Mass Transport Phenomena in Moist Porous Systems as Viewed from the Thermodynamics Of Irreversible Processes

HANS F. WINTERKORN, Professor of Civil Engineering, Princeton University

● THERE was an atmosphere of stimulation and creativeness in the scientific world of the middle of last century. Perhaps the main cause of this was the recognition even by the more conservative minds that heat was a mode of motion. The new truth sparked the thinking and experimenting of many scientists and led to the finding of a multitude of new experimental facts as well as to the theoretical evaluation of the new and the old knowledge on the various forms of energy and their correlation. A common characteristic of the scientific leaders was their wide scope of interest and application which covered all the known modes of energy and their interrelations and ranged from celestial dynamics to the vital forces of plants and animals.

Concerning the Essence of Classical Thermodynamics

When the time came to systematize the old and new knowledge on the different types of forces and energies and on their interrelationships, as well as on the processes by which one type of energy is changed into one or more other types, Clausius pointed out that for every natural system there exists a typical function that in all changes concerning the system alone either remains constant (reversible process) or increases (irreversible processes). Clausius called this function the entropy of the system (1). Planck (2) classified all independent processes that can occur into:

1. Natural processes, that actually occur in nature and proceed in a direction toward equilibrium while the entropy increases;
2. Unnatural processes that proceed in a direction away from equilibrium involving a decrease in entropy and which do not occur in nature; and
3. Reversible processes which are the limiting cases between the natural and unnatural processes and proceed without change in entropy (3).

Obviously, there was nothing that could happen in this world which was outside the scope of this new science that, according to Faraday, contained "the highest law in physical science which our faculties permit us to perceive—the conservation of forces (energy)." Since there is in the normal physical world no energy system that does not contain a considerable amount of thermal energy and whose state is not actually controlled by it, the new science was properly called thermodynamics in the widest sense of the term. It was logical that the first and central theoretical structure of this new science would be concerned with reversible processes. To choose and secure this central position in the tremendous expanse of thermodynamics, bespeaks not only the genius but also the wisdom of the pioneer systematizers of thermodynamics. This central position was to provide a solid starting point for the attack on the vast surrounding terrain of natural and unnatural processes. It was, of course, impossible for the pioneers in thermodynamics to conquer and cultivate all this terrain, but in the face of overwhelming evidence to the contrary, it is ridiculous to assume and act, as some contemporaries are doing, as if the pioneers in thermodynamics did not realize the vastness of the realm of thermodynamics, and to try to restrict the achievement of the pioneers to the construction of their fortress which they want to call thermostatics, claiming as their own the vast region which to conquer the fortress was built.

Whenever human beings are engaged in joint or interrelated endeavor, there are differing views among individuals and groups about the proper scope, the strategy and the tactics of their enterprise. It is natural then that even within the central fortress of thermodynamics different factions can be observed each of which emphasizes a particular portion of the sum total of the philosophy and endeavor of the group. Max Planck,

in the first edition of his famous book on thermodynamics, points out the existence of three distinct thermodynamic methodologies (4). The first is represented by the kinetic theory of heat as founded by Joule, Waterstone, Kronig and Clausius and brought to maturity by Maxwell and Boltzmann. According to this theory, heat is the manifestation of the movement of atoms and molecules, the discrete mass components of matter. The theory attempts to give a mechanistic explanation of the laws of thermodynamics. In its simple form it holds well for ideal gases and dilute solutions, but it becomes increasingly and often forbiddingly complex when applied to solids and liquids. Its reliability is not of an a priori character, but must be checked in each area against the principal laws of thermodynamics which embody in a more abstract manner the vast empirical knowledge on energy and its transformations collected by the human race.

The difficulties and involvements of the kinetic approach are avoided by Helmholtz and his followers who, accepting the kinetic nature of heat, refrain from the formulation of mechanical models. The founders were fully aware of the importance of the latter as heuristic tools, but they sacrificed them for the sake of greater certainty and correctness of the method and of a logically more satisfactory interconnection and systematization of the factual content of the theory. By excluding the intuitive and unproven elements of the pure kinetic theory, the established scientific system is essentially an intrapolation and correlation of the several general laws that had been derived directly from experience.

The third and so far most fruitful approach has been the one employed by Planck. Strongly founded on a vast body of empirical knowledge and on the rational abstraction of this knowledge in the form of the basic principles of thermodynamics, it utilizes the imaginative creative tools of the kinetic theory to make pioneering inroads into dark areas and the purer rational tools of Helmholtz to systematize the newly secured areas. This approach has proved extremely valuable in the development of modern physics and chemistry.

The fundamental principles of thermodynamics are:

1. The law of the conservation of energy;

2. The second law which may be formulated after Clausius as follows: For every natural system there exists a typical function that in all changes concerning the system alone either remains constant (reversible processes) or increases (irreversible processes). This function is called the entropy of the system.

3. The Nernst theorem which postulates that at the absolute zero temperature, the temperature coefficients of the free and the internal energy both become zero. The theorem, therefore, permits the calculation of absolute entropies if the specific heats of the components of the system are known for the entire range from absolute zero to the working temperature.

In order to establish under these laws the central theory governing the reversible processes, a working assumption has to be made that during a reversible process the system is in equilibrium not only at the beginning and the end of the process, but at each infinitesimal intermediate stage. Practically, this means that all the energy is employed for the specific process and that no side or coupled reactions occur in which energy transformation takes place which does not contribute to the purpose of the process. For mechanical systems, this requirement stipulates that they are frictionless. Practically, the difference between actual processes and their reversible prototypes is expressed by the terms of yield and efficiency. Obviously, this restriction to equilibrium conditions and to single processes rules out the central theoretical structure from direct usefulness in the treatment of reaction rates and also of processes in which two or more reactions are coupled with each other.

For the purpose of calculating rates of reactions from first principles, the theory of activation was developed which obeys the laws of thermodynamics, but makes use of certain model concepts that are germane to the kinetic theory (5, 6). For the purpose of treating coupled reactions, the classical central thermodynamic structure was extended in a natural and logical manner. This extension is often and perhaps too dramatically called the thermodynamics of irreversible processes.

Concerning the Thermodynamics of Irreversible Processes

The essence of irreversible processes is the production of entropy; this production is the natural focal point of their theoretical treatment. According to de Groot (7), the methodology of the thermodynamics of irreversible processes is based on the following four points:

1. The entropy production σ is positive definite; this is an expression of the Boltzmann H - theorem.

2. The entropy balance and hence also the entropy production are calculated from the Gibbs equation.

$$Tds = du + Pdv - \Sigma_k \mu_k dc_k \qquad \text{in which}$$

s, u and v are specific entropy, energy and volume
T = temperature
μ_k = chemical potential of component k
c_k = concentration of component k

3. The phenomenological laws written as linear relations between fluxes J and forces X. The term force is given to any "cause" of irreversible processes such as temperature and concentration gradients, and chemical affinity, while the term flux is used for the resulting phenomena such as mass transport or energy flow. The general type of these relations is

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \qquad (i - 1, 2, \ldots n)$$

This equation states that any flux is caused by contributions of all forces. L_{ik} are phenomenological coefficients, the L_{ii} representing single action coefficients, as for straight thermal and electrical conductivity or ordinary diffusion, while the L_{ik} ($i \neq k$) represent interference phenomena as in thermal diffusion.

4. The Onsager reciprocal relations which state that, provided that the fluxes J_i and the forces X_i are properly chosen, the matrix of coefficients L_{ik} is symmetric, that is

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \ldots n)$$

This is an expression of the assumption of microscopic reversibility of interference phenomena.

Several excellent books are available on the theoretical basis and the practical application of this methodology of treating irreversible processes (7, 8, 9). Its use has led to more elegant solutions than previously available of such coupled phenomena as thermoelectricity in bimetallic joints (Thompson effect), the "fountain" effect in liquid Helium II, the Nernst effect (a cross electrical potential gradient resulting from a temperature gradient in a magnetic field normal to both gradients) and other coupled phenomena of greater or lesser complexity. Application to thermoosmosis through porous solids was made by Hutchinson, Nixon and Denbigh (10). This methodology appears to be particularly well suited to the theoretical treatment of the complex irreversible phenomena occurring in moist soil systems. However, it must be kept in mind that the phenomena, for which this treatment has so far given the most elegant available solutions, had been known and studied experimentally and theoretically for a long time and that more cumbersome theoretical solutions were available. For worthwhile application to new territory, dependable experimental data must first be available. If this is not yet the case, the new methodology can be of great value in the planning of experimentation in a direction that it will lead to the type of data most suitable for the theoretical treatment. At any rate before a worthwhile theoretical treatment of complex phenomena can be undertaken, one must know as much as possible of the physical facts of the system and the processes that take place in it. As a first step in providing a basis of possible future theoretical treatment by this methodology of natural soil materials under conditions representative of those actually encountered in soil engineering, typical soil systems and irreversible processes occurring in them are described in the following sections.

Typical Soil Systems of Interest in Highway Engineering and Irreversible Processes Occurring in Them

A number of soil and other porous systems and irreversible processes occurring in them have been treated in an excellent manner in preceding contributions to this symposium. Considering the high quality of these papers, it would be not only superfluous but utterly presumptious to go over the same ground. Therefore, care will be taken to avoid such duplication except in cases where the continuity of presentation and the logic of argument would be seriously impaired by omissions. With due respect for the frame and purpose of this symposium, the soil systems considered will be in such conditions as are typical in highway use as subgrades and bases where irreversible processes are most likely to occur in practice and where their effects are most consequential. This means that the general state of reference will be the maximum density and the optimum moisture of compaction of the soil systems under consideration. This condition is exemplified in Table 1 on seven soils representative of a wide range of granulometric composition and surface-chemical activity. It is significant that in this condition the air volume as a percentage of the total voids volume (air plus water) is 8 percent for the heavy clay soil, about 13 percent for a lean sandy, silty clay, around 20 percent for several sandy and loamy soils including a loessial silt and about 37 percent for a very poorly graded sand. With such volume relationships, continuity of the air phase is extremely improbable. As a matter of fact, numerous samples of sandy soils compacted in the laboratory to maximum density at optimum moisture content in containers with closed bottoms showed surface exudation of a considerable amount of free water after they were placed in the oven for drying. The preponderant portion of this effect is undoubtedly due to the thermal expansion of the discontinuous air phase within the sample.

The envisaged moisture-density condition results in an air capacity of from 3 to 7.2 percent for all soils in Table 1 except the very poorly graded sand which has an air capacity of 14.7 percent. Keeping in mind that air capacities of 6 to 10 percent are required for the growth of sweet grasses, of 10 to 15 percent for that of wheat and oats and of 15 to 20 percent for that of barley and sugar beets, it is easily understood why agricultural soil physicists have not given primary attention to the theoretical study of these low air-capacity conditions which are of predominant interest to the highway en-

TABLE 1

CALCULATION OF ABSOLUTE VOLUMES OF THE SOLID, LIQUID AND AIR PHASES FOR SEVEN SOILS AT THEIR MAXIMUM DENSITY AND OPTIMUM MOISTURE CONTENT FOR COMPACTION[1]

Soil Texture and Plasticity Data							
No.	Description	Sand	Silt	Clay	L. L.	P. I.	P. L.
1	Well graded loamy sand	88	10	2	16	NP	
2	Well graded sandy loam	72	15	13	16	0	16
3	Medium graded sandy loam	73	9	18	22	4	18
4	Lean sandy silty clay	32	33	35	28	9	19
5	Loessial silt	5	85	10	26	2	24
6	Heavy	6	22	72	67	40	27
7	Very poorly graded sand	94		6		NP	

Soil No.	1	2	3	4	5	6	7
Dry density, pcf	135.6	127.6	120.0	114.0	105.2	103.2	100
Moisture percent of dry weight	7	9.6	11.5	15	17.5	21	16.3
Moisture, pcf	9.5	12.2	13.8	17.1	18.4	21.7	16.3

Absolute Volumes in Cu Ft per Cu Ft at Maximum Density and Optimum Moisture							
Solids	0.815	0.768	0.722	0.686	0.633	0.622	0.602
Moisture	0.152	0.195	0.221	0.274	0.295	0.348	0.261
Air	0.033	0.047	0.057	0.040	0.072	0.030	0.147
Volume ratio: air/water	0.217	0.241	0.258	0.146	0.244	0.086	0.563
Percent total (air plus water) voids	18.5	23.2	27.8	31.4	36.7	37.8	0.398
Percent air of total voids volume	17.8	20.2	20.5	12.7	19.6	8.0	36.9

[1] Basic data taken from HRB Bulletin 58, Compaction of Embankments, Subgrades and Bases, National Academy of Sciences, page 3 (1952).

gineer, but have concentrated on getting soils out of these conditions. Achievement of the agriculturally desirable higher air capacity also means a greater probability for continuous air phases and it is such systems that have been so excellently treated by agriculturally oriented soil physicists in several papers of this symposium.

Characterizing as soils the porous systems to be considered in this paper implies that they can support plant growth if in the proper physical condition for it. This means that the systems have dissolved ions either as "impurities" or as a result of interchange reactions between the solid surfaces and the contacting water phases. In this general picture should also be included the presence of living or dead organic matter especially since in some important soil groups, clay minerals and organic matter are so intimately combined that they cannot be separated without destruction of both components. While physically the condition of highway soil systems is distinctly different from that desirable for agricultural soil use, highway soil systems exhibit many similarities, especially in the case of high moisture and high clay contents, with living and dead biological systems (11).

The systems under consideration are further identified by the stipulation that they shall contain a sufficient amount of clay to make a predominant contribution to their internal surface. Considering the fact that 1 cu cm of a solid when subdivided into cubes of 1 mm size produces a total surface of 60 sq cm and one of 6 by 10^5 sq cm if subdivided into cubes of a size of 10^{-5} cm, this stipulation does not necessarily involve a large clay content. The clay may be of any type or a mixture of several as long as it possesses ion exchange properties or as long as the liquid phase contains ions in solution. The mass transport to be considered is that of water and of aqueous solutions. Sufficient information has been presented in this symposium on the geometrical and electrical features of the structure of both the water substance and the surfaces of soil minerals, and on the consequences of these features with respect to interactions at the solid-liquid interphases, to indicate the pertinence of these phenomena with respect to water movement in soil systems of the type that are under discussion. However, it may not be amiss to illustrate some of these consequences by physical examples.

Mineral Surfaces in Equilibrium with Water Vapor and with Liquid Water

Dry clay minerals establish different equilibria when brought in contact with the water substance in the gas or in the liquid phase as long as no capillary condensation takes place in the former case. This is not surprising since water in the gas phase consists mainly of the monomer H_2O while in the liquid phase the entire coherent mass of available water may be considered as one polymeric water molecule. Putnam clay, for example, at 30 C in contact with saturated water vapor came to equilibrium with 0.26 gm of water per gram of clay while when completely dispersed in water, the particles surrounded themselves with a water hull of modified properties amounting to 5.22 cc of water per gram of dry clay; if a dry powder of this clay was placed in contact with a liquid water surface in the absence of a hydrostatic head and without mechanical dispersing work, 0.81 cc of water were absorbed per gram of clay (see Table 2).

The addition of water in successive increments to dry clays is accompanied by the release of heats of wetting, the magnitude of which decreases with each increment of water while the total heat of

TABLE 2

WATER ADSORPTION BY CLAY MINERALS FROM THE VAPOR AND LIQUID PHASE AT DIFFERENT TEMPERATURES (12)

(a) Adsorption from the Vapor Phase at a Pressure of 30 mm Hg

Clay Mineral	H₂O adsorbed in weight percent Temperature, C			
	30	40	50	80
H - Bentonite	32.7	12.0	7.5	2.1
H - Putnam	25.8	10.8	5.7	2.3
H - Davidson	21.4	3.5	2.6	1.2
H - Permutite	28.4	16.9	4.9	3.1

(b) Hydration Calculated from Viscosities of Dilute Suspensions

Hydration in cc H₂O per gram of clay

Ionic Type	Li	Na	K	Ca	Ba	H
Temperature, C			Putnam Clay			
30	5.3	5.3	4.1	9.8	5.0	5.2
50	3.7	4.6	3.6	3.9	3.7	3.5
70	2.5	2.5	2.3	2.0	2.9	2.2
99	2.3	2.5	2.2	0.9	2.2	(2.7)
			Wabash Clay			
30	7.4	7.5	7.0	6.7	6.7	18.0
50	6.4	6.3	6.2	6.1	6.2	16.1
70	5.0	5.1	4.8	6.4	4.4	14.8
99	3.9	3.7	3.4	(7.1)	3.4	9.7

wetting tends asymptotically toward a limiting value. The heat of wetting can be conceived as the difference between the sum of the heat capacities of the separate clay and water components and the heat capacity of the combined system in which the water is under restraint through interaction with the mineral surfaces. The heat of wetting of clays is primarily a function of the type and amount of exchangeable ions on the clay mineral surfaces (12, 13). It has a negative temperature coefficient which fact is significant with respect to the behavior of clay-water systems subjected to thermal gradients.

The case of water vapor absorption at low relative humidities on soil mineral surfaces (and also the case of soil organic matter) apparently involves a solution of the H_2O monomer in the active surface of the solid soil particles, that is, with a solid solution. In the other extreme of aqueous suspensions, there is a solution of exchange ions in a hydrosphere surrounding the dispersed particles. In the absence of other dissolved ions, this solution differs from common ionic salt solutions by the fact that in clay dispersions the negative ionic charges are located on and in the solid surfaces. Hence, Donnan type equilibria will influence the solution picture. At low moisture contents sufficient to form continuous films on the soil particles, but insufficient to provide much free water, in addition to that needed for the hydration of the exchange ions, that pass out of the solid surface as water becomes available to them, this surface film is in a melt-like condition. This condition extends to the vicinity of the plastic limit at which point the water molecules in the layers most distant from the particles pass from a restrained condition to the low viscosity and lubricating properties of free water. The extension and characteristics of the different water phases are temperature dependent (14).

At an extremely large water content exemplified by aqueous clay suspensions, there may be water simultaneously in the following conditions.

1. In solid solution in the surface layer of the mineral particles just like water is soluble in solid silver nitrate. The extent to which this phenomenon may proceed depends upon the lattice structure of the mineral;

2. In oriented condition on the surface of the solid resulting from a superposition of a purely geometrical wall effect and an impression tendency of the packing of the O^{--} and OH^- ions of the solid surface into the vicinal layers of water molecules. This effect may perpetuate itself onionskin-like through a large number of water layers. In the case of montmorillonite, the density of this water is lower than that of free water and similar to that of normal ice (15).

3. Water molecules may be strongly held or at least oriented by the charges of exchange and other ions in the liquid. This corresponds to the phenomenon of hydrate formation in the case of cations or of predominantly geometrical influence in the case of anions. The cation hydration is usually associated with heat of wetting and the density of the hydration water is usually greater than that of bulk water; the latter phenomenon is called electrostriction.

4. Relatively free water between the hydrated exchange ions and the surface of the clay particles from which they issued and in whose attraction sphere they are held by electrostatic forces. This type of water has been termed osmotic water, since it is due to the osmotic tendency of the cations to get as far away as possible from the charged surfaces (16).

5. Free water at great distances from the particles and outside of their ionic atmospheres in relatively dilute dispersions, and

6. The oriented water at the air-water interface which according to McBain is several hundred molecules thick at normal temperatures (17).

While differentiation has been made between these various states of water, there is usually a transition zone at their areas of contact. The molecules in all zones, as is general between water molecules, are associated by hydrogen linkage which according to Rodebush and Buswell makes an entire coherent mass of water behave as one single macro-molecule.

In drying an extremely wet system to lower moisture contents, the least restrained water is lost first and the most strongly held last. Hysteresis phenomena occur at low

moisture contents when the exchange ions try to return to their original places in the surface layer of the crystal lattice and find them occupied by water molecules. A reverse type of hysteresis occurs in the incremental wetting of dry clays.

Mass Transport Phenomena of Major Importance in Highway Soil Systems

The available evidence shows that water in a soil system may simultaneously be present as vapor, as a liquid of varying viscosity and as a solid of varying plasticity. Also, except in the vapor phase, water possesses a well developed structure of highly electrical character due to its own nature and also under the influence of the electrically charged surfaces and of the ions in solution. Since the thermal energy of the molecules and ions of the aqueous solutions acts counter to the structure forming factors, the water structures and their physical and physico-chemical consequences are thermosensitive. This leads to a tremendous complexity and to interrelationships between all physical and physico-chemical factors in soil-water systems. Recognition of the marvelous complexity of water is not a recent achievement, but has found lucid and inspired expression by men like Tyndall (18), Cazin (19) and other of similar stature during the last century.

In view of the manifold properties of the water substance and their modifications in the soil environment, water in soil responds to the imposition of any energy gradient may it be mechanical, electric, thermal or other and responding to one exhibits coupling effects indicative of the disturbance of the other energy fields. Such response usually results in mass transportation phenomena. Gradients producing the latter are:

1. Hydrostatic potentials;
2. Potential due to the hydration energy of ions, related to the heat of wetting;
3. Potential due to the osmotic energy of ions either held in a kind of Donnan equilibrium on the solid particle surfaces or free in the aqueous solution;
4. The so-called capillary potential due to the surface tension of water and the size and geometry of the soil pores;
5. Applied electric potentials;
6. Thermal gradients; and
7. Vapor pressure potentials.

In real systems, none of these potentials acts alone, nor is there enough knowledge on coupling factors to attempt a quantitative treatment of all effects that result from the application of one specific gradient Therefore, the best that can be done at the present time is to present what might be called general phenomenological case studies of a few mass transportation processes in soils that are important in engineering. These shall be:

1. The mechanism of the attack of liquid water on dry cohesive soil systems;
2. The drying of wet cohesive soil systems;
3. Response to application of electric potentials; and
4. Consequences of application of thermal gradients.

Mechanism of Water Attack on Dry Cohesive Soils

The entrance of water into a porous system is due to its affinity for the internal surface of the system. Thus water rises into a glass capillary placed into a body of water with a free surface, while mercury is depressed in the capillary under analogous conditions. If the affinity between the liquid and the capillary wall is equal or greater than that between the liquid molecules, then the liquid film absorbed on the capillary wall may carry a liquid column to a height which is determined by the surface tension of the liquid. When a dry cohesive soil specimen or clod is brought into contact with free liquid water, then the resulting phenomena are governed by the following factors:

1. The driving force or the affinity of the internal soil surface for water the magnitude of which is indicated by the heat of wetting and which is the product of the amount and activity of the internal surface area.
2. The total porosity and the pore size distribution, which determine the perme-

ability to water and the ease or difficulty of escape of free and adsorbed air in the original soil system.

3. The rate of destruction of the bonds between the solid particles which changes the geometry of the pore space, and

4. The swelling capacity of the clay minerals which may result either in internal swelling that decreases the permeability or may be large enough to result in surface exfoliation of the systems (20, 21).

If the escape of gas is prevented, a type of failure may occur which possesses great similarity to an explosion although, of course, not liberating as large an amount of energy as is usually associated with this term. The concept that the affinity of the internal soil surface is the driving force for the water attack makes it easy to understand why certain moist cohesive soils may be exposed to free water for any length of time without observable change. In such systems, the water affinity of the soil is satisfied and no driving force is left. The described penetration of liquid water into the dry soil is accompanied by thermal and electrical effects.

Depending on the type of soil considered, its location and possible confinement, water attack may result in erosion, mud flows, slides or just in a general loosening of the soil and in the formation of secondary structure especially if wetting and drying cycles follow each other.

The Drying of Wet Cohesive Soil Systems

In the case of purely granular soils, entrance or exit of water has little or no effect on the packing of the soil except in the case that the granules are soluble; for example, with limestone and gypsum and similar sands and gravels. Although the previously discussed interaction of water with soil mineral particles holds for gravel and sand-sized particles as well as for clay particles, the specific surface of the latter is relatively small so that for gravel and sand water adsorption normally is of the order of magnitude on one and two percent by weight of the dry material while the large specific surface of clays and their ionic activity may result in a water interaction which is of the magnitude of the sizes of the clay particles themselves and may, therefore, reach 100 and more percent. Obviously, in the macro world, the interaction between gravel and sand particles and water does not influence soil structure and water movement to any considerable extent. This, of course, is quite different for cohesive soils since the property of cohesion is closely linked to water affinity which results in volume change of the soil system as a result of change in moisture content.

Structural Consequences of Drying

As a wet or moist cohesive soil system loses water, the soil particles move closer and closer together. If the drying proceeds from the surface down as in a mud flat, the dehydrated surface layers shrink while the shear resistance between the upper and lower layers and in the layers themselves prevents an adjustment to the volume decrease of the surface layer. As a result, tensile stresses are developed in the surface layer. These stresses finally relieve themselves by the formation of shrinkage cracks that break up the surface layer into pieces of more or less distinct geometric shape. If the soil material is homogeneous, the pattern of shrinkage cracks will be hexagonal in accordance with the law of the triple angle which is a special expression of the law of least energy. This cracking pattern produces the greatest stress release with the least amount of work. If the soil system is non-homogeneous as in the case of the presence of organic matter possessing less water affinity than the mineral soil constituents, then the hexagons will tend to become rounded and the organic matter will tend to become concentrated at the surfaces of the fissures. The drying of a film of varnish dissolved in dry alcohol will result in the same type of shrinkage pattern while disturbing the homogeneity of the solution by addition of a small amount of water will tend to round the corners of the polygons (22).

The actual size and shape of shrinkage structures formed in soils depends on a number of factors of soil composition and condition as well as on the rate of drying,

but the basic principle remains that soil structure formation is genetically related to the shrinkage process even if the drying is not caused by evaporation, but by the migration of water within the soil to growing ice lenses as in the freezing of silty and clayey soils. The great importance and widespread occurrence in nature of polygonal, especially hexagonal, patterns has been thoroughly discussed by Thompson (22). Excellent photographs on soil structure formation are contained in the symposium paper by Czeratzki and Frese.

Effect of Structure on Water Movement

With respect to water movement in liquid or vapor form through natural soils, the secondary structure of the soils and its stability is of greater importance than the primary soil components and their individual interaction with water. The reason for this is that the pores and fissures formed by shrinkage and located between the secondary aggregations or soil crumbs possess much larger dimensions than those between individual soil particles within the aggregates. According to Poiseuille's law the coefficient of permeability increases as a function of the fourth power of the radius of a pore.

Where drying and concomitant structure formation are due to freezing, the latter does not proceed uniformly throughout the soil mass, but the freezing occurs at locations where the specific water condition is most suitable for nucleus formation. Thence, ice formation proceeds along preferred directions, it often being easier for water to move to the growing ice crystals than for the freezing front to penetrate farther into the soil. The actual ice structures formed may range from Kammeis to rhythmic ice-banding and lensing. The causes of these phenomena have been understood since the work of Beudant (23), Faraday (24), Tyndall (25), Tomlinson (26), Liesegang (27) and others, but are presently being rediscovered by soil engineers. Ice structure formation is different for sandy, silty and clayey soils. Aside from factors of pore geometry, moisture content and of general environment, including presence or absence of a moisture reservoir and its distance from the freezing front, the difference is caused to a large extent by the fact that the water located at the basal planes of the clay particles resists the formation of normal ice and migrates toward places where ice is already being formed under different conditions.

For the understanding of the mechanism of mass water transport in soil drying, the symposium paper by Dr. Hallaire is of greatest significance and deserves thorough study. Hallaire points out that when the water lost by evaporation on the soil surface is equal to that brought there by film and capillary transmission, then the yield of water is due to a movement of the entire system of moisture films bringing into play the cohesion forces of the water substance. Thus, water in the deeper layers is displaced toward the surface even if it must pass through a zone of greater moisture content. This corresponds well with the concept described by Rodebush and Buswell that the entire mass of coherent water may be considered as one giant macro-molecule. In some way, such a coherent water mass in a porous hydrophilic system may be likened to a giant amoeba that tries to retain its form even though substance is lost at the surface. If the evaporation exceeds the water supply from below, then the soil dries out on the surface, forming a mulch of lower moisture conduction capacity. According to Hallaire, the reduction of this capacity is a function of the probability of the rupture of the water films in the drying soil layer.

Some Remarks on Water Transport in the Vapor Phase

The theory of distillation-condensation type water movement in the vapor phase has been treated in an excellent manner in several papers of this symposium. However, a few supplementary remarks may be permitted.

Water may move into, through and out of soil in the solid, liquid or vapor phase. Vapor phase movement may be due to gradients in relative humidity of the soil air (caused by differences in temperature, moisture content and in the water affinity of the internal soil surface), to passing air currents, or to the pumping of air into and out of soil as a result of changing barometric pressure in the outside atmosphere. Vapor phase movement by diffusion alone is normally not very important; movement by con-

vection, however, may acquire great significance under certain special conditions. To oft-repeated action of this type must be ascribed the failure of an asphalt paved road in Imperial Valley by water accumulation beneath the pavement which occurred despite the fact that the surrounding soil was dry, that no precipitation had fallen during the short lifetime of the road and that the ground water level was at a distance of more than 100 ft (28), too far for capillary conduction of the amounts of water actually encountered. The mechanism involved in this water accumulation appears to be essentially identical with that employed in the aerial wells of the Greek colonial city of Theodosia in the Crimea about 2,000 years ago (29). These aerial wells consisted of aggregations of calcareous rock fragments erected on the heights overlooding the city. The landward water-laden night winds from the Black Sea passed through these open stone pyramids and the cold stones adsorbed moisture from the passing air; during daytime, the heat of the sun warmed the stone and decreased its water-holding capacity sufficiently to change the adsorbed water into free water which, under the influence of gravity, seeped down in the interior of the pyramids. The ruins of these structures which were 30 by 20 by 10 meters can still be seen. They represented a city water supply furnishing an estimated daily quantity of 15,000 gallons of water for drinking and irrigation (30). This mechanism of water accumulation deserves renewed study.

Some Remarks on Water Transport in the Liquid Phase

Water transmission or shifting in the liquid state may occur within a wide range of moisture and complementary air contents of a porous system, starting theoretically with complete pore saturation and zero air content to a moisture content which, though low, is sufficient to provide a continuous liquid film over the internal soil surface. The air phase may be continuous or the system may contain entrapped air. The importance of the latter in the slaking of dry soils has been pointed out above; its effect on water conduction in soils is acknowledged by the care with which entrapped, and even dissolved air that might become free and entrapped, is removed in laboratory experiments. However, in natural soil systems such removal is impossible and while the effect of air entrapment in soil is not as dramatic as the bends in "sand hogs," it is important and often serves as a buffering and regulating mechanism. Its potential effect should be assayed in any experiment in which entrapped air is present and especially in cases where thermal gradients are set up in a soil system containing entrapped air.

It has been pointed out that water, in addition to possessing general liquid properties, has a highly polar character which together with hydrogen linkage leads to definite structural properties already of pure water and to the establishment of complex though ordered electrical and meterial structures in interaction with surfaces which also possess a well defined electric structure and especially those that contain exchangeable ions. This structure represents a compromise between the ordering and attraction effect of the forces between electric charges of opposite character and the disordering and dispersion effect of the kinetic energy of the ions and molecules composing the system. This structure is, of course, temperature sensitive. The thermosensitivity of the soil water system is also indicated by the positive heat of wetting of dry soils, the decrease of the heat of wetting with increasing temperature and the decrease of the water affinity and swelling capacity of soils with increasing temperature. Considering these properties, it is logical that soil water systems respond not only to mechanical (pressure and tension), but also to electric and thermal potentials and that mechanical, electric and thermal effects are coupled with each other in moist soil systems. This becomes the more evident, the greater are the amount and electric activity of the specific internal soil surface (14). The indicated effects and interactions make themselves noticed in both saturated and unsaturated water conducting systems with the additional influence of the water-air interface in the case of the latter (31).

For isothermal saturated flow under hydraulic pressure gradients, it has been shown by Winterkorn (20) and pointed out by Schmid in his symposium paper that the water-mineral surface interaction and its effect on the flow process can be treated phenomenologically by the assumption of a restrained liquid volume vicinal to the internal surface of the system.

The problem of unsaturated flow under suction potentials has been studied intensively and extensively during the last 25 years by agricultural scientists and by highway engineers. Several papers on various aspects of this problem and on its application to highway engineering are contained in the present symposium. Essentially the same general type of equations as used for saturated flow holds in this area except that the transmission constant is predominantly a function of the extent and character of the internal surface and of the moisture content.

Water Movement upon Application of Electric Potentials

The movement of water through capillaries and pores as a result of the application of electric potentials was first described by Reuss (32). The classical explanation of this phenomenon as due to the existence of an electric double layer between pore wall and liquid was given by Helmholtz and was developed subsequently into the Helmholtz-Perrin-Smoluchowski theory (3). This theory holds quite well for pores that are not too small and for walls whose electric double layer is not too diffuse. Within this class fall the natural silty soils and also clay soils whose permeability resembles that of silty soils because of aggregation and formation of a secundary soil structure. The theory does not hold well for very fine pores in material of great water affinity such as animal membranes and structureless clay soils. For the former, Schmid has developed a new theory under the assumption that the exchange ions are uniformly distributed in the pore water. Subsequently, this concept was applied successfully to electroosmosis in structureless clay-water systems (33). The Helmholtz concept leads to the following simplified equation for the electroosmotic transmission constant of a soil: $k_e = C_e \ n$ in which k_e = volume of liquid moved per second across a section of
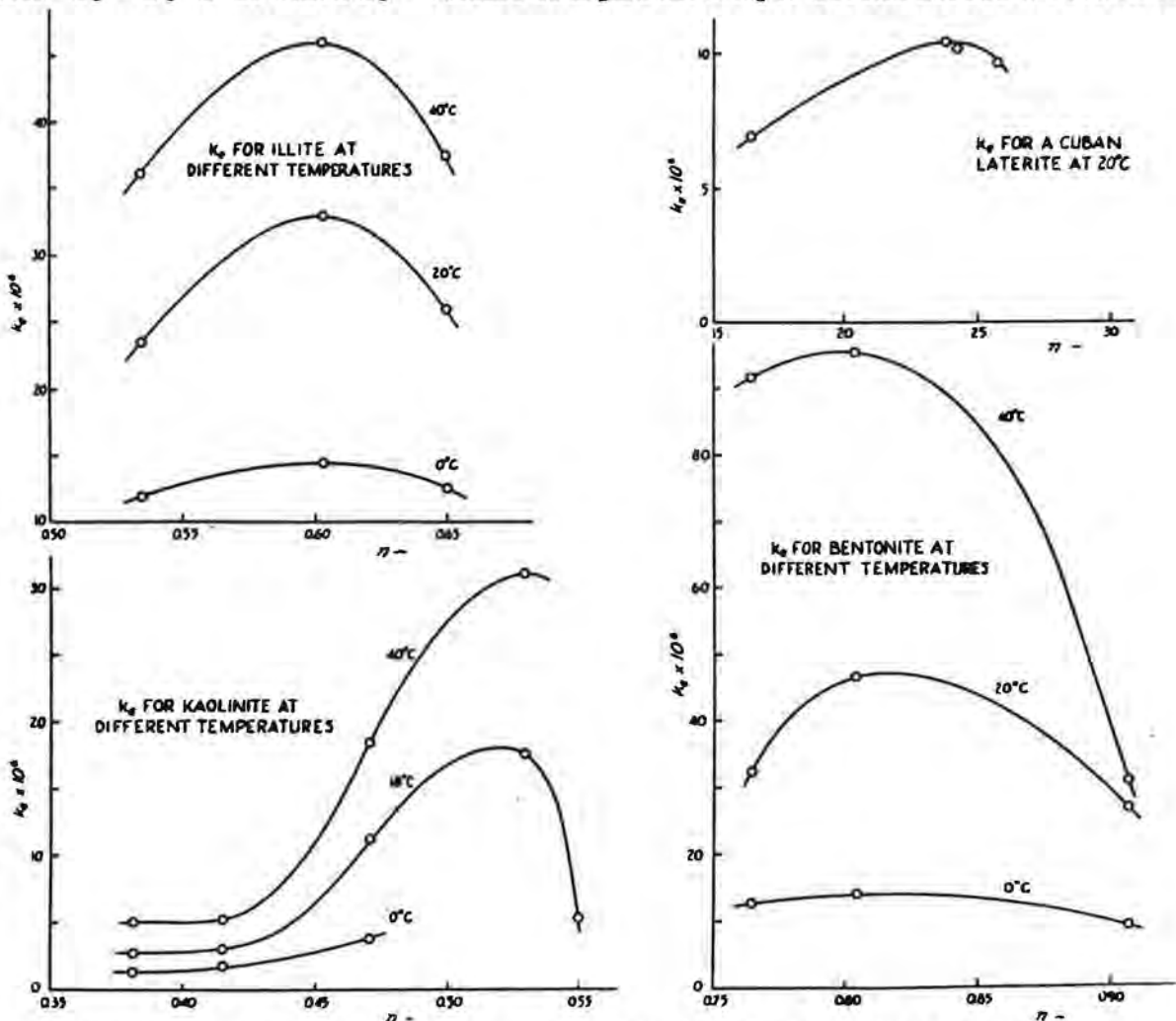

Figure 1. Electroosmotic transmission constants as functions of porosity.

1 sq cm under an electric potential normal to the section of 1 volt per cm, C_e = constant which incorporates geometrical and electric surface-liquid interaction factors, and n = porosity of the system as a fraction of the total volume.

Substituting in this equation a porosity of 1, that is, all pore space and no walls, would give a maximum k_e value. This is clearly illogical since the very presence of electrically charged walls is the "conditio sine qua non" for electroosmosis.

Application of the Schmid concept to electroosmosis in soils leads to the Winterkorn equation: $k_e = C_e (1 - n)^{2/3} n$, where C_e is again a constant expressing geometrical and surface-liquid interaction factors, and k_e and n possess the same meaning as previously. This equation correctly leads to k_e values of zero for systems of zero porosity, at one extreme, and for systems of 100 percent porosity, that is, no walls, on the other, with a maximum value at an intermediate porosity. The actual location and numerical value of k_e maximum is influenced by a number of factors such as degree of hydration and mutual interaction of hydrated ions that are not contained in the derivation of the general equation. Hence, experimental determination is indicated (33) (see Fig. 1). In actual engineering application of electroosmosis, there is coupling or interference with electrolytic, thermal and other phenomena.

Water Movement upon Application of Thermal Gradients

The most complex and least understood area in the field of moisture transmission in soils is the movement of water upon the application of thermal potentials. The complexity is illustrated by the following factors:

1. In the condition in which a cohesive soil yields a maximum amount of water under a thermal gradient (compaction at a moisture content in the vicinity of the plastic limit), there can be little doubt about the presence of significant amounts of entrapped air that expands on the warm side and contracts on the cool side of the specimen and thus produces a hydrostatic pressure gradient.

2. Almost immediately upon the application of a hot face at one end of a cylindrical soil specimen and of a cold face on the other, long before the temperature gradient within the specimen has become uniform, an electrical potential gradient of quite uniform character is established in the soil system. From the magnitude and characteristics of this electric potential, it may be concluded that it is essentially a thermoelectric potential that with the aid of the electric structure of the soil-water travels ahead of the thermal disturbance and of the thermal moisture movement in a similar manner as nerve fibers carry to the brain signals of the thermo-sensitive cell mechanisms of the living skin. This electric potential is of much greater magnitude than electric flow potentials, which are caused by any water movement whatever be the causative factor, and seems to be little affected by such flow potentials which must be superimposed (14) (see Fig. 2).
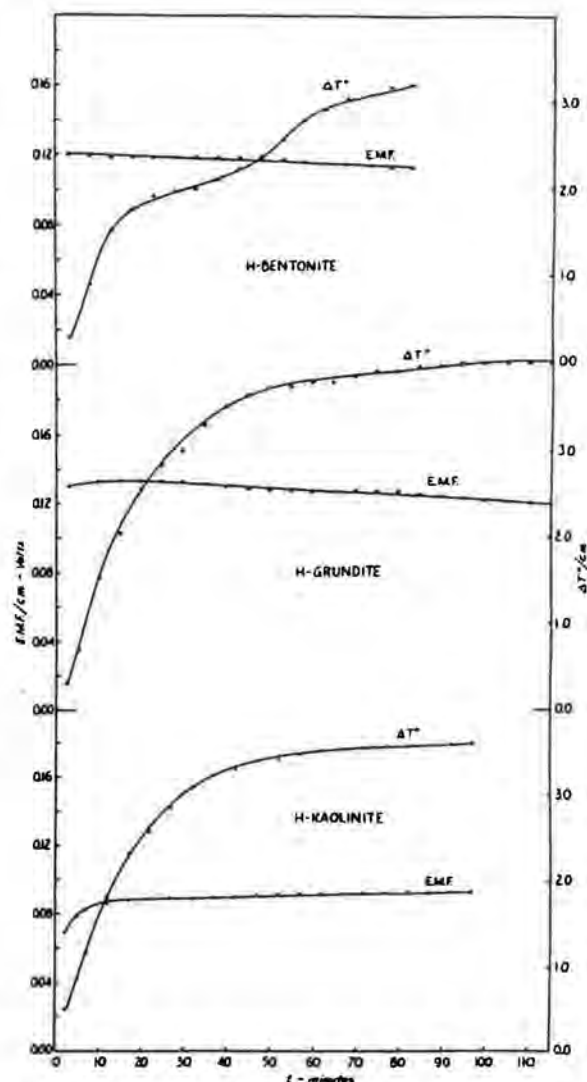

Figure 2. E.M.F. and temperature gradients developed in thermoosmosis experiments with clay minerals.

3. Micro-distillation and even micro-convection phenomena may occur in the entrapped and continuous air phases within the system and add their share to the total water transmission.

4. Application of the temperature gradient causes gradients in the surface tension of the water films, in the thickness of the ion atmosphere on the internal soil surface, in the hydration of the exchangeable ions, in the solubility of water in the solid surface and in the geometrical structure as well as in the dissociation and association of the water substance itself.

As formidable and as important a problem as the elucidation and proper coordination of the phenomena involved in the conduction of moisture through hydrophilic porous systems under thermal potentials should be attacked as a full time job by coordinated efforts of well staffed, well equipped and well financed laboratories. As a matter of fact, most of the important work done on this problem has been by scientists and engineers busy with other work obligations who grappled with whatever part of the problem was causing trouble in the pursuit of their official duties. Like an elephant occupying the crossing of many jungle paths, this problem was in the way of many scientific and engineering pursuits and at each path a different portion of the anatomy of the elephant was recognized, described as the obstacle and passed over without anybody finding the time to look at, much less to describe and analyze, the entire animal. This situation seems to be the perfect exemplification of the parable of the seven blind men and the elephant. It is hoped that the present symposium, by juxtaposing many different facts and concepts bearing on the various phases of the total problem of the effect of temperature gradients on moist soil systems, will aid in the clarification and ultimate theoretical organization of this extremely important scientific area.

SUMMARY AND CONCLUSIONS

Coupled irreversible mass transportation phenomena in highway subgrades and bases and in similar porous hydrophilic systems are of vital interest to the highway engineer especially if the material transported is water. These phenomena have so far been studied mainly experimentally and justifiably so. Their theoretical treatment has been essentially phenomenological with some influence of kinetic reaction and activation energy concepts. Due to the irreversible character of the phenomena, their classical thermodynamic treatment or their treatment as semi- or quasi-reversible systems has been either cumbersome or has led to results that did not touch the essence of the problem.

The new methodology of the thermodynamics of irreversible processes holds considerable promise for more adequate theoretical treatment. However, before such treatment can be applied with good expectation of success, a great deal of additional experimentation is needed to supply the necessary physical parameters in the most useful form for such treatment. Hence, in the planning of future experimentation, it will be worthwhile to keep in mind the methodology of the contemplated theoretical treatment of the data. For this reason, the essence of the methodology of the thermodynamics of irreversible processes has been indicated and references have been given for its study in detail which is necessary for its application.

In order to show the large potential area of application of this new methodology in the field of soil science and soil engineering, a number of examples were given of coupled mass transfer phenomena in soils of a type and occurring under conditions that are of distinct interest to highway engineers. Of course, within the frame of this paper, the description of these examples could not be exhaustive, but it is in sufficient detail to indicate the various forces that are coupled together in each case to produce the general reaction picture.

The coupling of mechanical, thermal and electric effects observed in soil-water systems of large surface to volume ratios brings to mind the similar phenomena observed in living systems and shows that essentially the same problems are faced by the plant and animal physiologist as by the soil scientist and engineer. Close cooperation between all disciplines concerned with the properties of the water substance and its interaction with materials and energy in various forms is clearly indicated.

The better understanding thus gained of the water substance and its reaction to energy gradients should aid in the solution of many scientific and engineering problems. In addition, it should show the way for better water utilization, with concomitant lessening of the ever growing problem of securing an economical water supply sufficient for present and future needs. Such coordinated study should also shed light on many problems of normal and abnormal life and growth and may well become the basis of a more scientific and more effective approach to the problem of health and disease (11).

ACKNOWLEDGMENTS

REFERENCES

1. Clausius, R., Pogg. Ann., 125:390 (1865).
2. Planck, Max, Ann. d. Phys. Lpz., 30:563 (1887).
3. Guggenheim, E.A., "Thermodynamics." North Holland Publishing Company, Amsterdam (1957).
4. Planck, Max, "Thermodynamik." Walter de Gruyter and Co., Berlin and Leipzig, 8th edition, p. 335 (1927).
5. Arrhenius, S., Zsch. f. phys. Chemie, 4:226 (1889).
6. Trautz, Max, Zsch. f. phys. Chemie, 66:496 (1909).
7. de Groot, S.R., "Thermodynamics of Irreversible Processes." North Holland Publishing Company, Amsterdam, pp. 220-4 (1952).
8. Prigogine, I., and Defay, R., "Etude Thermodynamique des Phénomènes Irreversibles, Liège (1947).
9. Denbigh, K.G., "The Thermodynamics of the Steady State." Methuen and Co. Ltd. (1951).
10. Hutchinson, H.P., Nixon, I.S., and Denbigh, K.G., "The Thermoosmosis of Liquids through Porous Materials." Discussions of the Faraday Society, No. 3, pp. 86-94 (1948).
11. Szent-Gyorgyi, Albert, "Bioenergetics." Academic Press Inc., New York (1957).
12. Winterkorn, Hans F., and Baver, L.D., "Sorption of Liquids by Soil Colloids." I. "Liquid Intake and Swelling by Soil Colloidal Material." Soil Science, 38, No. 4 (1934). II. "Surface Behavior in the Hydration of Clays." ibidem, 40, No. 5 (1935).
13. Winterkorn, Hans F., and Eckert, George W., "Consistency and Physico-Chemical Data of a Loess Pampeano Soil." I. "Physico-Chemical Properties of Samples from Different Depths of a Profile." Soil Science, 49:73-82 (1940). II. "Properties of Natural and Homoionic Samples of Soils and Clays." ibidem, 49:479-488 (1940).
14. Winterkorn, Hans F., "Potentials in Moisture Migration." Proc. Conf. Build. Mat. October 1953, Ottawa, Canada, Bull. No. 1, Div. Build. Res. Nat. Res. Council of Canada, pp. 86-101 (1955).
15. Low, Philip F., "Movement and Equilibrium of Water in Soil Systems as Affected by Soil-Water Forces." Highway Research Board, Special Report 40 (1958).
16. Winterkorn, Hans F., "Studies on the Surface Behavior of Bentonites and Clays." Soil Science, 41, No. 1 (1936).
17. Henniker, J.C., and McBain, J.W., "The Depth of a Surface Zone of a Liquid." Technical Report N 6 ori 154 T.O. 11, Stanford Research Institute, Stanford, California (1948).
18. Tyndall, John, "Heat Considered as a Mode of Motion." D. Appleton and Co., New York, pp. 122-143 (1868).

19. Cazin, Achille, "The Phenomena and Laws of Heat." Charles Scribner and Co., New York (1869).

20. Winterkorn, Hans F., "Mechanism of Water Attack on Dry Cohesive Soil Systems." Soil Science, 54: 259-273 (1942).

21. Winterkorn, Hans F., and Choudhury, A. N. Dutt, "Importance of Volume Relations in Soil Stabilization." Proc. Highway Research Board, 29: 553-60 (1949).

22. Thompson, D'Arcy Wentworth, "Growth and Form." Cambridge University Press, pp. 465-565 (1942).

23. Beudant, F. S., "Recherches sur les causes qui peuvent varier les formes crystallines d'une substance minerale." Annales de Chimie, VIII, pp. 5-52 (1818).

24. Faraday, Michael, "On Ice of Irregular Fusibility." Phil. Trans., p. 228 (1859).

25. Tyndall, John, "Forms of Water." p. 173 (1872).

26. Tomlinson, C., "On Some Effects of Small Quantities of Foreign Matter on Crystallization." Phil. Mag. (5) XXXI, p. 392 and other papers (1891).

27. Liesegang, R. E., "Colloid Chemistry and Geology." Colloid Chemistry, Theoretical and Applied, Jerome Alexander, editor, Vol. III, pp. 251-60. The Chemical Catalog Co., New York (1931).

28. Winterkorn, Hans F., "Climate and Highways." Trans. Am. Geogh. U., 25: 405-11 (1944).

29. Chaptal, L., "La lutte contre la sécheresse. La captation de la vapeur d'eau atmosphérique." La Nature, No. 2893, pp. 449-54 (1932).

30. Winterkorn, Hans F., "A Research Program on the Aerial Well." The Engineer's Bulletin, Denver, Colo., Vol. 39, No. 11, pp. 10, 11, 25 (1955).

31. Winterkorn, Hans F., "Water Movement through Porous Hydrophilic Systems under Capillary, Electric and Thermal Potentials." ASTM Symposium on Permeability of Soils, Spec. Techn. Publ. No. 163, pp. 27-35 (1955).

32. Reuss, "Memoirs of the Imperial Russian Naturalist Society." Moscow, 2: 327-37 (1808).

33. Winterkorn, Hans F., "Surface-Chemical Properties of Clay Minerals and Soils from Theoretical and Experimental Developments in Electroosmosis." ASTM Symposium on Exchange Phenomena in Soils, Spec. Techn. Publ. No. 142, pp. 29-43 (1943). See also (14).