1 = n_1 RT_1 W_{40^{\circ}} = Pv_2 = n_2 RT_2$$

where p = pressure of water vapor in atm. v = volume of water vapor in liters.

 $n_1$ ,  $n_2$  = mols. of water vapor involved. R = gas constant 0.082 lit. atm. per deg. T = absolute or Kelvin temperature.

The difference in free energy of adsorption of 1 g. of Putnam clay at 30 and 40 C. respectively is then:

$$W = R(n_1T_1 - n_2T_2), \text{ and using the respective} values for R, and those for the mol. numbers and temperatures viz:
$$n_1 = \frac{0.258}{18} = 0.0143$$
$$n_2 = \frac{0.018}{18} = 0.006$$
$$T_1 = 303 \text{ deg.}$$
$$T_2 = 313 \text{ deg.}$$
$$W = 0.202 \text{ lit. atm.}$$
$$W = 0.202 \text{ lit. atm.}$$
$$W = 2.03 \times 10^6 \text{ crg.}$$$$

The clay under consideration had been found to possess an internal surface of  $6.16^5$ sq. cm. per g. Consequently the above calculated energy differential can be expressed for a unit surface area as:

W per sq. cm. = 
$$\frac{2.03 \cdot 10^8}{6 \cdot 10^5}$$

=  $3.4 \times 10^2$  erg per sq. cm. per 10 deg. C.

This amount of energy  $(3.4 \times 10^2 \text{ erg per} \text{ sq. cm.})$  is available for water movement in whatever form this movement may take place. If this movement be in the liquid or film phase, then for the case considered, there would exist per unit length of perimeter at right angle to the direction of moisture movement and temperature gradient, a pulling force of  $3.4 \times 10^2$  dyne for a thermal gradient of 10 deg. per cm.

Assuming that the pulling force results in a film flow along the walls of a capillary of radius r, the pulling force P becomes:

$$P = 2r\pi \times 3.4 \qquad 10^2 \text{ dynes}$$

For such flow and for a film thickness d the frictional resistance F becomes (in the cgs. system):

$$F = 2r\pi\eta \frac{\Delta v}{\Delta r} \text{ in which }$$

 $\eta = viscosity coefficient of water$ 

 $\frac{\Delta v}{\Delta r}$  = velocity gradient at right angle to flow

## direction;

assuming, furthermore, a linear velocity gradient:

$$\frac{\Delta v}{\Delta r} = \frac{v}{d}$$
$$P = 2\pi r\eta \frac{v}{d}$$

The average thickness d of the moving water film is equal to one-half of the difference in equilibrium water content per g. of clay at 30 and 40 C., respectively, divided by the surface over which this film is spread (6  $\times$  10<sup>5</sup> sq. cm.). This thickness is then:

$$d = \frac{0.075}{6 \times 10^6} = 1.25 \times 10^{-5}$$

For steady flow conditions, the pull P and resistance F must be equal to each other, therefore: .

$$2r\pi \, 3.4 \times 10^2 = 2r\pi\eta \, \frac{v}{d}$$

 $\eta$  for 35 C. is  $0.7225 \times 10^{-2}$  when the pressure is expressed in cm. of H<sub>2</sub>O; expressing the hydrostatic head in dynes  $\eta$  must be multiplied by 981 (gravitation constant); consequently:

$$v = \frac{1.25 \times 3.4 \times 10^2}{0.723 \times 981 \times 10^7 \times 10^{-2}}$$

cm. per 10-deg. gradient

=  $0.6 \times 10^{-5}$  per 10-deg. thermal gradient and

=  $0.6 \times 10^{-6}$  per 1-deg. thermal gradient.

The volume V of water moved per sec. per cm. perimeter length of capillary, under a thermal gradient of 1 deg. C. per cm., is then for the soils and moisture conditions considered:

$$V = \frac{v}{2} \cdot d$$
  
= 0.3 × 10<sup>-6</sup> · 1.25 × 10<sup>-7</sup>  
= 0.38 × 10<sup>-13</sup>, or approximately  
= 0.4 × 10<sup>-13</sup>

The sum of capillary perimeters contained in a cross section of 1 sq. cm. of a soil is numerically identical (in the cgs. system) with the internal surface per cu. cm. Assuming a porosity n of 0.5 for the system considered, a density of the clay mineral of 2.65 g. per cu. cm. and an internal surface of the clay of  $6 \times 10^5$  cm. per g., we obtain as the sum S of perimeter lengths per sq. cm. cross section:

 $S = 2.65 \cdot 0.5 \cdot 6 \times 10^5 = 8 \times 10^5$ 

The amount of water  $V_i$  moved in unit time through a cross section of 1 sq. cm. of the claywater system under a thermal gradient of 1 deg. C. per cm. is then:

$$V_t = SV$$

 $= 0.4 \times 10^{-13} \cdot 8 \times 10^{5}$ 

=  $3.2 \times 10^{-8}$  cu. cm. per sq. cm. per deg. C. per cm. per sec.

 $V_i$  represents a coefficient of water movement under a thermal gradient; representing this coefficient as  $k_i$  we can write the respective relationships in a form analogous to that employed in the Darcy formula for hydrostatic gradients. As a consequence, all experience concerning form factors which have been correlated with the Darcy formula can be applied, "mutatis mutandis," to flow under a thermal potential.

Comparison of Theoretical with Experimental Data—It is of interest to compare the order of magnitude obtained for  $k_t$ , by using the Putnam clay data and the proposed hypothesis, with the results obtained in the aforementioned English tests on a clay soil.

The following data were given in the English report:

Thermal gradient applied = 1.6 deg. C. per cm.

Length of soil sample = 11.0 cm.

Average increase in percent  $H_2O$  (on the basis of the dry weight of soil) on the cold side, or the average decrease on the warm side = 2.3 percent.

Average moisture content = 18 percent. Average temperature = 34 deg. C.

Duration of experiment = 120 hr.

Dry weight of soil = 97 lb. per cu. ft.

Considering a cross section area of 1 sq. cm., normal to the direction of the gradient, in the center plane of the specimen, it can be seen from the data that both the temperature as well as the water content remained constant at this location and that an amount of moisture equal to the product of the average moisture percentage increase and of the amount of dry soil contained in a rectangular block of 1-sq. cm. base area and 5.5-cm. length, moved through this element during the time of the experiment.

1. According to the data given, about 1.54 g. of dry soil was contained in each cu. cm. of the considered soil-water system.

2. The total amount of water moved through a cross sectional area of 1 sq. cm. at the center plane was then  $0.023 \times 1.54 \times 5.5 = 0.195$  cu. cm.

3. This amount was moved in 120 hr. =  $4.3 \times 10^5$  sec. under a thermal gradient of 1.6 deg. per cm.

Consequently, the volume of water moved per second through a unit surface under a thermal potential 1 deg. per cm., i.e. the coefficient  $k_i$  of thermal moisture movement, is for the soil considered:

$$K_t = \frac{0.195}{1.6 \times 4.3 \times 10^5} = 2.8 \times 10^{-7}$$

The theoretical calculation for the Putnam clay gave a value of  $k_i = 3.2 \times 10^{-8}$ . While the temperature and the average moisture content for which the calculation was made was about the same as employed in the English experiments, the Putnam clay represented an extracted clay with no particle larger than 0.005 mm., while the English clay soil contained less than 50 percent clay. The English soil at 18 percent moisture was much closer to the optimum for thermal movement than the Putnam soil. For this reason, it can be said that the values calculated by means of the proposed hypothesis appear to correspond closely to those obtained by experiment.

Further Considerations on Thermo-Osmosis— The question whether moisture movement under a thermic potential takes place by means of film flow or by transfer in the vapor phase is not only of academic but also of great practical interest. If water must be evaporated on one side, transferred in the vapor phase and condensed on the other, this process requires not only the energy needed for the transference proper, but also the heat of evaporation (or condensation). Therefore, if transfer takes place in the liquid or film phase much less total energy is involved, resulting in a greater energy economy of the process. In fact, the ratio of heat transfer to water transfer is the crux of the whole problem from a theoretical as well as from a practical point of view.

It is of great theoretical interest that the optimum water transfer for a certain thermal potential occurs at a moisture content which is quite close to the optimum moisture content for compaction as obtained in the Proctor procedure. Physically spoken, the optimum moisture content for compaction is that at which the water molecules most distant from the solid mineral surfaces have acquired lubricating properties. In other words, the optimum moisture content signifies a distance at which the strong water attractive forces have come to an end and where only weaker attraction forces rule up to the liquid limit.

Because of the polarity of the soil mineral surfaces, of the exchangeable ions, and of the water molecules, soil water relationships may properly be designated as a branch of applied electrostatics. However, because of the geometrical factors involved, we do not deal with a system of point charges to which simple Coulomb considerations may be applied. but rather with an electric field representative mainly of scatter valences in the regions of low attraction. As the decrease of the dielectric constant of water with increase in temperature indicates, such a field is very sensitive to increased kinetic activity of the corpuscular field components. This concept explains the change of absolute water affinity of clay material with temperature.

## INTERRELATIONSHIPS BETWEEN ELECTRO-OSMOSIS AND THERMO-OSMOSIS

To summarize the evidence available with respect to electro- and thermo-osmotic phenomena:

1. A dielectric liquid moves through a porous system upon application of an electric potential;

2. A dielectric liquid moving through a porous system under a hydrostatic head creates an electric potential (streaming potential):

3. Water moves through a soil system under a thermal potential, in which the moving force is the difference in water-affinity of the soil at high and low temperature, respectively;

4. The water-affinity of a soil is closely related to the amount and type of exchangeable ions, and because of the electric charge of the ions and the dipole nature of water, must be considered an electrostatic phenomenon.

The evidence indicates that thermo-osmosis is a special form of electro-osmosis.

The experimental data presented in the first part of this paper give a coefficient of electroosmotic permeability:

 $k_o \approx 1 \times 10^{-5}$  cm. per sec. per volt per cm. The English data give a coefficient of thermoosmotic permeability:

 $k_i \approx 1 \times 10^{-7}$  cm. per sec. per deg. C. per cm.

From a purely phenomenological point of view it may be concluded that: 1 deg. C. per cm. corresponds to approximately 10 millivolts per cm. Experiments underway at the present time in the writer's laboratory, performed by Mr. Gowda and Mr. Shenoy have not only verified the existence of the predicted electric potential but appear to check closely with the predicted order of magnitude of the potential.

In the experimental arrangement, N. J. Hagerstown soil was compacted at the plastic limit into a 2-in. diameter lucite tube, and subjected to a thermal gradient. Electrodes were inserted at the hot and cold side respectively and the voltage measured. Corrections were made for the different solution pressures of the electrode metal at the two temperatures. The electrode on the cold side became positive with reference to that on the warm side.

The physical explanation of this phenomenon is that the exchangeable cations possess a greater activity (or are more dissociated) at the cold than at the warm side; they cannot move to the warm side because they are held by the negative charges of the mineral surfaces. The only way to decrease this concentration potential is by movement of the water from the warm to the cold side.

Detection of the electric character of thermo-osmotic flow proves its film nature and refutes the mass vapor convection concept of Smith. As mentioned previously, this is a matter of very practical interest. If the water had to be evaporated at the warm side and condensed at the cold side, transfer of one gram of water would involve a heat transfer of about 600 calories. In a film flow, not necessitating this evaporation and condensation the actual heat transfer is appreciably smaller, resulting in a much more economical water yield. Another important conclusion whose portent for many other fields and problems cannot yet be entirely visualized is the fact that temperature waves penetrating into soil are accompanied by electrical waves. What are the consequences of this with respect to electrolytic corrosion of metal pipes and other metal installations within the zone of thermal wave penetration? What are the consequences with respect to plant growth and other biological and physiological phenomena?

It appears that a new and important field of inquiry has been opened which promises to those who cultivate it a rich harvest of theoretical knowledge and of practical application.

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# FURTHER METHODS FOR THE ANALYSIS OF DATA TAKEN IN THE HVEEM STABILITY TEST

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## SYNOPSIS

The third and fourth of a series of papers concerning the analysis of data taken in the triaxial test for Hveem stability of bituminous road materials and their application to problems of design. In the first two of these papers<sup>1</sup> certain special methods of analysis and correction of the data have been presented. The first of these papers consisted chiefly of a review of the familiar graphical solution for combined static stress known as the Mohr Circle diagram with some applications to the analysis of data taken in the Hveem test for stability, and the second outlined another somewhat similar solution, with restricted application, the results being equivalent to those obtained in the Mohr diagram method. The third of these papers is given as Part 1 of this article. It describes a graphical method of correction of lateral stress readings for lateral surface voids and for measuring lateral deformation of the specimen at any stage of the test. The fourth, Part 2 herein, describes and illustrates proposed methods for the determination of the physical constants of road materials from data taken in the Hveem stability test.

## PART 1

## A GRAPHICAL METHOD FOR CORRECTION OF LAT-ERAL STRESS AND MEASUREMENT OF LATERAL DEFORMATION OF A SPECIMEN IN HVEEM'S TEST FOR STABILITY

A scientific method of design utilizing any construction material must include consideration of two factors: the relation between physical properties of the material; and its qualities requisite for good performance. The design method, to be adequate, requires accurate measurement of these properties and qualities and involves statistical analysis of a large body of data taken in laboratory and field tests in order to correlate the two factors.

No such method appears to have been developed for asphaltic concrete and an investigation was undertaken by the writer in an attempt to solve the problem. Data

<sup>1</sup> Published in *Proceedings* Highway Research Board Vol. 26, (1946) p. 100.

were used from several hundred tests for Hveem stability on various asphaltic concrete mixes.

About seven hundred diagrams have been constructed employing the methods outlined in the previous papers, and the shear resistance on the plane of failure, obtained from the constructions, has been correlated with Hveem percent stability, yielding a correlation coefficient of approximately 0.90.

In the present paper, a graphical method for measuring lateral deformation of the Hveem specimen, and for correcting the lateral strcss readings for surface voids is described and illustrated with data taken in the Hveem test for stability.

Method of Taking Data and Construction of Charts—Because of a certain quantity of air always present in the Hveem stabilometer system during a test for Hveem stability, and also due to such miscellaneous factors