Concerning a Mechanism for Soil Moisture Translocation in the Film Phase upon Freezing

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This paper reviews the electric double-layer theory, which serves as a basis for understanding soil moisture translocation in the film phase upon freezing. Based on this theory, hints are given as to a possible mechanism for the upward migration of soil moisture in the film phase under freezing conditions and some assumptions as a working hypothesis are outlined. Some of these assumptions are supported by observations from soil freezing experiments. Upon freezing a soil system, induced electrical potentials between 40 and 120 millivolts were measured, and subpressures of the soil moisture films as high as 32 cm mercury were measured.

All processes occurring in the freezing soil system are in some way connected with the surface phenomena of colloidal particles. Water in the form of soil moisture films is the medium where many changes in soil take place when subjected to temperature changes. The property of a colloidal soil particle of carrying on its surfaces an electrical charge and the functioning of the soil moisture as an electrolyte are of fundamental significance in the process of the translocation of soil moisture in the film phase when the soil system is subjected to an external, primary, freezing thermal gradient.

• A GOOD transportation system for high speed and mobility demands highclass roads and airfields. Because roads are built upon, and their fills are constructed by means of soil materials, it becomes necessary to understand thoroughly the properties and performances of highway soils under load and in relation to water and temperature. It is also necessary to understand the induced moisture migration processes in soil, particularly under freezing conditions, inasmuch as freezing and thawing affect highways and their soils adversely.

Owing to the significance of the liquid phase of soil (that is, the considerable contribution which the substance water makes to the performance of soil under freezing conditions), an attempt is made:

1. To review the available knowledge in the physical sciences as it pertains to some engineering problems; for example, to highway and airfield construction. 2. By means of this knowledge to try to explain certain processes which take place in a freezing soil system, thus providing also a scientific liaison between the physical and engineering sciences.

3. Specifically, it is hoped that the available knowledge would permit one to formulate in a scientific discipline a hypothesis in order to explain certain phenomena which are not yet quite well understood. Among these are the various soil moisture transfer mechanisms under freezing conditions, especially in the film phase. For the development of a scientific discipline on freezing soil systems, the hypotheses are to be tested by research and experiment. The experimental results should be thoroughly buttressed by theoretical analyses. Development of a scientific discipline takes place usually through (a) observation and measurement, (b) inductive reasoning from facts thus obtained, (c) deductive reasoning based on hypotheses and theories, and (d) experimental research to prove or disprove the theoretical deductions.

4. To illustrate some of the processes which take place in freezing soil systems by results obtained from the author's experimental research.

An insight into the phenomena and processes associated with the freezing soil system is of particular interest to the scientific technologist in soil engineering, enabling him to choose and to deal correctly with soil as a construction material under freezing conditions.

OBJECTIVE

Interaction of Physical Forces

In studying frost effects upon soil and its performance it must be remembered that there is something else involved than merely the solid particles of the soil (viz., soil texture). Soil in its natural condition usually consists of three phases: the solid phase (soil particles), the liquid phase (soil moisture), and the gaseous phase (air, or gas, or aqueous vapor). Thus, in the soil freezing process an important factor, among others, is the soil moisture. Soil moisture in a freezing soil system, it is safe to say, is relatively more important than the solid particles of the soil themselves, although, unquestionably, certain physical processes in soil depend also on the nature of the solid particles and their surface characteristics. More important, however, is the interaction of physical forces between the surface of soil particles and the soil moisture films surrounding the soil particles. This is of especial significance in studying processes in hydrophylic soil systems; for example, the soil moisture transfer in the film phase from one place to another when the soil is subjected to a freezing temperature gradient.

Some possible mechanisms of the upward migration of soil moisture under treezing conditions are discussed elsewhere (1, 2, 3). The manner in which the soil moisture translocates through a porous system such as soil during a freezing process is termed here the "mechanism of soil moisture transfer."

Changes Induced in a Freezing Soil System

If a vertical column of a soil system is subjected to freezing from its top downward, as occurs in highway soils in winter, several changes take place in the following manner. A curvilinear temperature gradient sets in across the freezing soil system, from the top down (4). There takes place an upward heat transfer from a region of higher temperature in the soil system (ground water) toward a region of colder temperature (frozen layer of soil). The thermal energy, in its turn, commences in the porous soil system the upward migration of soil moisture; upon freezing of the soil moisture, latent heat is released. Likewise the thermal properties of soil, water, and ice change, as do the density, viscosity and dielectric constant of the water. Although water in soil is usually present in the form of liquid, the conditions are very complicated, because water is noted for several anomalies it displays in its physical properties. Thus, for example, when subjected to temperature variations water changes its density, being at its maximum at +4 C. Also, with increase in temperature, the viscosity of water decreases rapidly.

In addition, water in soil may be encountered in the gaseous, liquid and solid states. Thus, studying the freezing soil system, the changes of water from one state of aggregation into another are to be considered. Similarly, the properties of water in the form of film attracted to and existing around the soil particles are believed to be somewhat different from its properties when in bulk. Because the many properties of water are usually well known to the physicists, but perhaps, not so well known to the engineer, it is proposed to discuss here especially some of those factors which are necessary for the understanding of the phenomena and processes taking place in a freezing soil system. To do this let recourse be taken to some of the basic physical concepts known in physics and in colloid, capillary, and physical chemistry, and use them, as far as it is possible, in elucidating the phenomenon of the upward migration of soil moisture under freezing conditions in the film phase.

SOIL AS A DISPERSE SYSTEM

All surfaces of solid particles, among them also the surfaces of the finest colloidal soil particles, when moistened with a liquid, such as water, adsorb this liquid in the form of a thin hull or moisture film. Likewise, it can be assumed that under natural conditions soil particles are in a humid, or moist environment and adsorbing moisture. The importance of this in relation to the freezing of soil is that the soil particles are already coated with adsorbed moisture films before freezing sets in.

Considering the solid particles of soil and soil moisture, soil can be considered as a disperse system: the solid particles form the disperse phase, and the water, in which the soil particles are distributed and which thereby forms the continuous phase, is the dispersion medium.

The term "phase" is understood to refer to any homogeneous part of the system different from other parts and separated from them by abrupt transition (for example, the solid soil particles dispersed in water), thus giving the concepts of solid and liquid phases of the soil.

Also, the finely sized soil particles surrounded by the moisture films can be considered in one way as a colloidal solution. Hence, the concepts, problems and processes of colloid and physical chemistry are coming more to the fore in studying soil moisture transfer upon freezing. It is to be noted that, according to Ostwald (5), the colloidal state is independent of the chemical composition of the dispersed solids.

STRUCTURE OF A WATER MOLECULE

Polarity

According to Debye (6, 7, 8), a molecule of a substance can be represented as a system of electrical charges, and the water molecule has a polar structure. The term "polarity" is applied in connection with the actual arrangement or the mobility of the charges of which molecules are supposed to consist.

The polar structure of water molecules is due to a non-symmetrical distribution of electrical charges in the individual atoms comprising the molecules. Therefore, in a certain region of the molecule there is a surplus of positive electrical charge, but in others there exists a surplus of negative charge. One would expect that in the polar water molecules electrical poles would exist. Hence, water is designated as a polar substance. The polar molecules are called dipoles. Figure 1 is a simplified diagrammatic representation of the geometrical arrangement of the atoms in a polar water molecule. The plus and minus poles form a dipole. The electric charge at the electrical centers multiplied by the distance between these



Figure 1. Schematic diagram of a polar water molecule, showing (left) a simplified representation of the dipole and (right) a triangular model.

centers is termed the dipole moment of the substance.

It is interesting to note that according to Partington (9) the existence of separated positive and negative charges in molecules was assumed by Berzelius (36), who called this state polarization, comparing it with the polarity of magnets.

The polarity of water is explained by the triangular alignment, wherein the atoms are aligned at the vertexes of a triangle. The hydrogen ions are located at the shell of radius r, which is concentric with the oxygen ion. The angle 2β in the triangular orientation of the atoms, depending on the assumptions made in calculating the angle, is reported to be as follows:

 2β
 Reference

 105°
 Kronig (10)

 105°
 Partington (11)

 104°31'
 Brown (12)

 110°
 Debye (13)

If indeed such "polar" molecules exist, one must expect that the action of an energy field on the medium will disclose electric properties in it by virtue of the field's directive action, because it will tend to set the positive-to-negative axes of the molecule into the direction of its own lines of force. Thus, within the water molecule there must occur an orientation as well as a deformation.

The polarity property of water is important in that it gives water the ability to support ionization. Ionization is a process which results in the formation of ions in a certain medium, in this case water. The polarity of water can thus be considered a link in the mechanism of the soil moisture transfer in the moisture film phase.

Orientation of Water Molecules

Because of the presence of electrical charges the polar water molecules have among themselves a mutual electrostatic interaction and orientation; namely, the positive pole of one molecule is attracted to the negative pole of another molecule, and vice versa. For example, Figure 2



Figure 2. Mutual orientation of polar water molecules, showing stability (attraction) and instability (repulsion).

shows mutual attraction of two water molecules, said to be stable, and mutual repulsion between two water molecules, said to be unstable. As a result of mutual interaction, polar molecules of the same substance combine among themselves and form complexes with the ions leading to associations. Figure 3 illustrates the concept of attraction of dipole water molecules by a positive ion. In the case of a negative ion, the attraction and orientation of dipole water molecules is the converse of that shown in Figure 3.

Associating liquids, for example, are water, acetone, liquid ammonia, and other ionizing solvents.



Figure 3. Attraction and orientation of dipole water molecules by a positive ion.

BOUNDARY BETWEEN SOLID AND LIQUID PHASES OF SOIL

Ionic Atmosphere

Of particular interest in studying physical processes in soil is the boundary between the phase of the soil and its surrounding medium, whether liquid or gaseous, or a combination of the two.

Referring to the concept of soil as a disperse system, the soil moisture surrounding the solid soil particle represents a water hull or film in which an ionic aura or atmosphere exists. The ionic atmosphere extends from the surface of the solid particle into the bulk of the free water in the voids of the soil for some distance.

The concentration or electric density of the ionic atmosphere diminishes from the surface of the solid particle with the increase in distance. With increasing distance from the surface of the soil particle, the molecular attractive forces rapidly decrease and the bound water of the moisture hull gradually transforms into free (bulk) water. The distribution of ions in soil water close to the solid soil particle takes place under the action of electrostatic forces and by the presence of molecular heat movement.

Electrical Charge on Surfaces of Colloidal Particles

Water molecules forming moisture films are not the only factors that are adsorbed on the surfaces of solid soil particles. One of the conspicuous characteristics of a soil particle in a medium of water is that under certain conditions it carries an electrical charge, which, in contrast to heat, tends to reside on its surface.

The charge on the particles is usually the result of adsorption of ions. The soil particles acquire their electric charges from naturally occurring solutions which act as electrolytes, the molecules of which upon solution separate into electrically charged units or ions. The more finely the soil is dispersed, the greater is its specific surface. Consequently, more ions can be accommodated on the surfaces of the soil particles. However, it must be understood that this simple explanation of the manner by which soil colloidal particles acquire their electric charges is far more complex in reality.

The sign of the charge is different for various substances. However, the particles carry the same kind of charge if all of the soil colloidal particles are of the same matter in a certain solution. The nature and magnitude of the charge varies greatly with the liquid used as a dispersion medium. For instance, the character of this charge on the surface of a clay colloid particle in water is usually negative (14). The character of the charge of the soil solid particles can be approximately determined by Coehn's law (15). According to this law, a phase such as the surface of a solid particle acquires a negative charge if its dielectric constant, D_s , is less than the dielectric constant of the liquid, D_L , which comes in contact with the solid. The value of the dielectric constant, expressed in electrostatic units, is defined as the ratio of the mutual electrical capacity of a given pair of equipotential surfaces, fixed with reference to each other, when immersed in the dielectric to their capacity when immersed in a vacuum. The dielectric constant of water, not exceeding 100 megacycles per second at a pressure of one atmosphere, is independent of the frequency, and is about $D_w = 81.2$ electrostatic units at +17 C (16); that of the soil particles is $D_s = 5$ to 6. Thus, according to Coehn's law, it can be expected that on the surfaces of the soil particles there should reside a negative charge (=anions), but the soil moisture film surrounding the soil particles should then be charged positively (with cations).

Although considerable doubt has been cast, for various reasons, on the validity of Coehn's rule (17), it is certainly not of great value when ionizing solvents are concerned. However, it may have some use when the liquid is not an electrolytic conductor. The ionic atmosphere appears to involve oriented polar molecules. Thus, when the solid phase is in contact with a

pure solvent (for example water), in general, Coehn's law is valid (15).

Therefore, in studying freezing soil systems it is necessary to know the values of the dielectric constants of soil, water, and ice, at different temperatures.

ELECTRIC DOUBLE LAYER

The purpose of discussing the electric double layer is to relate it to an understanding of the orientation of the dipole water molecule and soil moisture migration when the soil system is placed in an electric field, or when subjected to a freezing thermal gradient.

Double Layer

If a soil particle is considered individually, and immersed in water, it can be deduced from the previous description that the solid particle is surrounded by an electric double layer. One layer of this double layer is formed by the negative charge on the surface of the soil colloidal (clay) particle. The negatively charged soil particles tend to surround themselves with ions of the opposite charge (cations) thus forming the second (outer) layer of the electrical double layer. This outer layer is formed by the excess of the oppositely charged ions in the solution (water). This means that polar molecules of water may be oriented at the interface between the solid soil particle and the dispersion medium, water.

Helmholtz's Electric Double Layer

Historically, Quincke (18) suggested that the solid particle in contact with the liquid becomes electrically charged in some way while in the immediate vicinity of the surface of the solid, but in the liquid there is a layer of electrical charges of the opposite kind, exactly equal in magnitude to the charge on the solid. This was the origin of the so-called theory conceived by double layer Ouincke, usually called the Helmholtz double layer because Helmholtz (19) formulated theoretically the concept of the existence of differently charged layers at the solid-liquid interface.

According to Helmholtz, an electrical double layer of a fixed thickness (of the order of magnitude of one molecule) forms at the interface of any phase in contact with a liquid. The outer layer of oppositely charged ions is mobile, and the inner layer, which lies in the liquid, is rigid, adhering firmly to the wall of the solid. The mobile layer neutralizes the oppositely charged surface laver. This simple concept of the Quincke-Helmholtz electrical double layer is shown diagrammatically in Figure 4. The double layer could be represented by two parallel, flat electrical condenser plates. Such electrical double layers are supposed to exist not only at plane surfaces but also surrounding the solid colloidal soil (clay) particles suspended in a liquid medium such as water.

It is also interesting to note that Helmholtz formulated the following:

The layer of water molecules in contact with the wall of the solid particles is immobile. It is fixed to the wall regardless of the physical forces imposed on the liquid. That is, there is no slip. The rest of the molecules in the double layer are mobile and subject to the ordinary laws of friction of normal liquids.

Zeta (ζ) Potential

It was seen that, in general, when two phases—solid and liquid—come in contact there is a separation of charges: one phase becomes negative in respect to the other. This separation of charges gives rise to an electric potential difference or a potential gradient at the interface between the two phases. According to Helmholtz, the gradient of this potential drop across the double layer is sharp and varies linearly with distance (Fig. 4a). The electric potential across the double layer is called the electrokinetic potential.

In recent years, however, there has been a tendency to use the noncommittal term zeta potential (ζ -potential) instead of electrokinetic potential because of the symbol conveniently used for its representation. The double layer was considered by Helmholtz as a parallel-plate electrical condenser with the spacing between the plates replaced by the thickness



Figure 4. The Quincke-Helmholtz electrical double layer, showing (a) electrical conditions at a charged interface (orientation of charges) and (b) a soil particle in water.

of the double layer, and with the ζ -potential existing between the plates.

The difference in cross potentials at the interface of two phases when there is no mutual relative motion is called the thermodynamic potential, or the Nernst potential (ϵ). Potential difference created at the interface upon the mutual relative movement of two phases is called the electrokinetic or zeta potential.

Usually the electrokinetic (ζ) potential is considerably less than the thermodynamic potential, ϵ , and under some circumstances can even be of the opposite sign.

The electrokinetic potential can be measured only under conditions of phases in motion relative to each other; that is, when electrokinetic processes are taking place. It is conceived that the ζ -potential has a major part in the electrical properties of colloidal (soil) systems. Also, it is most important because its value is often connected with the stability and viscosity of suspensions. The ions in the double layer attract water. The amount of water taken up will influence the viscosity. Thus, the viscosity of the liquid will not only be influenced by the quantity of electrolyte present, but also by the kind of ions.

One other point is important. There exists an important difference between surface tension and viscosity of a liquid; namely, surface tension is essentially a surface phenomenon, whereas viscosity is concerned with the internal properties of a liquid. Therefore, it can be expected that viscosity will respond with great sensitiveness to changes in the molecular configuration of the liquid. This explains the importance of the ζ -potential and viscosity of the dispersion medium (here water) in research.

The concept that the colloidal soil particles carry an electrical charge might give one the mistaken impression that the soil represents an aggregate of statically charged ideal spheres, and that therefore an electroscope, when brought close to the soil (*in situ*, or a laboratory sample), would show a deflection. However, this is not so. It must be remembered from the previous discussion that the electrical charges in the system are self-compensating. This principle finds its validity in the idea of the electrical double layer.

Gouy Double Layer

In the course of time it was revealed that the Helmholtz model of the double layer is inadequate because the thermal motions of the liquid molecules could scarcely permit such a rigid array of charges at the surface of the solid particle. Scientists came to the conclusion that the electrical double layer at the interface could not be rigid as was originally assumed, and of fixed thickness equal to the diameter of a molecule.

Gouy (20) thought that the charges of one sign in the liquid side of the Helmholtz double layer would attract charges of opposite sign. This attraction, in turn, would cause a non-uniform distribution of the charges in the liquid near the solidliquid interface that Helmholtz proposed. Gouy's ideas about the electrical conditions at the solid-liquid interface are principally as follows: the rigid part of the electric double layer lies in the liquid adhering firmly to the surface of the solid particle; the second part lies in the mobile part of the liquid and extends into the homogeneous interior of the liquid.

Movement of the liquid takes place against the liquid adhering firmly to the surface of the solid, and thus against the charges imbedded in it, but not against the solid surface directly. At very low temperatures ions are rigidly adsorbed on the surface, thus forming a true Helmholtz layer. With increase in temperature (to room temperature, for example) many of the adsorbed ions "dissipate" from the surface. However, these ions are unable to escape entirely from the influence of the charge on the wall.

The distribution of ions in the rigid part of the double layer is governed by the mutual interaction of electrostatic forces and specific energy of adsorption, as well as by the presence of molecular heat movement. The distribution of ions in the mobile part of the double layer is governed by electrostatic forces and by thermal action. Electrostatic forces concentrate the oppositely charged ions around the solid particle, but the forces of the molecular heat movement tend to distribute ions uniformly within the liquid phase.

Owing to these circumstances, a diffuse double layer results, where the negative ions are adsorbed primarily near the surface or wall of the solid particle, but the positive ions farther away from the wall. The ionic atmosphere in the immediate vicinity of the surface is fairly dense, and at greater distances from the surface the ionic density decreases until the net charge density is zero.

Although not all the ions in the diffuse double layer are of the opposite sign from those at the surface of the solid, the ions of opposite sign do predominate. Thus, Gouy (20) and Chapman (21) imagined the double layer as a diffuse distribution of electrification, an "ionic atmosphere." Also, Gouy supposed that the double layer frequently extends considerably farther out from the solid surface into the liquid phase than a distance of one molecule.

Gouy termed the outer part of the double layer diffuse because there the ion concentration decreases with the increase in distance from the surface of the solid particle. Consequently, the electrical density of the ionic atmosphere drops off away from the wall into the interior of the liquid according to an exponential law, in contradistinction to Helmholtz's linear rule, which calls for a sharp drop in the ζ -potential gradient at the inter-



Figure 5. Gouy-Chapman diffuse double layer.

face. The Gouy-Chapman diffuse double layer and the drop in ζ -potential are illustrated diagrammatically in Figure 5.

The thickness, δ , of the double layer, according to Rutgers (22), is of the order of 10^{-6} or 10^{-7} cm.

Because the diffuse layer extends some distance into the water phase it is necessary in soil moisture migration studies, particularly upon freezing, to take into account the dielectric constant of water. This constant may probably be assigned the value it has in pure water.

Stern Double Layer

More recently, Stern (23) showed that neither the sharp nor the diffuse double layer theory is alone adequate, and presented a view combining the essential features of both. As in the Helmholtz layer, in Stern's proposition there is a rigidly attached charge on the surface of the solid. Then, immediately adjacent to the surface, there exists a layer with a charge opposite to that which is fixed on the surface of the solid (Fig. 6). This



Figure 6. Stern's double layer.

layer adjacent to the surface is approximately one ion thick, and is almost rigidly adsorbed to the surface of the solid; thus, this thin layer can be considered as practically immobile. This layer is part of Stern's double layer. In this almost fixed layer there is a sharp drop, AB, in potential like the one that exists in the Helmholtz layer.

This sharp potential gradient can be considerably influenced, depending on changes which may take place in the adjacently adsorbed part of the double layer.

Adjacent to, and farther away into the bulk of liquid, from this single-ion layer, there is the second part of Stern's double layer which is diffuse in character. Here the charges may be of the same sign as, or opposite to, that of the adsorbed layer. Because the electrostatic field at the surface results in a preferential adsorption of the oppositely charged ions, the distribution of positive and negative ions in the diffuse part of the double layer is nonuniform. Thermal agitation in this part of the double layer allows the particles to translocate freely. Also, the diffuse part is free to move when the whole soil system is subjected to an externally applied potential difference.

Because the ionic concentration gradually decreases with the increase in distance from the solid surface, the ζ -potential drop across the diffuse part of Stern's double layer is more gentle, gradual, and curvilinear. Thus, the interfacial potential difference in Stern's double layer contains two parts corresponding to separate potentials across both Helmholtz' and Guoy's diffuse layers.

Triple Layer

Devanathan (24) further developed the Stern concept of the double layer and has postulated the structure shown in Figure 7. According to Devanathan, the Helmholtz layer is of duplex structure, consisting of unsolvated and solvated ions. The unsolvated ions are regarded as specifically adsorbed. Farther out from the surface, there is a layer of solvated anions and cations. The average plane through the electrical centers of these solvated ions marks the boundary of the Gouy diffuse layer, which substantially remains unaltered.

Devanathan's view is complicated by the effects of specific adsorption. However, according to Potter (24), Devana-



Figure 7. Triple layer of Devanathan.

than's concept takes into account the observed shape of the capacity-potential curves for mercury, a subject beyond the scope of this paper.

Freundlich (25) has some comments to make relative to the dependence of the electrokinetic phenomena upon the nature and concentration of the electrolyte present in the solution. It is his opinion that at high concentrations of electrolyte the electrokinetic phenomena will become insignificant and may disappear for the simple reason that the double layer will no longer reach far enough into the liquid and that at the point where the layer of liquid adhering to the wall passes over into the mobile liquid appreciable differences of potential will no longer exist. Besides the influence of concentration, the increase in conductivity causes a diminution in electrokinetic action.

STRUCTURE OF COLLOIDAL PARTICLE

In order to elucidate the nature of water-film attached to the surface of a colloidal (mineral) soil particle, it is necessary to familiarize one's self with the present-day concepts of the structure of a colloidal particle and the mutual interaction of mineral particles with the aqueous solution surrounding them. These concepts are borrowed from colloid science and are utilized for the explanation of the so-called electrokinetic phenomena in soils, particularly in fine-particled soils such as silts, clays, and clay colloids.

Micella

When solid particles such as those of a colloidal clay are dispersed in liquids, as may occur with soil *in situ*, there are many individual systems which consist of a charged nucleus surrounded by adsorbed and more or less extended diffuse ionic atmosphere (Fig. 8).

According to the suggestion made by Duclaux (25), the individual colloidal particle in a disperse system as previously described is termed a "colloidal micella." The disperse phase is termed the "intermicellar liquid," which is in equilibrium



Figure 8. Schematic diagram of a colloidal micella, showing positively charged ions, negatively charged ions adsorbed at surface of particle, and polar water molecules.

with the micella. The intermicellar liquid may contain electrolytes, as well as nonelectrolytes.

ELECTROKINETIC EFFECTS

The behavior of the diffuse component of the double layer is associated with another phenomenon called the electrokinetic effect. As the name implies, the electrokinetic effect is induced upon the motion of one phase of the disperse colloidal system relative to the other and is associated with the displacement of the electric charges within the diffuse double layer.

Electro-Osmosis

Fundamental Principle—Consider a cylindrical column ABCD (Fig. 9) of an ideal porous soil system, of which the particle S (shown idealized as spheres) are surrounded by moisture films m. Assume that this soil system is placed between the two electrodes 1-1 and 2-2 in an electrical field E brought about by a source of direct electrical current. This is to say that the soil system is subjected externally, at its ends, to an electric energy or to an electrical potential difference. Upon the application of an external primary electric potential, the



Figure 9. Translocation of ions and soil film moisture under the influence of an electrical potential.

positive charges (cations) in the diffuse double layer are attracted by the negative electrode (cathode) and thus will tend to translocate in the electric field toward the cathode, and the negative ones (anions) toward the anode (Fig. 9).

The positive ions of the electrical diffuse double layer translocating upward in the pictured soil system drag with them the oriented water molecules, thus setting the positively charged water layer (or the mobile part of the moisture film) into upward motion and dragging the rest of the liquid along the immobile part of the moisture film. The direction of flow depends on whether the liquid carries positive or negative charges, and on the position of the poles of the direct-current source. The tendency of the positive charge in the water to set itself in motion and to translocate the water along with it, together with the enclosed column of neutral water (free water, or water in bulk) is resisted by the viscosity of the water. The resistance to motion of the water molecules is assumed to follow Newton's law of viscous flow. Hence, the movement of the mobile part of the moisture film over the immobile part of the moisture film surrounding the soil particle is a tangential slip by overcoming the shearing resistance of the liquid.

The velocity of the soil moisture flow in the film phase depends on the magnitude of the applied electric potential difference and the viscosity of the liquid medium. The amount of moisture transferred by means of film flow is also proportional, among other things, to the specific surface area of the soil particles in a unit of a given volume. The finer the soil particles, the more specific surface there is in a unit of volume, or in unit weight, which in turn means more films, and hence more film moisture transferred.

The term electro-osmosis is used to describe the electrokinetic phenomenon of liquid (water) moving through a system of a porous medium relative to a fixed solid (that is, the colloidal soil particles are prevented from moving) under the influence of a primary externally applied electrical field. The derivation of this term is based on an analogy with osmotic phenomena which takes place through organic and inorganic membranes, diaphragms or porous plugs. Therefore, such a movement of liquid through a porous plug under the influence of an electric potential is called electro-osmosis. The porous system, such as soil, may be thought of as bundles of complicated interconnecting passages of diverse ways.

From the foregoing discussion it can be understood that in electro-osmosis the mechanism for the translocation of soil moisture is possible due to the existence of the electric diffuse double layer in a moist soil system. The application of an electric potential at the ends of the soil system results in the displacement of the charged mobile moisture films relative to the immobile ones. Because the mobile part of the moisture film is free to move whereas the soil particles are not, a flow of moisture takes place. The direction of moisture flow depends on whether water is charged with positive or negative ions.

Historical Notes—The electro-osmotic phenomenon was discovered by Reuss (14) in 1808, but he did not explain the phenomenon. Systematic research on electro-osmosis was performed by Wiedemann (26) in 1852. Quincke (27) made in 1859 and 1860 quantitative measurements at a single capillary. Quincke also realized that the electro-osmotic phenomenon has a connected phenomenon, termed the "streaming potential." The phenomenon of the streaming potential is the converse of electro-osmosis.

Also, Quincke gave the original electrical double layer theory and explained it.

As may be gathered from the review

of the various double layer theories, Quincke's original theory is a fundamental one to which, generally, only a few improvements were made and a few extensions were added.

Quincke's theory was formulated mathematically in 1879 by Helmholtz (19). With the introduction of the dielectric constant in the Helmholtz double layer theory by Smoluchowski in 1893 (28), the Helmholtz theory by and large is still valid, particularly as a special case, or as a component part in other theories.

Application in Engineering—The application of the electro-osmotic phenomenon to soil and foundation engineering has been studied by Casagrande (29, 30), Schaad and Haefeli (31), Winterkorn (32), Preece (33), Vey (34), and others.

Electro-osmosis is utilized for the dewatering of silty and clayey soils difficult to drain by gravity. These soils cannot be drained by gravity because the relatively large surface tension forces of water in such soils tend to retain water in their voids.

Dewatering of soil is pursued to facilitate laying of foundations in a dry pit or excavation, for the stabilization of soil in natural or artificial slopes, as well as for other purposes.

The principle of dewatering fine-particled soils electrically is shown in Figure 10. To keep the excavation dry, positive electrodes in the form of rods are installed near the toe of the slope of the excavation. The negative electrodes are installed in the mass of soil away from the slope of the cut and are made in the form of perforated pipes resembling wellpoints. Their function is to collect the water flowing from the positive electrode when a direct-current field exists in the soil between the electrodes. The water collected in the negative electrode is pumped out and discharged.

One well-known example of the successful application of electro-osmosis in soil mechanics is the dewatering of a silt with unfavorable physical properties by the Germans during World War II at



Figure 10. Principle of dewatering of a fine-particled soil by electro-osmosis.

Trondheim, Norway, for the construction of U-boat pens.

Induced Electrical Potential

Streaming Potential—In electro-osmosis, the application of a primary electrical potential causes in a moist porous system (which may be imagined as a fixed porous plug inside an imaginary cylinder) the motion of the liquid relative to the fixed solids.

Conversely, the motion of a liquid forced mechanically through a fixed porous plug, say a clay diaphragm, by means of a certain driving pressure, induces an electrical potential difference (or electromotive force) between the two ends of the plug. A process of soil moisture translocation brought about by means of a thermal potential is termed "thermoosmosis."

Because the film liquid is electrically charged, translocation of the liquid through the porous system is accompanied by an induced electric current. The electric diffuse double layer is swept along by the flow of the mobile film, so that opposite charges are built up at opposite ends of the system of the porous plug. This induced electric potential difference in a thermo-osmotic process is termed the "streaming potential," which may be regarded as the converse phenomenon of electro-osmosis.

Hence, it can be expected that an ex-

ternally applied primary potential (for example, a thermal potential) will induce between the two ends of the porous system a secondary (electric) potential upon displacing the mobile moisture film. This was discovered by Quincke in 1859 (18). The streaming liquid displaces the positive charges of the water molecules relative to the solid particles and thus induces an electrical potential along the height of the column of the moist, porous soil system. The induced E.M.F. is connected with the ζ -potential (35). Likewise, the amounts of film moisture transferred are thus connected with the ζ -potential. This phenomenon, converse to electro-osmosis, seems to be less known to the engineering profession than electro-osmosis. Yet, the phenomenon of induced electric potentials gives one an important basis on which to rest the theory of the mechanism for the translocation of soil moisture in the film phase, particularly upon freezing.

Freezing Soil System-If a freezing thermal gradient is applied across a vertical column of a soil system, there also exists a temperature gradient in the liquid or soil moisture. This, in general, sets up a concentration gradient in the liquid acting as an electrolyte, inducing the liquid to translocate from higher concentrations to lower concentrations; specifically, from places of higher temperature to places of lower temperature. In turn, the mobile moisture layers carry the ions with them. Thus a primary potential, in this case a thermal potential, induces between the warm and cold fronts of the soil system an electric potential, termed a secondary potential. It arises as the result of a mechanical flow of liquid through a porous medium. The induced electric potential is proportional to the driving pressure of the liquid. Generally, in a freezing soil system such as is dealt with here, energy in the form of heat flows upward, commencing the upward translocation of the soil moisture. In other words, here heat provides the motive power, the driving pressure. Moreover, the application of thermal energy to the soil system has two effects; namely, loosening of the water

molecules, and increasing the thermal motion of the loosened molecules.

During the course of upward migration the flowing water loses some of its driving pressure. This means that the driving pressure in the system's flow performs some mechanical work, which is lost. Thus, in doing external over-all work the entire freezing soil system loses some of its energy, so that the system in nature does not work with 100 percent efficiency. It also appears that the factors governing the energy losses (or drop in driving pressure) accompanying the upward migration of soil moisture upon freezing are not quite susceptible to exact mathematical analysis. Therefore, to understand the frost effects in soil, the freezing soil system must be studied experimentally.

THE SOIL FREEZING EXPERIMENT

Purpose

The main purpose of a soil freezing experiment is to learn the interrelationships of the various factors involved in the soil moisture translocation and freezing processes, and to try to find a relationship between the driving pressure and the amount of soil moisture supplied from the ground-water via the moisture films to the freezing zone of the soil. The amount of water transferred should be a well-defined function of the driving pressure to permit reasonable calculations of frost problems on roads. Also, these studies would permit one to learn and to describe the mechanism for the upward translocation of the soil moisture in the film phase in a freezing soil system.

Method of Study

To learn the interrelationships of the various factors involved in damage to roads by frost in interaction with soil moisture, particularly when the translocation of soil moisture from warmer regions to colder ones is more effective than the other moisture transfer mechanisms, a certain soil was subjected to freezing experiments. Because of the many unknown and obscure factors involved in the behavior of a freezing soil system, such systems were studied in their entirety, evaluating their performance by the total net end-result of the system—as a whole between the entrance and exit of the system.

Principle of Experiment

The freezing soil system should be studied as an organic entity; that is, the freezing experiment should be so arranged as to simulate nature as closely as possible. If in the field ground-water is available from which, upon freezing, the soil can "draw" water, the experiment should be set up accordingly. Likewise, if in the field the soil freezes from the top down, the experiment should be so arranged. If it can be assumed that in the field there is no lateral flux of heat through the soil, proper boundaries should be provided in the experimental freezing soil system to assure such a condition. If the organic entity of soil in the field suggests an open system, the soil freezing experiment should be performed with an open soil system. If there is no ground-water source present in the field, or the ground-water is inaccessible for the supply of water to the downward freezing ice lenses, the experiment should be performed accordingly. Also, moisture transfer from places of higher concentration to lower ones upon freezing in the vapor phase, or by capillarity, or by film flow, or by a combination of all of these mechanisms, must be clearly kept in mind and the experiment arranged accordingly.

It is useless to freeze a soil sample from all sides by simply placing it in a freezing chamber without due regard to the organic soil environment in the field; that is, the location and position of the soil, soil moisture conditions, as well as the temperature conditions concerned. The foregoing clearly discloses the complexities of the various processes in soil induced by a freezing thermal gradient, as well as the difficulties in experimental research on freezing soil systems.

Experiments

The pilot freezing experiments on soil systems prepared of Dunellen soil (a siltcontaining glacial outwash soil in New Jersey) were performed so as to simulate as closely as possible average field conditions most frequently encountered. The freezing of the soil system is accomplished by applying an external, primary potential, cold (a freezing thermal potential) to the upper horizontal surface of a vertical soil cylinder 12 in. high and 6 in. in diameter, the lower end of which is inserted in a water bath (at +8 C, which is the average annual ground-water temperature at the "frost yard" of Rutgers University, at University Heights, N. J.) to simulate the source of ground-water or perched ground-water. Hence, the soil system is an open one. Immediately after the commencement of freezing, measurements are made of temperature within the soil and its environment, driving pressure differences, induced electrical potential differences (E.M.F.) across the soil system (secondary potential), the supply of ground-water consumed from a burette during freezing, and frost heave.

The freezing equipment with auxiliary apparatus for performing such soil freezing experiments is shown in Figure 11.

Pilot Experiment Results

In the pilot soil freezing experiment described here, the following data were recorded in sequence:

1. Time.

2. Developed subpressures.

3. Soil temperatures at various levels.

4. Surface temperature above the soil specimen.

5. Ground-water temperature.

6. Laboratory air temperature.

7. Quantity of water transferred from the ground-water reservoir into the soil specimen upon freezing.

8. Induced secondary electrical potentials.

9. Frost heave.

Figure 12a shows the positions where temperatures, subpressures, and induced



Figure 11. Equipment for soil freezing experiment.

electrical potentials were measured. Figure 12b shows the pilot soil freezing experiment data. This graph indicates that as the temperature in the soil decreases the subpressure and the induced electrical potential between both ends (1-5) of the freezing soil system in-

creases. The order of magnitude of the induced electrical potentials has been measured by the author in various freezing soil systems as from 40 to 120 millivolts. The subpressures, depending on the physical conditions of soil, temperature, pressure, and humidity environment, have



Figure 12. Soil freezing experiment data.

been observed for the Dunellen soil as high as 32 cm mercury.

ASSUMPTIONS UNDERLYING THEORY

The studies previously performed on freezing soil systems have convinced the author that the electric diffuse double layer theory may be considered as the basis for studying freezing soil systems and hints at a possible mechanism for the upward translocation of soil moisture in the film phase upon freezing.

At the present stage of studies, some of the assumptions upon which the theory of the mechanism is based can be summarized as follows:

1. Water is the continuous liquid phase in the porous soil system.

2. There exists in the water around the solid soil particles an electric diffuse double layer of the Gouy-Chapman or Stern type.

3. The surfaces of the solid soil particles are ordinarily charged negatively; the negative ions are adsorbed on the surfaces.

4. There are free positive charges in the diffuse part of the double layer.

5. The complex network of voids in the soil is assumed to be bundles of ideal, straight capillaries.

6. Through the voids of the soil an idealized, laminar flow of soil moisture can take place in a direction parallel to the axis of the cylindrical column of soil; the flow is slow enough for the inertia factors to be neglected; the flow should, however, be considered as an over-all system's flow.

7. The motion of soil moisture in the film phase is induced by means of an external, primary potential; specifically, a thermal potential—freezing, for example.

8. The translocation of the soil moisture takes place by friction; that is, a viscous flow takes place within the double layer and in the bulk of the free liquid.

9. There is no slip of film water at the boundary surfaces of the solid particles.

10. The thickness of the double layer (that is, the distance normal to the inter-

face over which the ζ -potential differs appreciably from that in the bulk of the liquid) is small compared with the radius of curvature at any point of the surface.

11. The mobile part of the moisture film is set in motion tangentially past the immobile part of the film by a freezing temperature gradient.

12. The translocating moisture, displacing the positive ions of the water molecules, induces an electric (secondary) potential along the columnar system of soil.

13. Soil freezing experiments have shown that upon freezing and at the proper packing water is transferred from ground-water via the soil moisture films to the cold front.

14. Also, experiments have shown that upon freezing an electrical potential is induced between the two ends of the freezing soil system.

15. There exist certain relationships between the experimental driving pressure, induced electrical potential, and amount of water translocated; these relationships are still to be studied.

Comments

Logical and appealing though the aforementioned theory may be, there appear to be some difficulties in it, the most pronounced of which are as follows:

1. In closely packed, fine-particled colloidal soils one can imagine the possibility of overlapping of the diffuse parts of the double layers of two adjacent soil particles, thus reducing considerably the ζ -potential. This might be disconcerting because it may severely limit induced potential work unless superposition in the overlapping parts is permitted, or a satisfactory working hypothesis and corrections in certain details of the theory are introduced (the simple, unrealistic assumption of the parallel-plate condenser should be remembered).

2. Swelling of the colloidal soil in water can be imagined as decreasing greatly the translocation of soil moisture through the voids of the soil.

3. It seems that the moisture translo-

cation in soil does not occur by a singular transfer mechanism; for example, by films or by vapor diffusion. Most likely and naturally, several moisture transfer mechanisms act simultaneously (in a combination of surface tension forces and vapor diffusion). No sharply defined boundary for the onset of the various mechanisms is possible. In nature, such processes as are here dealt with are transitional and gradually changing. Also, under certain physical conditions one mechanism may be more effective than the other. It is extremely difficult to ascertain in what proportion each of the mechanisms contributes to the amount of soil moisture transferred. However, by judicious experiment, there is visualized the possibility of establishing certain ranges which may indicate at which porosities of the soil one mechanism is more efficient than another.

CONCLUSIONS

The discussion in this article on the theory of a possible mechanism for the soil moisture translocation upon freezing, and the review of the electric double layer theory show that the property of a colloidal soil particle of carrying on its surfaces an electrical charge, and the functioning of soil moisture films surrounding the particles as an electrolyte, are of basic significance in the process of the translocation of soil moisture in the film phase set in motion by an external primary thermal potential—that is, freezing.

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REFERENCES

- JUMIKIS, A. R., "Formulation of Upward Soil Moisture Transfer upon Freezing by Various Moisture Transfer Mechanisms." Frost Action Research Memo., 1948-56. Submitted to Eng. Research Advisory Comm., Rutgers Univ. (Dec. 1956).
- JUMIKIS, A. R., "Soil Moisture Transfer in the Vapor Phase upon Freezing." HRB Bull. 168, pp. 96-115 (1957).
- 3. JUMIKIS, A. R., "Some Concepts Pertaining to the Freezing Soil Systems." HRB Special Report 40, pp. 178-190 (1958).
- 4. JUMIKIS, A. R., "The Soil Freezing Experiment." HRB Bull. 135, pp. 152-165 (1956).
- OSTWALD, W., "A Handbook of Colloid Chemistry," p. 2. (Trans. from 3rd German ed. by M. H. Fisher) Blakiston, Philadelphia (1915).
- "The Collected Papers of P. J. W. Debye," p. 142. Interscience Publ., New York (1954).
- DEBVE, P., "The Structure of Matter." (Trans. from German by F. M. Denton) Univ. of N. Mex. Bull., Vol. 1, No. 2, p. 24 (Oct. 1, 1934).
- DEBVE, P., "Polar Molecules," pp. 3, 7. Chem. Catalog Co., New York (1929).
- PARTINGTON, J. R., "An Advanced Treatise on Physical Chemistry." Vol. 5 (Molecular Spectra and Structure; Dielectric and Dipole Moments), p. 364. Longman, Green and Co., London (1954).

- KRONIG, R. DEL., "The Optical Basis of the Theory of Valency," p. 175. Macmillan, New York (1935).
- PARTINGTON, J. R., "An Advanced Treatise on Physical Chemistry." Vol. 5, p. 35. Longman, Green and Co., London (1954).
- BROWN, G. I., "A Simple Guide to Modern Valency Theory," p. 91. Longman, Green and Co., London (1953).
- 13. DEBYE, P., "Polar Molecules," p. 69. Chem. Catalog Co., New York (1929).
- REUSS, F. F., "Sur un Nouvel Effet de l'Électricité Galvanique. 30. Notice lue le 15 Avril 1808." Memoirs Moscow Imperial Soc. of Naturalists, Vol. 2, p. 332, Imperial Univ. Press, Moscow (1809).
- Сöhn, A., AND RAYDT, U., "Über die quantitative Gültigkeit des Ladungsgesetzes für Dielectrika." Ann. der Physik, Fourth Series, Vol. 30, Part 14, p. 804. Joh. Ambrosius Barth, Leipzig (1909).
- DORSEY, N. E., "Properties of Ordinary Water—Substance," p. 359. Reinhold, New York (1940).
- RUTGERS, A., "Zur Erklärung des Cöhn-Raydtschen Ladungsgesetzes." *Physica*, 5:No. 1, 58. Martinus Nijhoff, The Hague (Jan. 1938).
- QUINCKE, G., "Über die Fortfuhrung materieller Teilchen durch stromende Elektrizität." Poggendorff's Ann. der Physik und Chemie, 113:No. 8, 513-598. J. A. Barth, Leipzig (1861).
- HELMHOLTZ, H., "Studien über electrische Grenzschicheten." G. Wiedmann's Ann. der Physik und Chemie, New Series, 7:338. J. A. Barth, Leipzig (1879).
- GOUY, M., "Sur la Constitution de la Charge Électrique à la Surface d'un Électrolyte." Jour. Theor. and Applied Physics, Paris, 9: 457-468 (1910).

- CHAPMAN, D. L., "A Contribution to the Theory of Electrocapillarity." *Philosoph. Mag. and Jour.* of Science, London, Sixth Series, 25:No. 148, 475-481 (Apr. 1913).
- 22. RUTGERS, A. J., "Physical Chemistry," p. 404. Interscience Publ., New York (1954).
- STERN, O., "Zur Theorie der elektrolytischen Doppelschicht." Zeits. für Elektrochemie und angewandte physikalische Chemie, p. 510. Verlag Chemie G.m.b.H., Leipzig—Berlin (1924).
- 24. POTTER, E. C., "Electrochemistry," p. 159. Macmillan, New York (1956).
- FREUNDLICH, H., "Colloid and Capillary Chemistry," p. 371. (Trans. from 3rd German ed. by H. S. Hatfield) Dutton, New York.
- 26. WIEDEMANN, G., "Über die Bewegung von Flüssigkeiten im Kreise der geschlossenen galvanischen Säule." Poggendorff's Ann. der Physik und Chemie, 87: No. 11, 321-352 (1852); 99:No. 10, 177-233 (1856).
- QUINCKE, G., "Über eine neue Art elektrischer Ströme." Poggendorff's Ann. der Physik und Chemie, 4th Series, 107:No. 5, 1-47 (1859); 110:No. 5, pp. 38-65 (1860).
- SMOLUCHOWSKI, M., "Elektrische Endosmose und Strömungsströme." In "Handbuch der Elektrizität und des Magnetismus," (Graetz) Vol. 2, p. 366, J. A. Barth, Leipzig (1914).
- 29. CASAGRANDE, L., "Die elektrische Entwasserung feinkerniger Böden." Deutsche Wasserwirtschaft, 36:556-559 (1941).
- 30. CASAGRANDE, L., "The Application of Electro-Osmosis to Practical Problems in Foundations and Earthworks." Building Research Tech. Paper No. 30, H. M. Stat. Off., London, 16 pp. (1947).

- 31. SCHAAD, W., AND HAEFELI, R., "Elektrokinetische Ersheinungen und ihre Anwendung in der Bodenmechanik." Mitteilungen aus der Versuchsanstalt für Wasserbau und Erdbau an der Eidgenossichen Technischen Hochschule in Zürich, No. 13, 18 pp. Leeman and Co., Zürich (1947).
- 32. WINTERKORN, H. F., "Fundamental Similarities Between Electro-Osmotic and Thermo-Osmotic Phenomena." *HRB Proc.*, 27:443-455 (1947).

- 33. PREECE, E. F., "Geotechnics and Geotechnical Research." HRB Proc., 27:384-416 (1947).
- VEY, E., "The Mechanics of Soil Consolidation by Electro-Osmosis." HRB Proc., 29:578-589 (1949).
- ALEXANDER, A. E., AND JOHNSON, P., "Colloid Science," Vol. 1, pp. 340-343. Clarendon Press, Oxford (1949).
- 36. BERZELIUS,, "Essai sur la Théorie des Proportions Chimiques et sur l'Influence Chimique de l'Electricité." P. 68. Paris (1819).