HIGHWAY RESEARCH BOARD

Special Report 40

Water and Its Conduction in Soils

An International Symposium

organized and edited by

Hans F. Winterkorn, Chairman
Committee on Physico-Chemical
Phenomena in Soils

presented at the
Thirty-Seventh Annual Meeting
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1958

Washington, D. C.

Dedicated to

ERNST A. HAUSER

1896—1956

Pioneer in the study of colloidal phenomena, particularly as related to siliceous materials such as clays and soils.

Author of numerous books and papers on colloids and allied fields.

Recipient of citations and honors from scientific societies throughout the world.

Profound philosopher and sympathetic teacher, vitally interested in the education of American youth.

Department of Soils, Geology and Foundations

Foreword

The Chairman of the Highway Research Board Committee on Physico-Chemical Phenomena in Soils is sincerely grateful for the excellent cooperation enjoyed by him from everybody concerned in the organization and presentation of this International Symposium on Water and Its Conduction in Soil.

First of all, thanks are due to the contributors of papers from all parts of the globe who took time out from their busy professional lives to prepare for us these excellent contributions. Certainly this symposium is unique with respect to the wealth of information, observational, experimental and theoretical, brought together in one volume and there can be no reasonable doubt concerning its immediate value to all those interested in soil and water as well as its continuing importance as a catalyst in the search for new knowledge.

Great appreciation is expressed to the Highway Research Board and its staff, and to Frank R. Olmstead, Chairman of the Department of Soils, who passed away before he could see the completion of this symposium in which he was so deeply interested, for their sincere interest and effective help in making this symposium a reality and a success.

Organization and presentation of this symposium would have been impossible without the keen interest shown and the effective help given in many ways by W. Mack Angas, Vice Admiral U.S. Navy, ret., Chairman of the Department of Civil Engineering, School of Engineering, Princeton University. The Department of Civil Engineering and the Soil Thermal Resistivity Research Project sponsored at the Department's Soil Physics Laboratory by the American Institute of Electrical Engineers shared the expenses for secretarial halp, reproduction of papers, translations and illustrations needed for advance circulation and for a number of other items incidental to this type of undertaking. For this generous help grateful acknowledgment is expressed to the American Institute of Electrical Engineers, its Committee on Insulated Conductors and the various sponsoring organizations that financed the research initiated by this Committee, as well as to Admiral Angas, Chairman of the Department of Civil Engineering, J.C. Elgin, Dean of the School of Engineering and Robert F. Goheen, President of Princeton University.

Hans F. Winterkorn, Chairman

Committee on Physico-Chemical Phenomena in Soils

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Introductory Remarks

HANS F. WINTERKORN, Director, Soil Science Laboratory, Princeton University

● GOD CREATED the unit, the system, with its infinite number of aspects and interrelationships. Man, trying to understand God's creation, has as his only tool his limited mind. This tool varies from person to person in type and degree of refinement. Paraphrasing the words of the Earth Spirit in Goethe's Faust, it may be stated that our mind understands only those aspects of the world around us to which it resembles or whose basic theoretical structures are already performed in it. Hence, the work of many different minds is required if one wants to collect pertinent information on a complex natural system and to organize it into a body of knowledge that is at once sufficiently comprehensive to satisfy the searching mind and sufficiently detailed to be practically useful.

Water and soil are not only the most important materials in this world, but also the most complex ones, each in its own category, water as a liquid and soil as a multi-phase dispersed system. As a matter of fact, this very complexity of water and soil is the reason for their importance in engineering as well as in biology. If water and soil are combined to moist soil systems, then the complexity of each is multiplied by that of the other. At this point, the learned coward gives up; the conscientious scientist and engineer goes on. He observes and describes his observations; later, he classifies and systematizes facts found by himself and others; still later, certain simple mechanisms can be recognized and, if they are simple enough, be described by means of mathematical formulae. The total complexity, however, remains and any theory or hypothesis that is sufficiently simple to permit mathematical formulation is either so general as to be obvious, or it is applicable only to a limited area of the total field.

With the conscientious scientists and engineers go many others. The fools, of course, we shall always have with us, as well as those that want to be fooled. We have the impatient intellectuals that escape into theories in order to avoid the complexity of reality and then attempt to force reality into the straight-jacket of their premature creations. Then, we have the fellow-travelers that put their trust in formalized methods rather than in observing and thinking. Still, there are many well-trained, able and conscientious men working quietly on the soil-water problems. The best of them know that in order to make real progress in a chosen field of research, a man must first be true to himself; he must reproduce the world in his own mind and according to the structure of his mind.

Progress in knowledge is made by scientists and not by science. There are scientists whose minds approach the purely intuitive type, and others that are almost pure analysts. There is the majority whose mind partakes of both intuition and analysis in the wide range between the extreme types. There are scientists in whose memories can be stored a tremendous number of facts that somehow order themselves into structural units of connected knowledge, and others whose memories may hoard the same facts, but these remain inert and never enter into fruitful mutual relationships. There are men that have practically no memory, but possess a discerning and dissective genius that can detect the flaws of a mental construction if placed before them. All types of creative minds are needed in order to produce a mental facsimile of the phenomena that is wanted to understand and use for the benefit of our fellow men.

Much loose thinking and talking is currently going around about science and science education. The great present danger of this is that seductive half-truths may crystallize into legislation and further impede our scientific and engineering advance. Most of the proposals forget that it is man who makes science and not science that makes man. Man has been aptly described as an animal that has his head among the stars and his feet in the mud. This description highlights the glory and the tragedy of man, but it should not be forgotten that head and feet are only extremities of a physical, intellectual and spiritual unit in which balance and equal development of all parts is the prerequisite for harmonious functioning. Science, too, consists not only of head and feet, but must have a well developed body if it is to be of greatest use. This body must include all pertinent knowledge in a given field, the qualitative, the semi-quantitative and the quantitative,

to our present living science. The danger of doing this is real and present. As a result of the widely spread misconceptions about science and scientists, the creative scientific thinker, who grappels with problems too complex to yield to simple mathematical formulation, either by himself or by others, is being pushed out of the serene atmosphere of the basic sciences, and is supposed to join the ordinary inventor of gadgets and patent medicines in the noise and squabble of the market-place. Qualitative thinking, the thinking in picutres, or the geometrical thinking as Poincaré calls it, which is the prerequisite and first step in scientific discovery and invention, is being discouraged, and this under the pretense of doing something for science. It is high time that there is an understanding of science as it really is—a search for truth in which a man uses all the knowledge and all the material and mental resources at his disposition and in which the means of attack and the formulation of the results vary with the nature of the problem and its understanding by the scientist. This formulation shows the kinship of science with philosophy and art, in short, the kinship of all analytical and creative human endeavor to understand the world around us and to give expression to this understanding. In order to have more creative scientists in the future, there must be an improvement in the education of our present youth not only in science, but also in philosophy, in the arts and in the humanities. In addition, the illusion of a germane relationship between mathematical and general scientific talent and creativeness, must be erased. In so doing, the ability to detect in our country much more scientific talent and, possibly, even genius than suspected, would be greater. The wholehearted admission of gifted qualitative thinkers into scientific research presupposes, of course, that their ability to think qualitatively has been proven by education and performance and not just by a lack of gift in mathematical thinking.

Three years ago, the Committee on Physico-Chemical Phenomena in Soils of the Highway Research Board decided to bring together in one place as much pertinent knowledge on water, its interaction with solid surfaces, and its conduction in soils as could be collected by reasonable effort. This information was to represent as many facets of the soil-water problem as possible and, at the same time, as many different approaches as have yielded good and usable knowledge up to the present time, with the approaches ranging from the purely descriptive to the highly mathematical.

The Chairman of the Committee on Physico-Chemical Phenomena in Soils was authorized by the Committee and by the Highway Research Board to ask individual scientists and engineers as well as research institutes that have established reputations in the areas to be covered by the Symposium for contributions that would represent either original work or concise appraisals of the knowledge available in a specific scientific area. Worldwide representation was sought and a certain overlapping of treatment was considered desirable because of the complexity of the problems and the natural disagreement to be expected under such circumstances. In fact, it was reasoned that juxtaposition of contrary points of view in the printed symposium and their discussion would help to define and ultimately resolve areas of controversy.

It seemed desirable to have the entire publication in English; however, in order to alleviate the burden of contributors not fluent with this language, it was decided to accept also papers written in French, German, Italian, Portuguese and Spanish, to have such papers translated into English by the Chairman of the Committee and to print these translations only after they had been checked by the original authors.

While this undertaking was planned as a symposium-in-print, three opportunities were made available for personal presentation or summarization and discussion. These were as follows:

1. A meeting in the Building Research Laboratories of the National Research Council of Canada in Ottawa, October 9, 1957. Contributors able to attend this meeting presented their papers in person, while papers received at that time from contributors unable to attend any of the meetings were read by the Committee Chairman.

2. Two program sessions during the 37th Annual Meeting of the Highway Research Board in Washington, D.C., January 7, 1958, for formal presentation of papers and a committee meeting on January 6, 1958 for complete or summarized presentation by the Chairman of papers from contributors unable to attend.

the wealth of material properties and phenomena and the central nervous system of mathematical theory.

Now, some vociferous single-trackers want to create a central nervous system without a body and feed it with special food like a queen bee, with lesser nourishment provided for the common workers in the hive. Mathematical talent is to be the criterion by which to recognize and select those that are to become our future scientists, who are supposed to restore our leadership in those scientific and engineering fields in which we have lost it. The truth is that overemphasis on the theoretical and mathematical aspects of science and insufficient cultivation of the more qualitative and of the experimental material phases in American science education are among the major causes of the present deplorable situation. In freshman physics and chemistry, we have been teaching theory before the students were made acquainted with the actual phenomena whose explanation and correlation is the noble and extremely practical task of theory. Instead of introducing the students first to the living body of material phenomena and teaching them observation and experimentation until the mass of accumulated knowledge is too much for the memory and cries for organization by abstraction and theory, they are given a skeleton of abstractions and expected to put on it the flesh of reality. It is hoped that they will recreate God's work from the meager condensate of the abstractions of man's limited mind.

Natural science is based on observation and experiment; this basis has been more fruitful in providing real and useful knowledge than the purer thinking of the scholasticists. Should this proven basis be left for a new mathematical scholasticism? These comments should not be construed as an attack against the wonderful science of mathematics, the inventions of which may range from esthetic creations of the beauty and balance of a Greek statue to extremely useful and dependable tools of the natural scientist. Rather, they are made for the purpose of extricating mathematics from an imposed role of being either the highest form of natural science or the only acceptable language, and, at the same time, only a language of natural science. The real place of mathematics in the scheme of science, philosophy and art has been discussed beautifully by Poincaré in his popular writings.

Much misunderstanding is abroad, also, on the place and function of theory. Theory comes from the Greek word for "seeing". After contact has been established between a human mind and a physical phenomenon, the first step towards its explanation in terms of a more abstract body of knowledge is the qualitative or intuitive "seeing" of a correlation or mechanism. If the picture seen is very simple, a mathematical formulation may suggest itself immediately; if it is more complicated, but still relatively simple, one may find a formulation fitting the case among the inventions of the pure mathematicians, or the physical problem may stimulate a Newton to invent or develop a new branch of mathematics. Sometimes the picture is so complex that it does not yield to mathematical treatment. Whatever the case may be, the mathematical formulation, though of tremendous value because of its "correctness", represents a training and dressing up of the "new baby" to make it more presentable in scientific society, but is of itself hardly ever of the essence of discovery and creation in natural science. On the other hand, mathematical formulation of a theory can make it more precise and more useful and is something definitely to be desired and earnestly sought.

However, it should be remembered that mathematical genius or even talent is not a prerequisite for creative genius in natural science. This is well shown by the great discoveries in natural science by people devoid of mathematical talent. Nernst, the father of the heat theorem, is reported to have said that: God had favored him with such an intuitive understanding of the physical world that it would be immodest to ask for mathematical genius in addition. Voltaire, who had considerable mathematical talent, used it well to spread the new Newtonian physics in France, but did not add to it; while Goethe without such talent could not understand Newton, but in trying to refute Newton's color theory, did enough excellent observational and experimental work and thorough qualitative thinking to become one of the founders of physiological optics just as he was one of the originators of philosophic botany and osteology.

Favoring only the mathematically minded in our science education will deprive us of a large and important section of creative scientists of a type that has contributed much

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3. A final committee meeting at Princeton University on April 2, 1958 for presentation, summarization and discussion of papers that became available after the Highway Research Board Meeting.

The area covered by the symposium may be divided into four parts, as follows:

1. The properties of the water substance which must be known before any real understanding can be attained of the behavior of water in soils and similar porous hydrophilic systems.

2. The interaction of water with solid mineral and organic substances, normally found in soil and in living systems, knowledge of which is basic for an understanding of the phenomena that occur in these systems and that are decisive for the life of individuals and nations.

3. The response of soil and similar systems to the application of physical and chemical potentials, and the movement of water as a resultant phenomenon.

4. The application of the collected knowledge to the rational design of highways and similar structures.

There is an old designation at German Universities that includes all members of the academic community from the president, or rector, to the greenest freshman. It is "Kommilitone", or fellow soldier in the search for knowledge and truth. The term is so old that it can refer only to the patient and enduring foot soldier, not to the dashing cavalryman or the modern bird man. This term "Kommilitone" seems to be most fitting for those that have contributed to this symposium. They are devoted and proven scientists and engineers who in their work and search have learned to appreciate the great complexity of the phenomena occurring in soil-water and similar systems and who have become aware of the limitations of their own knowledge and of the need for exchange and pooling of knowledge. They have produced this symposium as humble searchers and workers without fanfares or festivities, and without special appropriations, just adding one more task to their other toils. Speaking for them as just another Kommilitone, I should like to conclude these introductory remarks with the following credo:

"We are not aristocrats that believe in science for the sake of science alone. We are humble searchers for the truth, which is at once beautiful and useful. We hope to have approached this truth sufficiently that our work will be useful and an aid toward solving the many important water problems in engineering, agriculture and other human activities. We hope that our efforts will lead to a better life for all and especially for the humble people of this world. May God bless us in this undertaking."

Properties of Water Substance

WORTH H. RODEBUSH, Research Professor Emeritus, University of Illinois, and
ARTHUR M. BUSWELL, Research Professor of Chemistry, University of Florida

Introductory Remarks by Chairman

Occam (1300-1349) is usually credited with introducing into science the principle of necessary and sufficient assumptions—"Essentia non sunt multiplicanda praeter nessitatem." This has been called "Occam's Razor" with which to slash away unnecessary assumptions. In dealing with complex actual systems, it is often practically impossible to carry along in the theoretical treatment of the entire system even all the necessary and sufficient available knowledge on the components. Hence, a practical decision must be made on how much we can carry along and how much we can slash away. With respect to the behavior of water in soil, it seems that a number of contemporary soil physicists have slashed away too many of the real properties of the water substance. This situation manifests itself in lack of agreement between actual experimental findings and certain theoretical conclusions. The remedy, of course, is to go back and add to the basic assumptions more of the real properties of the water substance even if this makes the calculations more bulky. The paper by Rodebush and Buswell summarizes in a simple and concise manner present knowledge on the properties of the water substance. The time has come when this knowledge must be part and parcel of the equipment of every soil physicist and must be built into the foundations of his theoretical structures.

●WATER is the only liquid with which we are really familiar. There are many substances that exist in liquid form and it is noteworthy that water is in no sense a typical liquid. It is best described by discussing those properties which differentiate it from the general class of liquids.

Water is a polar liquid (Fig. 1). Other examples of polar liquids are hydrogen fluoride and hydrogen cyanide, which are indeed bizarre substances. Polar liquids are made up of small molecules containing hydrogen which is sufficiently mobile or active to serve as a link between molecules. The molecules linked together in this manner by hydrogen bonds orient in an electric field and exhibit the property of high dielectric constant.

Ambivalence of Hydrogen. The hydrogen atom is capable of forming but one primary valence bond. When this is formed between hydrogen and oxygen, the oxygen atom appears to accumulate an excess of electronic charges and the hydrogen with a deficiency of electrons appears to have a positive charge. The positively charged hydrogen is capable of attracting an oxygen atom from another molecule, forming the so-called hydrogen bond which is, compared to the primary valence bond, a weak bond. The hydrogen atom in this bond lies between the two oxygen atoms, but not at equal distances from the two. It is much closer to the oxygen atom to which it is attached by a primary valence bond and to which it may be considered to belong (Fig. 2).

The Association of Water. The association of water has been the subject of many misconceptions. For example, it has been supposed that liquid water consisted of dihydrol or trihydrol, that is groups of two or three molecules. Such a concept is
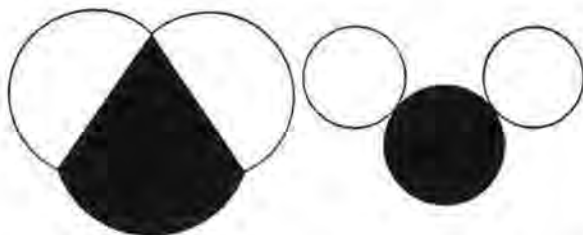
Figure 1. Molecule of water consists of one oxygen atom (black) and two hydrogen atoms (white). The distance between the center of the oxygen atoms and the center of each of the hydrogen atoms is 0.9 Angstrom unit (one Angstrom unit: 0.00000001 centimeter). The angle formed by the two hydrogen atoms is 105 degrees. These dimensions are fitted together in the drawing at left. In the more schematic drawing at right the size of the atoms has been reduced. This representation of the molecule is used in the following drawings.

absorption. A hydrogen bond shows a primary absorption at a wave length of about three microns. Liquid water shows this absorption even in the thinnest layer so that if the eyes were sensitive to the infrared region water would appear jet black. One may assume that the higher harmonics show absorption extending into the visible region, thus accounting for the familiar blue-green color characteristic of liquid water. It is not possible to determine the degree of association of liquid water by absorption experiments, but one may assume that water is highly associated, that is to say, there are practically no unassociated molecules present. The best clue to the structure of water is by a consideration of the structure of ice. The structure of ice is itself reasonably well understood although certain details are still in doubt.

Ice Water Structure. The only properties which differ markedly for ice and water are density and viscosity and closely related properties. The infrared absorption, the dielectric constant, and the degree of association change in a continuous manner through the melting point. Even the heat of fusion is much smaller than might be expected.

Water is one of the few substances which shows a greater density as a liquid than as a solid, and it is perhaps the only substance

now known to be erroneous. Water is a liquid with structure such that the molecules are linked together by hydrogen bonds so that they are not free to rotate as, for example, are benzene molecules in liquid benzene. From this point of view, therefore, the whole mass of liquid water constitutes the molecule. The molecular weight depends on the size of the containing vessel.

The method par excellence for the detection of hydrogen bonds is infrared
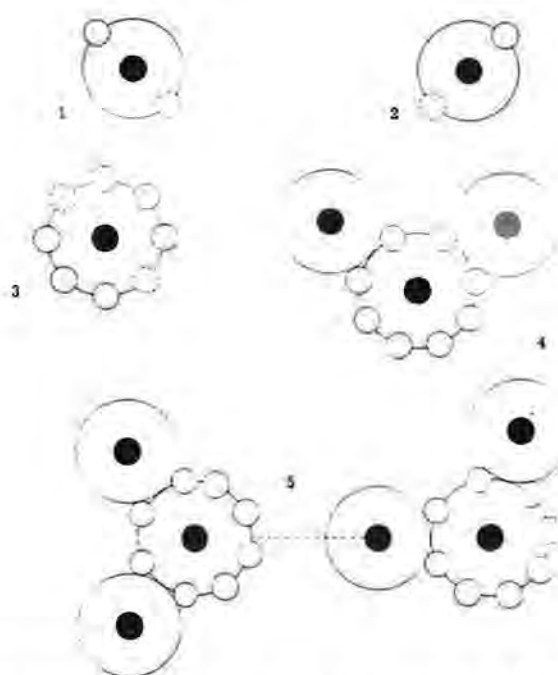
Figure 2. Electrons and protons of the water molecule account for most of its physical and chemical properties. The hydrogen atom (1 and 2 in this highly schematic picture) consists of one positively charged proton and one negatively charged electron. The oxygen atom (3) has eight electrons, six of which are arranged in an outer shell. Because the shell of hydrogen has room for one more electron (broken circle), and the outer shell of oxygen has room for two more electrons, the atoms have an affinity for each other. In the water molecule (4) the electrons of the hydrogen atoms are shared by the oxygen atom. Because the positively charged proton of the hydrogen atom now sticks out from the water molecule, it has an attraction for the negatively charged electrons of a neighboring water molecule (5). This relatively weak force (broken line) is called a hydrogen bond.

that exhibits a maximum density a few degrees above the freezing point. In order to understand this behavior it is necessary to consider the crystal structure of ice (Fig. 3). Ice forms hexagonal crystals but it is rarely seen in perfect forms of greater than microscopic size. The hexagonal symmetry is exhibited by snow flakes which occur in an infinite variety of forms (Fig. 4). The normal form of the snow flake would be a flat hexagonal plate, and the skeletal forms are due to the fact that the crystal grows in an atmosphere which is really very dry so that water vapor is present in small amounts. The crystal growth is greatest at the extremities of the crystal axis leading to the star-like forms.

It is the internal arrangement of the molecules in the crystal which is the primary concern. By means of X-rays, the position of the oxygen atoms in the crystals can be determined and the positions of the accompanying hydrogen atoms can be inferred. Ice might be expected to crystalize in the regular or cubic system, but the tetrahedral angle required involves a strain of the bond angles of the water molecule which is in some way relieved in the hexagonal crystal. The two hydrogens in the vapor phase water molecule are at an angle of about 105 deg. Each water molecule is surrounded by four nearest neighbors, the group forming a tetrahedron with one molecule at the center and the other four molecules at the apices of the tetrahedron. X-ray determinations show that the distance between oxygen atoms is 2.76 deg Angstrom units. Since the distance between the oxygen atom and the hydrogen atom is about 0.9 deg Angstroms, it follows that the hydrogen atoms lie on a line jointing the oxygen atoms but one not halfway between. Each hydrogen atom belongs, therefore, to one oxygen atom (forming a water molecule) and is joined to another oxygen atom by the relatively weak hydrogen bond. Each water molecule is, therefore, joined to its neighbor by four hydrogen bonds. If the number of hydrogen bonds per molecule were counted there are only two instead of four since each hydrogen bond is shared between two molecules. If ice is vaporized the work of separating
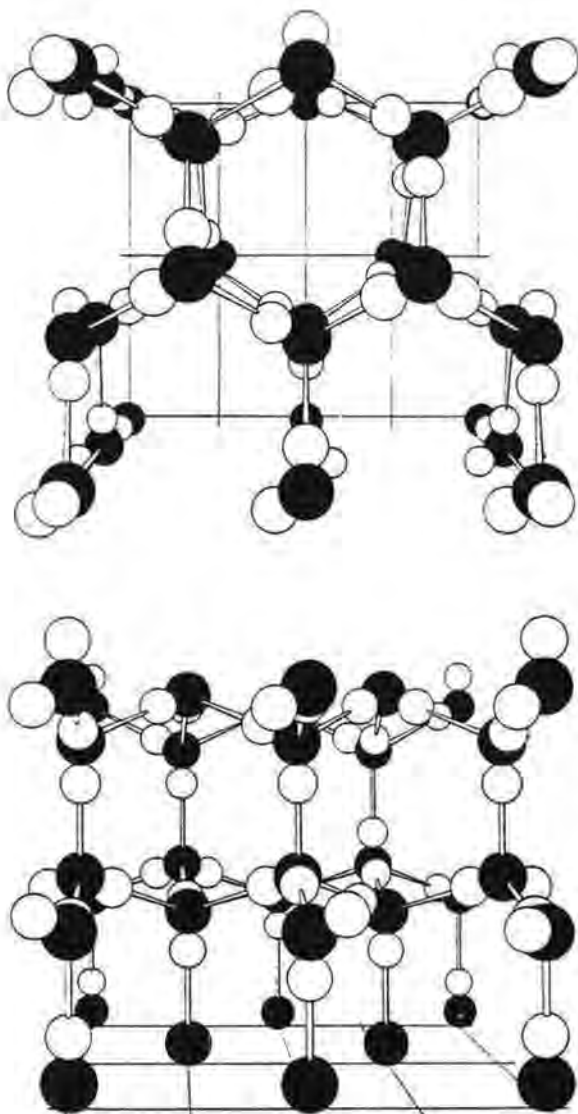

Figure 3. Ice consists of water molecules in this arrangement. The top drawing shows a model of ice seen from one direction. The bottom drawing shows the same model seen as if the reader had turned the top drawing forward on a horizontal axis in the plane of the page. Some hydrogens have been omitted from the molecules which touch the grid. Each hydrogen in each molecule is joined to an oxygen in a neighboring molecule by a hydrogen bond (rods). In actuality the molecules of ice are packed more closely together; here they have been pulled apart to show the structure. In a similar model of liquid water the molecules would be much more loosely organized, farther apart and joined by more hydrogen bonds.

all the molecules from each other must be done and, assuming that this work is entirely used up in separating the hydrogen bonds, 12,000 calories is the heat of vaporization of one mole (18 grams) of water. Then the energy of one mole of hydrogen bonds would be 6,000 calories.
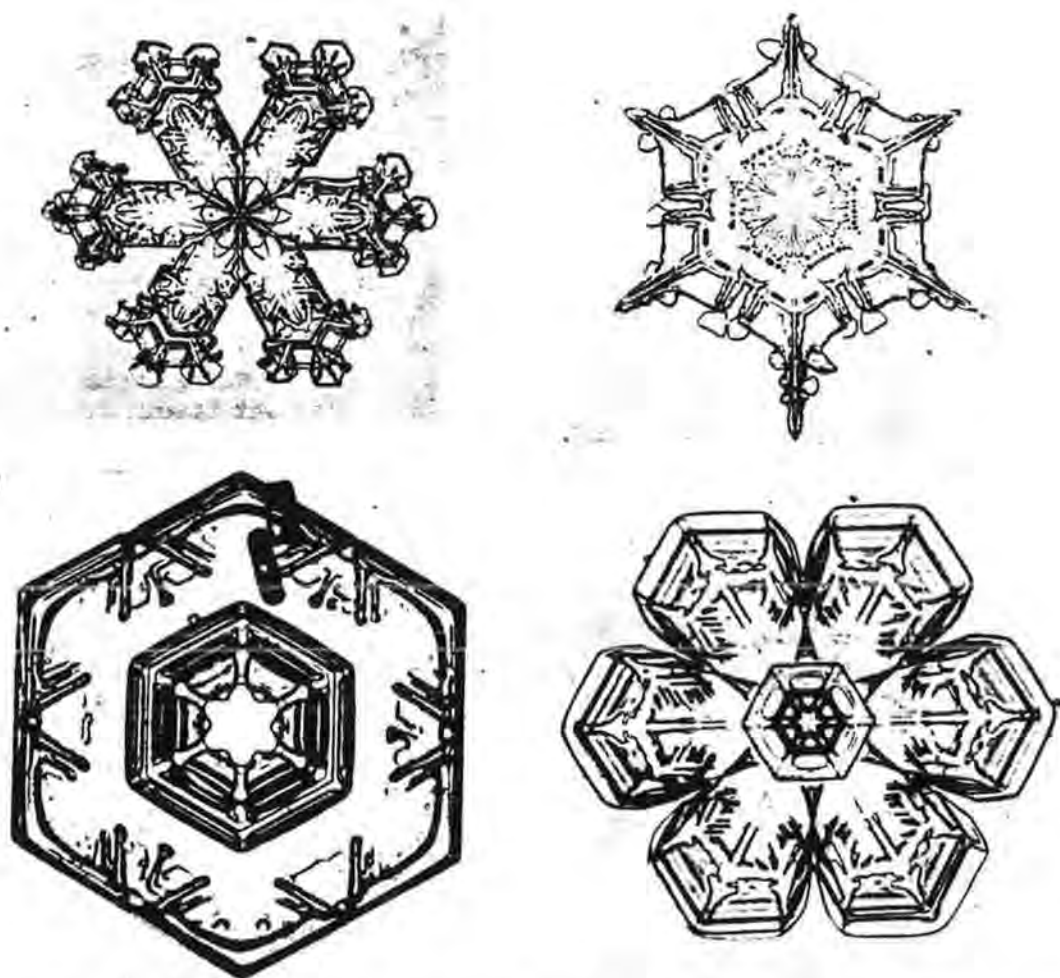
Figure 4.   Snow crystals are enlarged in these photomicrographs by Vincent J. Schaefer of the Munitalp Foundation in Schenectady, N.Y. The hexagonal symmetry of the crystals is due to their molecular structure.

The exact arrangement of the water molecules in the ice crystal is not known with certainty, but it is known that the water molecules are arranged in hexagonal rings which form a network or lattice. Since each molecule is surrounded by only four others, the packing is not very close and ice is a relatively not very dense crystal.

When ice melts to liquid water the hydrogen bonds are stretched and the molecules move farther apart. X-ray studies show that the distance between oxygens is now increased to about 2.9 deg Angstroms on the average. The effect of this stretching would be to decrease the density and to produce a large absorption of energy which would disappear at the heat of fusion were it not for a compensating effect. This is a crowding together of additional molecules. The regular structure disappears and instead of each molecule being surrounded by four neighbors in a regular arrangement, the number of nearest neighbors is increased to five or more on the average in an arrangement that is constantly shifting. This crowding together of the molecules means a closer packing and an increase in density. The number of hydrogen bonds is also increased so that the heat of fusion is less than might be expected. This chaotic disorder in which water molecules exist in the liquid state is difficult to picture since it is continually shifting, but it may be described as an average state rather than as a series of instantaneous states. The water molecules retain their identity. That is, two hydrogen atoms are bound to each oxygen atom and remain so for long periods of time. The electrons are more closely associated with the oxygen atom and the hydrogen atoms are separated

somewhat further from the oxygen atom than in an isolated water molecule and appear more as isolated positive charges. The water molecule becomes more flexible in that the angle between the two hydrogen atoms no longer remains fixed at or near a right angle, but becomes variable. Each oxygen atom, in addition to the two hydrogen atoms which are firmly attached by primary valence bonds, now attracts by electrical forces not two additional hydrogen atoms as in ice, but three or more hydrogen atoms. Thus, an oxygen atom is surrounded by five or six hydrogens and a hydrogen atom is surrounded by as many as three oxygens. This may have a closely packed, closely knit structure which is flexible with continuously shifting hydrogens displacing one another and the whole body of liquid has the property that if a hydrogen is displaced anywhere the displacement is propagated in chain or zipper fashion throughout the liquid. This has consequences which affect the viscosity, dieletric constant, and electrical conductivity.

Viscosity. In an ordinary unassociated liquid such as benzene, the molecules slide past each other when the liquid flows, encountering a certain amount of resistance resulting from the fact that they have to move around each other. In liquid water the molecules are attached by hydrogen bonds and one at least must be broken before any flow can occur. This means that the motion is rolling rather than sliding. Since the hydrogens of one molecule are now bonded on the average to the oxygens of two other molecules, it is not necessary to break both of these bonds at once, but rather one at a time so that the viscosity of liquid water is much less than might be expected from the fact that the molecules are bonded together. The greater viscosity of ice is due to the fact that each hydrogen is firmly bonded to a single oxygen atom from another molecule and this bond must be completely broken before any movement can occur. The temperature coefficient of viscosity indicates that the energy required to break the bond between water molecules is about 3,600 calories per mole. This is much smaller than that required for a normal hydrogen bond and supports the theory of the partial or multiple hydrogen bond where each hydrogen is bonded to two or more oxygens of adjacent water molecules. It is only necessary to break one of these partial bonds at a time in order to permit movement of molecules past each other.

Heat Capacity. The assumption of an increased ionic character for the atoms in liquid water receives additional support from a consideration of the heat capacity of liquid water. The heat capacity shows a remarkable discontinuous change at the melting point. The heat capacity of ice corresponds to that to be expected for an organic molecule. The oxygen atom should contribute four calories per mole, and the two hydrogen 2.3 calories each, and this is about what is observed. For liquid water the heat capacity is 18 calories per mole, which is high and remarkably constant from the melting point to the boiling point. It has been commonly assumed that the abnormally high heat capacity is due to the dissociation of hydrogen bonds, but this explanation appears inadequate. Hydrogen bonds are not being dissociated and if they are it would scarcely account for a constant value over a range of 100 degrees. A striking fact is that the heat capacity corresponds to the Dulong and Petit value of 6.0 calories per atom. This is the value to be expected when the frequencies of vibration of the atom, which occur at the rate of three per atom corresponding to the three degrees of freedom, are low enough to be excited at the temperature prevailing. The significance of this is that the atoms must be more loosely bound than in ice where the structure is rigid. Part of this freedom of motion may arise from the bending of the water molecule from the normal configuration of approximately 105 deg angle. It is possible to accumulate energy in the hydrogen bonds without dissociation.

Liquid Structure. The infrared absorption of liquid water indicates a high degree of association. The high dielectric constant is additional evidence for this conclusion, but the strongest evidence is perhaps obtained from energy consideration. Even at the boiling point the heat of vaporization is abnormally high. This means that the boiling point is actually lower than it would otherwise be if it were not for the large increase in entropy resulting from the dissociation that takes place when the liquid vaporizes. On the other hand, the low heat of fusion indicates hydrogen bonding in the liquid to a degree almost as great as that in ice. This causes the melting point to be higher than might otherwise be the case.

Water as a Solvent for Electrolytes. The picture of water as a largely associated structure of high dielectric constant accounts very well for the extraordinary ability to act as a solvent for electrolytes. Ice has no space in its lattice to permit ions to dissolve but the water molecules can arrange themselves in such a way as to largely neutralize the forces between ions, the hydrogen surrounding the anion and the oxygens the cation. The only discordant note in this picture is the extremely small electrical conductivity of pure water itself. This means that the water molecule has very little tendency to dissociate into free ions. The two hydrogens and the oxygen remain attached to each other.

The hydrogen bonded water molecule in the medium of high dieletric constant exists in essentially ionic form. But the oxygen ion is doubly charged and of small radius so that the Coulomb's law attraction is still large. Comparison with a molecule such as hydrogen chloride will make this clear. The chlorine ion is singly charged and of large radius so that the Coulomb's law attraction is small. Hence hydrogen chloride is largely dissociated into ions and behaves in water solution as a strong acid. The dissociation of the water molecule, while measurable, is small indeed.

Water is, therefore, to be thought of as a highly associated liquid with a semi-ionic structure. The molecular weight is indefinitely large, the molecule depending upon the total mass present. Because of its ionic nature and high dielectric constant, it is a solvent for electrolytes par excellence. When ions dissolve because of the powerful electrostatic forces which surround them, the structure of the liquid is broken down and undergoes modification. There is another class of substances for which the solubility is small which actually has the effect of augmenting the structure of water. These are nonpolar molecules which will be discussed below. There is a class of substances which are intermediate in their behavior in that the molecule includes both ions and nonpolar parts. An important example of these are protein molecules and the reaction between water and protein molecules plays an important role in living organisms. Proteins may be likened to plastics and water may be regarded as a plasticizer for proteins.

Solutions of Nonpolar Molecules. While water is primarily to be regarded as a solvent for electrolytes, more about water itself is learned from solutions of nonpolar molecules. A nonpolar molecule is a molecule that contains no potential ions and is not, therefore, surrounded by any strong electrical fields. Nonpolar molecules do not, therefore, attract other molecules strongly, either polar or nonpolar. The solubility of nonpolar molecules in water is, therefore, expected to be slight and this is the case. The interest in these solutions arises from the existence of solid hydrates which separate at temperatures well above the freezing point when the partial pressure of the gas above the solution is sufficiently high. These hydrates came to attention in a dramatic fashion when natural gas lines became clogged with a solid precipitate at temperatures as high as 20 C. Methane is, of course, a nonpolar molecule, but even more striking is the existence of hydrates with the inert gases such as argon and xenon. The noble gases form no compounds and fantastic explanations have been offered for the supposed attraction. Actually, it is clear that the reason for these compounds is the lack of attraction between the water and gas molecules. The water molecules form a cage around the gas molecules. Since this cage is only one layer thick, the strain which prevents ice forming a cubic crystal does not build up as it would in a continuous lattice. When the gas molecules in solution reach a certain concentration, these cages unite to form a cubic lattice. The reulting lattice is more stable than ice and has a higher melting point. It is not, of course, stable if the gas escapes from solution (Fig. 5).

The fundamental picture here is that the water molecules form a cage around the gas molecule with the oxygen atom turned inward and hydrogen bonds on the outer surface of the cage. The simplest of these structures is a pentagonal dodecahedron which contains 20 water molecules but larger cages are also formed. The heat and entropy of formation are comparable to that for ice. If the inert gas molecules were replaced by water molecules the attractive forces of the hydrogens would break the structure from within, causing it to collapse, and the situation would revert to the chaotic condition of liquid water. There are two lattices known for the gas hydrates

and the lattice constants are given in Table 1. It will be noted that the ratio of the number of molecules of water to gas is fractional, or odd. Furthermore, it appears that the holes in the lattice may not all be filled, giving rise to further variation.

There are two cubic lattices, one with a spacing of 12.0 deg Angstroms and one with 17.0 deg Angstroms. The smaller one contains 46 molecules and the larger one 136 molecules. The smaller lattice contains holes of 12 to 14 sides respectively, while the larger lattice contains holes of 12 to 16 sides. These holes are of different sizes and make it possible to explain the bewildering array of hydrates. It was formerly supposed that chloroform formed a hydrate with 16 molecules of water, but it now appears by counting the number of holes in the lattice that the correct number is 17. Furthermore, the different sized holes can be filled only with different size molecules and not all holes need be filled. Thus, fractional numbers of waters of crystallization and variability in these numbers are accounted for. Certain hydrates involve two different substances in a definite ratio, each substance filling a particular sized hole. Such a case is $CHCl_3 . 2H_2S . 17 H_2O$.

Figure 5. Hydrate is formed when a foreign molecule in water is electrically neutral and just the right size for the water molecules to collect around it in crystalline cage. This cage can then grow to a much larger crystal. It is part of a repeating unit of 136 molecules.

Before a crystalline hydrate can be formed the molecular clusters must exist in solution. These complexes which exist in solution are not observed by direct means but are of great significance. In the case of ions reliance must be entirely on inference since the solid hydrate cannot form because the powerful electrostatic forces between ions prevent the water molecules from entering the crystal in the same ratio that exists in the hydrate in the solution.

TABLE 1

PHYSICAL DATA ON THE TWO CUBIC HYDRATE LATTICES

	Diamond Type	Body-centered Type
Cell constant (approx.)	17 deg A	12 deg A
Number of H_2O molecules in cell	136	46
Number of dodecahedra (small holes)	16	2
Number of 14-hedra (medium holes)	none	6
Number of 16-hedra (large holes)	8	none
Hypothetical hydrative numbers		
(a) Filling all holes	136/24=5-2/3	46/8=5-3/4
(b) Filling only larger holes	136/8=17	46/6=7-2/3

Ionic Hydration and Mobility. The mobility for ions of like charge should vary inversely as the square of the effective diameter. If the mobility of the ions is considered a most peculiar behavior is observed in that the smallest ions appear to have the lowest mobility. A little consideration, however, shows the mobility depends upon the degree of hydration, i.e., the number of water molecules which are attached. The effective diameter of an ion is the diameter of the shell of attached water molecules.

While this is perhaps not always a definite number, certain positive conclusions can be drawn. Only the small cations are strongly hydrated.

The hydration of the cations is explained as due to a cage of water molecules formed in a manner similar to the gas hydrates. The cation which is positively charged attracts the oxygens of two water molecules quite strongly. If the cation is small enough (smaller than the potassium ion) so that the volume of the ion plus two water molecules is comparable to the volume of a methane molecule, then a cage of water molecules forms around this group as nucleus. The attraction of the ion for the oxygen atoms polarizes the central water molecules and increases the hydrogen bonding tendency so that a second layer of water molecules is attached in a symetrical rigid shell. The number of molecules bound may be very large.

If the cation is too large, the shell cannot form. Anions may attach one or more water molecules by hydrogen bonding, but the hydrogen bond does not propagate through adjacent water molecules and the shell does not form.

This theory works admirably until the case of the hydrogen and hydroxyl ions which have the highest mobilties of any ions and many times that of most ions is considered. Hence it is concluded that these ions exist in a cage of water molecules but that they manage in some way to escape from the cage of water molecules, leaving the cage behind. Actually, of course, they continually form a new cage as they travel. The mechanism for this is not hard to picture. It involves what is called proton transfer.

The hydrogen ion or proton is attached at any instant to one of the oxygens but it oscillates between the two oxygen atoms many times per second. Under the influence of an electric field the proton, therefore, jumps from one molecule to the next. When this has occurred its task is done and the hydrogen on the farther side of the water molecule takes up its part in the race like a relay runner and jumps to the next water molecule. Thus a succession of protons, each doing its bit, carry the current. This makes for a rapid motion since each proton moves only a short step. It is, however, different from the original theory proposed by Grotthius who supposed that a whole series of protons moved in step in a continuous motion.

The mechanism of the conduction of hydroxyl ions is explained similarly by proton transfer. The formula for the hydroxyl is: $HOH \longrightarrow OH^-$. The proton jumps toward the right which is in effect the motion of the hydroxyl ion toward the left.

Bound Water. It is clear from the preceding discussion that liquid water undergoes a change in structure in the presence of molecules or at the surface or interface of a solid phase. This may be the result either of hydrogen bonding with active groups or if no active groups are present a considerable structure may be built out of water molecules themselves. In the case of protein molecules, both effects probably occur. It is evident that this is a subject that requires further exploration.

There is plenty of evidence for this formation of hydrates. Most of the phenomena of this sort have been ascribed to "bound" water. "Bound" water is essentially a term covering ignorance but there can be no doubt that water tends to solidify or crystallize in the presence of foreign molecules.

The solidification of water by gel formation is a familiar phenomenon which occurs at ambient temperatures. The key to the swelling of proteins and the imbibing of water by large molecules is undoubtedly to be found in hydrate formation as a result of one or the other of the above mentioned processes. The jelly fish is said to be more than 95 percent water.

The most commonly observed phenomenon of solidification is the formation of ice at temperatures below zero centigrade. Ice occupies a larger volume than liquid water so that if freezing occurs in an enclosed space the walls will rupture unless they are capable of resisting enormous pressures. The damage to living cells from freezing is ordinarily explained as due to this effect, but the evidence indicates that it is a much more complicated affair. The simple analogy of the anti-freeze in an automobile radiator cannot be applied to the sap of a frost-resistant plant. The mechanical effect of freezing does, of course, play an important role in the action of frost on the soils in the northern and central United States. The productivity of these soils is greatly increased by the loosening action of winter freezing. This process, which amounts to a natural cultivation of the soils, becomes harmful, of course, in the case of road

materials. The disruptive action of freezing water extends to even the hardest material, such as granite, over geological periods.

One of the most important products of this geological weathering action is the group of complex materials known as the clays. These substances exhibit a bewildering variety of colloid behavior in which water behaves as a plasticizer. This plasticizing action involves the hydrogen bonding of water to the oxygen of the silica or alumina groups. Silica gel is, of course, pure silica plus water. This bonding of the water molecules is a more or less reversible process except when high temperatures are reached, in which case the molecules become so closely bonded that the water molecules cannot intrude. The analogy is very close between the burning of ceramic material and the denaturation of proteins by dehydration.

ACKNOWLEDGMENTS

Water Structure and Bioenergetics

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Introductory Remarks by Chairman

Strange as it may seem to the soils engineer, soil science is
usually listed as belonging to the biological sciences. Even if we
do not completely subscribe to the propriety of such classification,
natural soil systems represent a meeting ground par excellence
between animate and inanimate nature. In addition, the non-living
as well as the living components of soil normally contain an appre-
ciable percentage of water and owe their properties in a large de-
gree to the interaction of their well-developed internal surfaces
with the water substance. Dr. Albert Szent-Gyorgyi, an eminent
physiologist and Nobel Laureate, has kindly prepared the contri-
bution on "Water Structure and Bioenergetics." Since no unique
"life principles" are invoked in this treatise, the facts and con-
clusions presented hold true for non-living mineral soil systems
the same way as they do for organic living or dead systems. They
are, therefore, of greatest pertinence to the soil scientist and
engineer that really wants to understand what goes on between soil
and water.

● LIFE WAS born in water and is carrying on in water, 80 percent of our own body
being water. Water molecules have unique properties, and it seems most unlikely
that life should not have made use of them. Bio-chemistry has recognized the central
role played by water in bioenergetics. Water is the fuel of life. What the sunshine
(which is the ultimate source of our energies) does, is to separate the elements of
water. The gradual approach of these elements, H and O, and their eventual union to
H_2O with the gradual decrease in free energy is what is moving life. While admitting
the role of water in energetics, biology failed to concede any role to water in the ma-
chinery of life and looked upon water as a more or less inert matter filling the space
between the single parts of that machinery. This outlook on water had two main-
springs: the nature of coulombic forces and macroscopic experience. Electric forces
from charged points decrease with the square of the distance, and so the orienting
effect of charged points on the water dipoles could reduce the mobility of water mole-
cules only in layers of no more than a few molecules deep. Our every-day macroscopic
experience is that water, at room- or body-temperature, is a random fluid, unable to
build structures. The fallacy of this impression is born out by the fact that a decrease
of its kinetic energy by no more than 10 percent, a cooling from room temperature to
- 1 C, i.e. from 293 K to 272 deg, suffices to turn water into a rigid solid with a most
regular crystalline structure. This freezing is permanently going on, also at room
temperature, only the crystal lattice thus formed is smashed up by heat agitation and
so the size of the crystals formed does not exceed molecular dimensions. However,
the balance between heat agitation and the trend to unite to solid and regular structure
needs to be shifted but slightly to lead to extensive lattice formation. This lattice
formation is due to the H-bonds established between the H-s and the non-bonded ("lone
pairs" of) electrons of the different water molecules. So if a solid surface binds and immo-
bilizes one layer of water molecules, this layer will protect its neighbors both parallel
and normal to the surface from the heat agitation present in the bulk. This will stabi-
lize the H-bonds. This mutual protection from heat agitation will be cooperative and
thus can be expected to lead to the formation of extensive lattices, reaching under
favorable conditions thousands of molecules deep into the fluid, and if another parallel
surface is found within this distance, the water can be expected to freeze up altogether
between the two surfaces. So, in closely packed bilogical structures where the distance

between the various macromolecules is of the order of 100 $\overset{o}{A}$, we can expect to find "ice", lattice-ordered water, even if this ice does not share the rigidity of common ice. Even common ice is deformable, its bonds being easily broken and rebuilt, as can be demonstrated by the "dropping" of a steel ball through ice. This property, deformability, will be present in increased degree in the "ice" of our body, which will offer no considerable resistance to deformation or the diffusion of smaller ions.

A distinction must be made between two water structures. The one corresponds to the idea of the "bound water" which has occupied many a research worker in the past. This bound water is due to the attraction of charged points of the surface on the water dipoles. Coulombic forces fading out rapidly with the distance, these layers can be but very thin. Proteins, for instance, can appreciably immobilize, as a rule, a layer of water but one molecule deep. However, this immobilization of the water in the immediate vicinity of the surface may upset the subtle balance between the ordering influence of the inherent qualities of the water molecule and the disordering action of heat agitation, and may lead through a cooperative action to the formation of lattices reaching deep into the fluid.

This ice-formation belongs in no way in the realm of speculation, and it is strange that biology should have taken no notice of it. Henniker and MacBain collected, already ten years ago, 175 references to papers dealing with multi-layers around surfaces (5). Frank and Evans were led by entropy calculations to the conclusions that even dissolved molecules may be surrounded by "icebergs" (4). Bernal and Fowler took X-ray pictures of water a quarter of a century ago, introducing the idea of "structure temperature", by which they meant the temperature at which common water would have the same degree of structuredness as has the water around the surface in question (2). In this scale, most of the intracellular water is probably around 0 C.

In the last twenty years, the author was interested in the working muscle and could demonstrate that the contractile matter is a complex protein, actomyosin, which can be extracted, given the shape of a muscle fiber and made to contract by ions and ATP (adenosine triphosphate). Though mammalian muscle contains 10 percent actomyosin, owing to the great hydrophility of this protein, it is difficult to prepare actomyosin solution containing less than 97 percent water. Such an actomyosin solution, at physiological ionic concentration, forms a rigid gel. It is difficult to explain this strong binding of water in any other way than by the formation of "icebergs", water lattices formed around the fibrous actomyosin particles. On addition of ATP, this water structure collapses, and the actomyosin becomes a practically anhydrous material. This collapse of the water structure declares itself to the observer as a contraction of the actomyosin thread. If, within this thread, the actomyosin filaments had a random distribution, then the contraction takes place in every direction, and what we see is an extensive shrinking. If the actomyosin filaments were ordered paralled to the axis of the thread, then this latter becomes shorter only, behaving very similarly to contracting muscle. Essentially, this change observed in an actomyosin thread is identical with muscular contraction which is intimately connected with the collapse of a water structure, while the relaxation of the contracted muscle has to be connected with the rebuilding of the collapsed water lattices. The structures induced in the surrounding water by the actomyosin particles are thus just as much a part of the contractile machinery as the protein itself; the two make one single system. What is true of the generation of motion, one of the oldest and most basic signs of life, is probably true, also, for the other biological functions.

The assumption of water structures makes many biological phenomena appear in a new light. One of the most basic phenomena of biology, for instance, is semipermeability. This was hitherto explained by holes in the membrane, or by the presence of "careers" within the membrane. It seems likely that the membrane, with its pores, is covered by a sheet of "ice" while the substance which it has to let through is surrounded by an "iceberg". The latter's transmission through the membrane will thus depend less on the relative size of the hole and the permeating molecule or ion than on the nature of the two ices, the one covering the membrane and the one surrounding the dissolved particle. If the two ices are similar in structure and can fuse, then only will the substance be able to penetrate. The ice inside the cell will also resist the admission of

ions which disturb its structure, and it has been shown that the specific permeability of cells to potassium, as compared to Na, might be also explained by the lack of disordering effect in K^+, and the disordering action of Na^+ (1).

If a $10^{-4}M$ watery solution of Rhodamin B is frozen in dry ice, it shows practically no light emission, if observed in near ultraviolet light. The situation is not altered by the presence of O. 1 M KCL, but in presence of O. 1 M NaCl, an intense light emission is observed, coming from a triplet excitation of the dimer of the dye. The presence of Na-ions thus makes an electronic transition probable which was improbable in its absence, the transition from the excited triplet state into the ground state under emission of photons being "forbidden" by the selection rules. This perturbation is, in all probability, due to the disorder-producing effect of Na^+ within the thin sheet of lattice ordered water surrounding the water crystals. This simple experiment suggests an intimate relation between the excited state, transition probabilities and the lattice ordered nature of water, and it is not impossible that these water lattices are also instrumental in the energy transmission in biological processes. They may also make "proton conduction" possible, holding the water molecules in an orientation favorable for the transmission of H^+ from one molecule to the other.

Lattice ordered multilayers are also found in systems where no coulombic forces can be involved in the immobilization of the fluid around the surface in question. This is the case, for instance, when the liquid phase consists of a non-polar substance, as is the case with lubricants. We can expect that any solid surface will protect the adjacent liquid layer from heat agitation and thus immobilize it. That this is the case is shown by the fact that in streaming fluids, the layers adjacent to the solid surface are stationary. So we can also expect that around protein structures the water will be immobilized even at points where the protein has no charges. As shown by Rodenbush and Buswell at this symposium, the lattices, thus formed around non-polar groups will be different from the lattices formed around polar groups or formed in the bulk of water on cooling. This complexity of the situation, with its very subtle equilibria, makes conditions most colorful and begins to resemble the subtle complexity which characterizes life.

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Organization of Water on Clay Mineral Surfaces And Its Implications for the Properties of Clay-Water Systems

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Introductory Remarks by Chairman

There was a time when every leading physical chemist had his own favorite picturesque expression of the Second Law of Thermodynamics. The advantage of such similes or parables was that they stimulated the imagination and were easily retained by the memory. Their disadvantage was, of course, lack of precision. As everything potent, they had to be used with caution. However, if properly employed, such formulations can be powerful agents for the progress of knowledge and understanding. In this class, falls the statement by Harkins that whenever two different materials are in contact, an interface structure will be formed in such a manner as to make the transition from one material to the other the least abrupt possible. In the present symposium, we are vitally interested in the structure of the interphase between liquid water and solid mineral—especially clay surfaces. Proceeding from the better known to the lesser known, we may and should approach this interphase not only from the water side but also from the mineral side. It is, therefore, appropriate and gratifying to have as eminent a clay mineralogist as Professor Grim discuss the organization of water on clay mineral surfaces.

● THE OBJECTS of this paper are to gather together the evidence indicating that the water held on the surfaces of clay particles has some sort of definite geometric organization, and to discuss the implications of such water characteristics for some of the properties of clay-water systems.

In clay-water systems containing relatively large percentages of water, such factors as particle charge, shape, etc. may exert a controlling influence on the properties. On the other hand, when the percentage of water is relatively small, as in the case of systems in the plastic state, the thickness of the water film between particles is such that the characteristics of the water itself must play a significant role in determining properties. It is suggested that data obtained by studying highly fluid systems may not be applicable directly to plastic systems, because in the former case, the character of the water would be relatively unimportant, whereas in the latter case it would exert a controlling influence.

EVIDENCE FOR WATER ORIENTATION ON CLAY MINERAL PARTICLE SURFACES

The evidence for some regular orientation of the water particles held on the surface of the clay mineral particles comes from many directions. The characteristics of water molecules themselves, according to the work of Bernal and Fowler (1), Bernal and Megaw (2), and Cross et al. (3), indicate that the water molecules would tend to group into a definite network. In the present symposium the paper by Rodebush and Buswell on the "Properties of Water Substance" shows that the properties of water are such that orientation of water molecules develops at the surface or interface of a solid phase.

Forslind (4) has presented diffraction data which seem to provide direct evidence for orientation in the adsorbed water layers on the clay minerals surfaces. There is urgent need for investigation by neutron diffraction of this matter.

Studies of the properties of clay-water systems provide strong evidence for water

orientation. Grim and Cuthbert (7) have emphasized this point stating that it is extremely difficult to arrive at a satisfactory concept and explanation of such properties without assuming some water orientation. Many examples could be given, but a few will suffice. The heat developed (Heat of Wetting) when clay mineral surfaces are wetted is attributed largely (11) to a change in the nature of the water adsorbed on the surfaces of the clay minerals.

Many cases are known where there is an abrupt change in the physical state of a clay-water system with a slight change in water content. Thus, as increasing amounts of water are added to a dry clay, plasticity develops abruptly; there is a very narrow moisture range in which high bonding strength is developed in a clay-sand system, Figure 1 (7); as water is added to a dry clay, it cannot be extruded until a certain water content is reached when it suddenly becomes easily extrudable, Figure 2. These and many other attributes are easily explained if one considers that the initial water is adsorbed in a rigid oriented state, that as the adsorbed water layers become thick, there is a point at which the orientation is lost or at least greatly reduced in rigidity, and, that the oriented water molecules provide a bonding force between particles.

Figure 1. Schematic sketch of orientation of water molecules adsorbed on the basal surfaces of the clay minerals. Large circles represent oxygen atoms; small circles hydrogen atoms; small black or shaded circles silicon atoms (after Hendricks and Jefferson).

WATER ORGANIZATION STRUCTURE

Although students of clays are likely to agree that the water adsorbed on clay mineral surfaces does not have the physical characteristics of liquid water, there is no general agreement on the precise nature of the organization of such water molecules (5). A concept favored by many is that suggested by Hendricks and Jefferson (9) in which successive water layers are composed of water molecules joined into hexagonal groups of an extended hexagonal net. This structure gains credence because of its similarity to the well established structure of water molecules in ice; because of an epitaxial fit with the organization of the oxygen atoms
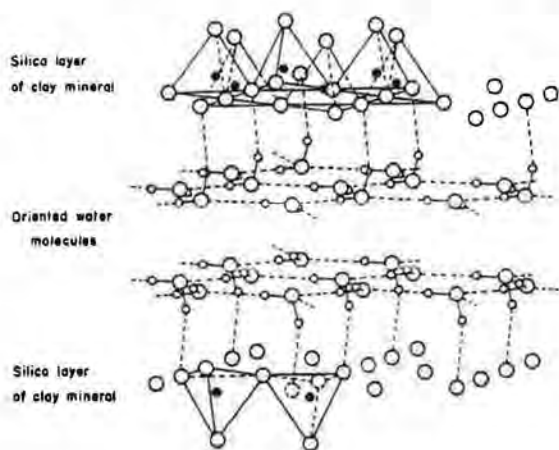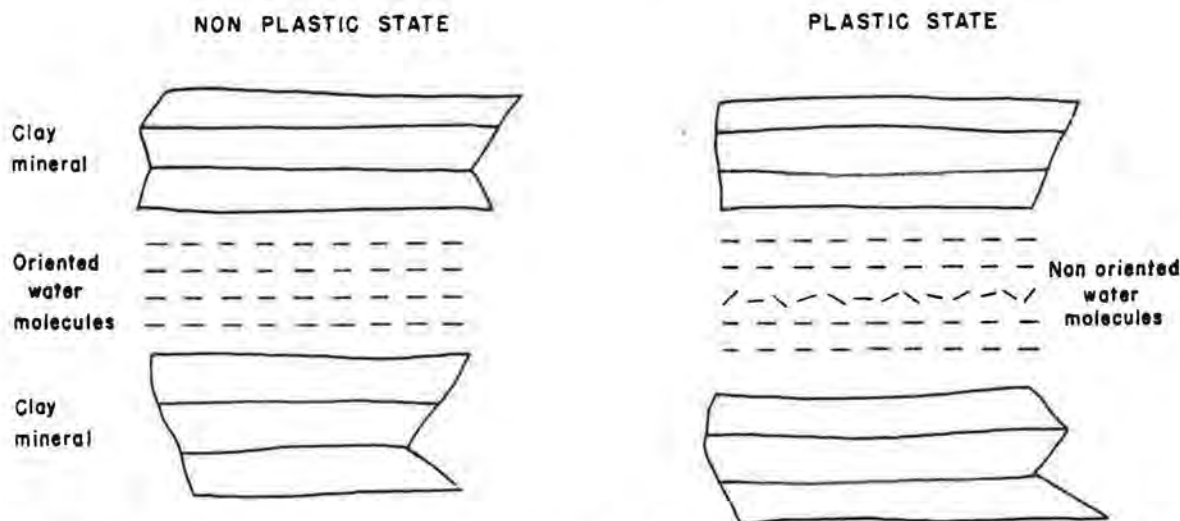

Figure 2. Schematic presentation of character of water in nonplastic and plastic states.

in the basal surfaces of the clay minerals; and because it is in accord with the requirements of hydrogen bonding between the water molecules themselves, successive water layers, and the clay mineral surface.

It seems quite certain, as will be discussed presently, that the water organization is not always exactly the same on all clay particle plane surfaces, and it may well be different on the irregular edges of clay mineral flakes as compared to basal plane surfaces.

The significant point is that the water adsorbed on the clay mineral surfaces and for some distance outward is not in the state of liquid water, but has some organization in which the water molecules are held together by hydrogen bonding.

INFLUENCE OF CLAY MINERAL COMPOSITION

It would be expected that the degree and perhaps kind of water organization would not be the same for all clay minerals, and therefore that the effect of this factor on physical properties would not be the same for all clay mineral compositions. Since the most probable water organization is a sheet structure, flat surfaces would be better than curved surfaces yielded by minerals without cleavage such as quartz, and probably these in turn would be better than the irregular broken edges of the layer-silicate clay minerals.

Some of the flat surfaces of the clay minerals are composed of oxygens, others are made out of hydroxyls. There seems to be no inherent reason why a flat oxygen surface should be better than a flat hydroxyl surface. Perhaps a somewhat different organization of water molecules would develop on the oxygen as compared to the hydroxyl surface. Thus, it might be expected that the structure suggested by Hendricks and Jefferson (9) would favor an oxygen surface because of a preferred epitaxial fit of the water net and the arrangement of oxygens in such clay mineral surfaces.

Another factor in the influence of the clay minerals is the difference in the ease of cleavage into thin flat flakes and/or the ease of penetration of water between the flakes. This factor, of course, determines the amount of flat surface available for water orientation, and it probably would be more important than the kind of surface.

Based on the foregoing considerations, montmorillonite clay minerals would be expected to show the largest amount of oriented water development. Next, but to a considerably smaller degree, would be vermiculite, and weathered degraded illites and chlorites. Next, and also to a considerably reduced degree, would be illites, chlorites and kaolinites, with the micas probably somewhat better than the kaolinites. The halloysite and allophane minerals would be expected to occupy a lower position because their particles may not be flake shaped, although in some cases their extremely small particle size would perhaps outweigh the shape factor.

The exact situation with regard to the fibrous clay minerals, attapulgite-palygorskite-sepiolite, is not certain, but in some cases, at least, their high cleavability and large surface area appears to permit considerable water orientation.

The phenomenon of "Quick" clays, well known to engineers dealing with soils, probably requires the concept of oriented water to provide a satisfactory explanation for their properties (6). Many of these materials are actually silts, and their mineral composition strongly suggests that oriented water can develop on granular particles as well as on the clay mineral surfaces.

INFLUENCE OF ADSORBED IONS

Adsorbed components on the surface of clay particles may serve as a waterproof coating thereby preventing the development of water in a non-liquid state. Common examples would be various types of ionic organic materials. Adsorbed components may also largely control the nature and the extent of oriented water development, and of these inorganic cationic components are probably the most important. Also their influence is best known, and hence, they will be discussed in some detail.

Adsorbed cations influence the development of non-liquid water in several ways as follows: They serve as a bonding force between particles, and thus may determine the available space between particles and the attractive force that growing layers of water

must overcome in pushing apart clay particles. They determine the thickness of the oriented water layers also by the manner in which the cations or the cation plus a hydration envelope can fit into the geometry of the water net. The fit or absence of a fit may serve to enhance or retard the formation of oriented water layers. The cation may determine the actual geometry of the water net, and of very great importance, determine whether the oriented water grades gradually into liquid water or is abruptly separated from liquid water.

In soils and clays the usual adsorbed cations are calcium, magnesium, sodium, potassium, hydrogen, aluminum, and iron.

Calcium, probably the commonest adsorbed cation, in the presence of an abundance of water tends to develop very well oriented water to a thickness of about four molecular layers with any additional water unoriented. There is a sharp break between liquid and non-liquid water. In an air dried state Ca^{++} tends to develop two molecular layers of well oriented water.

In general, and for our purpose, Mg^{++} exerts about the same influence as Ca^{++}. In detail there are some differences: The maximum possible thickness of well oriented water is probably slightly less, and in the air dried state, the geometry of the water is somewhat different so that the thickness of the water layer is slightly reduced.

The sodium ion favors the development of very thick layers (probably tens of molecular layers) if the water is available. Further, the oriented net seems not to be very rigid and there is no abrupt separation between oriented and liquid water. In an air dried state Na^+ favors the development of a single molecular layer, and thus there is a tremendous difference between the thickness of adsorbed water in an air dried state and the potential thickness if moisture is available. Obviously Na^+ clays have very high swelling potential and limit values.

For our purpose K^+, H^+, Al^{+++}, and Fe^{+++} may all be grouped together in that they form a tight bond between particles with very small potential for the growth of thick oriented water layers. In an air dried state very thin water layers would be expected. Precise data for some of these cations is difficult to obtain. For example, a prepared hydrogen clay contains Al^{+++} and possibly Fe^{+++}, and the preparation of a K^+ clay is likely to be accompanied by structural changes within the clay mineral itself.

Untreated clays or soils may contain a dominant single adsorbed cation or a mixture of cations. If there is a single cation present, a very uniform oriented water thickness may develop throughout the material which will cause considerable stability. If there is a mixture of cations, there may be variable water thicknesses which would favor instability. In Wyoming bentonites, it has been shown (13) that an adsorbed cation composition of about 70 percent Na^+ and 30 percent Ca^{++} produces the maximum potential dispersibility. Of importance is the point suggested by available data, that the gradual replacement of one cation by another may have no influence on adsorbed water development up to a certain point at which there is a sudden abrupt change in the stable thickness of the oriented water.

This factor of the abruptness of transition of water from one state to another is probably related to the distribution of cations on the clay mineral surfaces. It has been shown recently that in some clays containing both Ca^{++} and Na^+, the Ca^{++} are concentrated on some surfaces, and the Na^+ on others rather than having a random scattering of Ca^{++} and Na^+ on all surfaces. Since the population of any surface by Ca^{++} or Na^+ is probably never completely monoionic, it is logical that there could be a certain amount of exchange without influencing the adsorbed water layer stability. This is probably a factor in determining abruptness characteristics of changes in water orientation. It must be remembered that there is much yet to be learned regarding the relation of the distribution of cations within a clay or soil to adsorbed water characteristics.

Recently Slovinsky (12) has shown by means of continuous X-ray diffraction analyses that the loss of adsorbed water by montmorillonite clays takes place in a stepwise fashion rather than continuously. Thus, there is the loss of one molecular layer, then a second layer, and so on. This seem to be the case regardless of which of the common adsorbed cations are present. Such a stepwise dehydration must be accompanied by a stepwise abrupt change in volume and bonding strength between particles.

IMPLICATIONS OF ORIENTED WATER STRUCTURES

Oriented water molecules on clay particle surfaces undoubtedly act as a bonding force between the particles. Liquid water would be expected to produce comparatively little bonding strength. This difference in bonding strength is the essential factor regarding the state of the adsorbed water so far as the physical properties of clay - water systems are concerned. To this generality must be added the point that adsorbed ions and molecules on the surfaces of clay particles act directly by influencing the bonding force between the particles, and indirectly by influencing the organization of the water molecules and thereby its bonding force.

On the basis of the foregoing considerations the following statements seem warranted:

There could be materials with very high moisture contents which would have considerable strength. Such materials are likely to be composed largely of montmorillonite and carry sodium as the exchangeable cation. Soil materials and clays composed of attapulgite or very poorly organized clay minerals might also have these properties.

A material can exhibit tremendous difference in strength with a slight change in moisture content. If a material is holding about its maximum amount of rigid water, additional water would be in the liquid state with the likelihood that the water bond between the particles would be broken. Also, the loss of a slight amount of moisture by drying might well disrupt an equilibrium thickness of water layer so that strength would be destroyed.

A slight change in the adsorbed cation composition might well cause a destruction of the orientation of some water molecules because the replacing cation would not permit the same maximum amount of oriented water as the replaced cation. In the case of the replacement of Na^+ by Ca^{++} of H^+ the permissable oriented water thickness would be reduced—this might develop liquid water and immediate loss of strength, or the oriented water might continue to exist but in an unstable form which later would be changed to liquid water by the addition of more water, or perhaps by the application of some external abrupt shock force which would suddenly break the water net. In the case of an exchange of Na^+ for hydrogen or a multivalent cation, the maximum oriented water holding capacity would be increased, but the perfection of orientation and hence the bonding strength of the water net would be reduced. As a consequence of replacement with Na^+, one would expect, therefore, a more gradual loss of strength, and of course, if additional moisture were available, an expansion in volume or swelling of the clay.

As just noted above, there would be clays and soils where volume would increase with increased moisture control. Such expansion would be accompanied probably at first with only a slight decrease in strength and later with a substantial gradual decrease of strength. The gradual decrease is a consequence of the great thicknesses of oriented water layers possible when Na^+ is the adsorbed cation, and the gradual decrease in the degree of rigidity of the oriented water layers outward from the adsorbing surface. Montmorillonite would be the clay mineral component expected in swelling clays since it permits water to enter between the individual unit silicate cell layers, i.e. the swelling takes place within the silicate structure. Some swelling within the silicate particles might also develop in some poorly organized clay minerals. In clays composed of other clay materials the water is in pores and around large crystal units and particles so that the development of oriented water would not be expected to cause a substantial increase in volume, i.e. the expansion under ordinary conditions would be insignificant.

It follows from considerations of rigid water, that soils and clays can experience a reduction in volume, aside from any association with surface drying and without the application of an external force. This can occur following the liquification of adsorbed water if the setting is such that the liquid water may be removed, as by seepage downward into the ground water. Conceivably, such a reduction in volume could also occur without the removal of any water. Thus, there may be material with a water bond in which there are pores not completely filled with water. Also, if the structure suggested by Hendricks and Jefferson (9) is the correct one, the oriented water could have a density less than liquid water so that there would be a reduction in volume when the water structure was lost.

A consequence of the development of oriented water, which is somewhat unexpected, is the existence of a time factor in the development of the properties of clay-water systems. Thus it has been observed (7) that the compression strength of some moist clay-sand systems increases during a matter of hours after mixing and compacting into a test piece without any change in the moisture content. This is readily understandable on the basis that some time is necessary for the moisture to penetrate the clay mass to all potential surfaces and for the water structures to develop. The development of oriented water is a kind of crystal growth and, as is common in crystal growth, requires time. One would expect that the time factor would be particularly important in materials composed of mixed-layers, degraded illites and chlorites, and perhaps halloysites. Under certain conditions attapulgite clays should also show this phenomenon but for a somewhat different reason, since the bundles of elongate particles of this mineral are cleavable, but with some difficulty. As an attapulgite-water system is worked or agitated, the mineral particles are separated by cleavage thereby increasing the surface area for water adsorption. This same growth of surface by cleavage of particles takes place in all the clay minerals, but probably not to the extent or with as great an influence on clay-water properties as in the case of materials composed of attapulgite.

Materials whose properties would be most influenced by oriented water considerations would be likely to be those with high limits and high sensitivity. However, some materials of low activity, for example, some silts with a low clay mineral content, are also thought to have oriented water bonds which are responsible for their high sensitivity. In such materials the detailed factors of composition, both textural and mineral, which favor the development of the high sensitivity are not well understood. Rosenquist (10) has shown that an exchange of cations, as by leaching of Na+ plays a role, but it seems doubtful if all very sensitive silts have been subject to such leaching action.

It seems obvious from the foregoing discussion that an engineer needs to give particular attention to the moisture content of soils and clay materials with which he is required to deal, and to any potential cation exchange which might change the nature and the extent of the adsorbed water. Conceivably it might be desirable to go to great lengths to maintain the moisture content and to prevent an exchange reaction in order to insure that the water orientation and attendant strength would not change abruptly. Thus, drainage favoring a variable change in the adsorbed moisture content might not stabilize the slope but be disastrous because it might tend to alter the nature of the adsorbed cation and the strength of the water bond.

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Influence of Liquid and Clay Mineral Type
On Consolidation of Clay-Liquid Systems

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Introductory Remarks by the Chairman

In order to appreciate the special qualities of the water substance, it is advisable to experiment with non-aqueous liquids, especially with pure organic substances of well known molecular and bulk properties. Mr. Waidelich has done this and has determined with established engineering techniques the consolidation behavior, the Atterberg consistency limits and the apparent specific gravities of three clays in combination with six organic liquids and water, respectively. The data obtained and the conclusions drawn therefrom complement and illuminate the findings on soil-water interaction reported by other contributors to this symposium.

● THIS PAPER deals with the influence of physico-chemical factors on the compressibility of clays. It had previously been shown that the presence of exchangeable ions in clays is accompanied by repulsive forces between the particles and that the amount and type of exchangeable ions in a soil material influenced its consolidation behavior. To verify this fact and to learn about other physico-chemical factors, consolidation and supplementary tests were performed with three distinctly different clays and seven liquids; one of these was water, the others were organic liquids differing in molecular structure, dipole moment, and dielectric constants.

To verify Russell's findings (19), concerning the interaction of polar liquids with soil and lack of interaction in the case of non-polar liquids, specific gravity tests were run with all the soil-liquid combinations. It seemed probable that the soil-liquid interaction that shows itself in the specific gravity values of a soil if determined in different liquids would also affect the mechanical properties of soil-liquid systems, especially since Winterkorn had shown the relationship existing between the swelling of expanding lattice type clays and the dielectric constant of the liquid employed.

The experiments showed that the compression indices of the non-expanding lattice clays varied in the same manner as the dipole moment of the liquid used. The expansion indices also varied with the dipole moment of the liquids; in addition, they were affected by the size and structure of the molecules, the effect of the liquid upon the elasticity of the soil particles, and the dielectric constant of the liquid. The specific gravity of the non-expanding clays also varied with the dipole moment but was additionally influenced by the size and structure of the molecules of the liquid.

The compression indices of the expanding lattice clay varied in the same manner as the dielectric constant of the liquids used. The expansion indices were functions of the dielectric constant of the liquid but were additionally affected by the size and structure of the molecules and the other factors previously mentioned. The specific gravity of the expanding lattice clays also varied as the dielectric constant of the liquids but was additionally influenced by the size and structure especially of the larger molecules.

Of course, the physical properties are not the only factors governing the experimental results. The consolidation and expansion mechanism is quite complex and many secondary phenomena are coupled with the primary factors that have been investigated in the present work. A major contribution to the resolving of this complexity is the correlation found in this study between mechanical properties of soil-liquid systems and dipole moments of the liquids in the case of non-expanding lattice clays, and between mechanical properties and dielectric constants for expanding clays.

This investigation was motivated by the desire for a better understanding of the various factors involved in the consolidation of saturated soils upon loading. The general

theory of soil consolidation was developed by Terzaghi (1925) who recognized the analogy between the consolidation of a soil confined between strata of greater permeability by loss of water and the cooling of a hot plate by loss of heat. The mechanism of this type of consolidation is well described by the late Donald H. Taylor (24) who states:

"Any loading applied to a saturated mass of clay causes compression. However, the soil grains and the pore water are relatively incompressible, and as compression requires a reduction of the pore space, it can occur only as fast as pore water is able to escape. At the instant after the application of load, before any pore water has escaped, none of the added load can be carried by the granular network of the soil, since to carry added load this network must undergo compression. The load, therefore, must be carried, temporarily, by a pressure in the water, called 'hydrostatic excess pressure'. If water can escape at the surface of the clay, drainage begins and the hydrostatic excess pressures and their gradients gradually decrease. The stresses imposed by the loading slowly pass from hydrostatic excess pressure to intergranular pressures, with compression of the clay meanwhile occurring at a continuously decreasing rate. In time the load is carried entirely by the grain structure and no hydrostatic excess remains. It is this gradual adjustment process which is known in soil mechanics as 'consolidation'."

The Terzaghi theory as well as the Taylor statement represent only first macromechanical approximations to what is really happening in a consolidating soil. According to this picture the total consolidation is equal to the loss of water and the rate of consolidation is a function of the permeability of the soil system. The inability of this simple picture to account completely for actually observed consolidation phenomena has led to the development of auxiliary theories on secondary consolidation.

Actually, the consolidation process represents a complex interplay between applied stresses on the one hand, and frictional and cohesive resistance forces in the solid-liquid system on the other hand. The resistance factors themselves are functions of the granulometry of the solid components and the surface interactions between the solid and liquid phases composing the soil system. Such interactions fall within the realm of physical chemistry; their character and magnitude are functions of the physico-chemical characteristics of the surfaces of the solid components and of those of the liquid phase. For water as the liquid phase, it has been shown by Winterkorn that the consolidation process and the physical parameters, such as the coefficients of permeability, consolidation and compressibility calculated from the respective experiments, are functions of the type of soil, the type, percentage and base exchange capacity of its clay fraction, and the kind and proportions of exchange ions present (29, 30, 34).

Since water is a unique and complex liquid, its actual role in the consolidation process can be properly understood only by comparable experimentation with other liquids. With respect to interaction of soil mineral surfaces and liquids, it had been shown by Winterkorn and Baver (33) in the case of swelling experiments and E. W. Russell (19) in specific gravity determinations of clay involving various liquids that the polar character and the architecture of the molecules composing the liquids were of primary importance. On the basis of the available information, it was decided that significant data could be obtained by making consolidation experiments using three different well defined clays and seven different liquids with each clay.

EXPERIMENTATION

Materials Used in the Investigation

1. Clay Minerals. Three different commercially available clay materials were employed in the experimental part of this study. They are (a) Georgia Acid Kaolinite, (b) Goose Lake White Clay—predominantly Halloysite and, (c) Na—Bentonite (Montmorillonite) in pellet form.

Mineralogical identification of these materials was made by means of X-ray diffraction (1, 5, 10, 28, 29). A North American Phillips Co. X-ray diffraction machine was used with a Brown potentiometer which is a counter and graphic recorder of the amount of X-rays reflected. The X-ray machine rotated the X-ray beam one deg of arc per min. The graphic record was started at 36 deg, measured from the horizontal, and run to approximately four deg from the horizontal. This proved to be the range of

identifying peaks. Spectrograms were obtained for the three clay materials employed in the investigation as well as for kaolinite and dickite standards. The slides used for this purpose were made in the following manner: The mineral material was first pulverized in a small dish by means of a glass pestle. A small amount of the resulting powder was placed on a glass slide where it was mixed with a few drops of acetone.

A paper clip was used to mix the soil and acetone and also to spread the mixture evenly and thinly over the glass slide surface. The acetone evaporated rapidly and soon the slide was ready to be placed in the X-ray diffraction machine. The apparatus worked automatically once the machine was turned on.

RESULTS OF THE IDENTIFICATION TESTS

a. Georgia acid kaolinite

This material was supplied through the courtesy of the Georgia Kaolin Company, Dry Brand, Georgia. Kaolin, according to Ross and Kerr (18) is the name of a rock composed of white or nearly white clay minerals that have the approximate chemical composition $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$. Kaolinite is the name of the mineral that characterizes most kaolines. Other minerals falling within the same group are nacrite and dickite. The word "kaolin" is a corruption of the Chinese "kauling" meaning "high ridge", the name of a hill near Jauchua Fu, China, where the material was obtained centuries ago for porcelain manufacturing (10). Kaolinite crystallizes in the monoclinic system and in dense crystalline form has a specific gravity of 2.627. In less perfect crystals the specific gravity is smaller and of the order of 2.5. The crystal structure of kaolinite was first generally outlined by Pauling in 1930, worked out more thoroughly by Gruner in 1932, and substantiated by Brindley and his colleagues by X-ray analysis in 1951. It has a 1:1 lattice structure and a silica/sesquioxide ratio of two.

An X-ray diffraction analysis of the Georgia kaolinite used is matched in Figure 1 with that of a pure kaolinite standard and a dickite standard. Representatives of this clay mineral group can be identified as such by the two sharp "first order" peaks seen to be at approximately 7.14 A and 3.57 A. No other clay minerals have first order peaks at this location. The values given above indicate the lattice spacing in Angstroms.
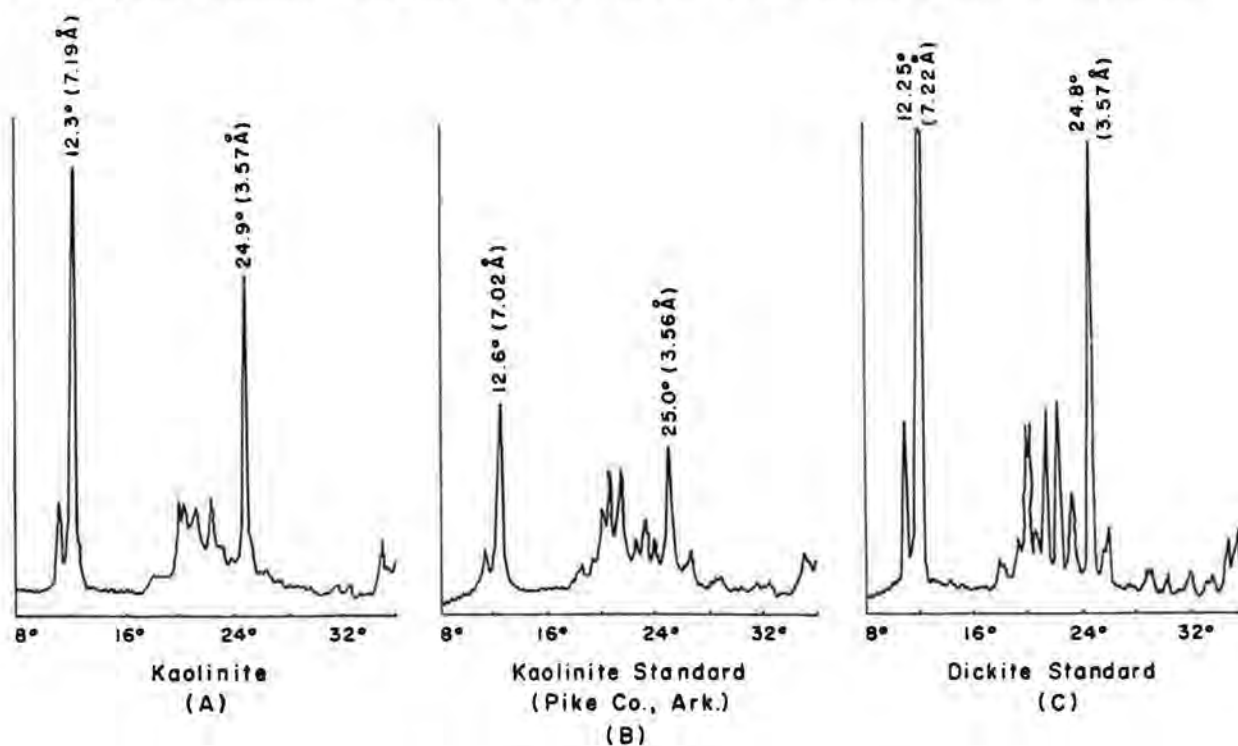

Figure 1.

Goose Lake White Clay
(A)

Goose Lake White Clay
Treated with Ethylene Glycol
(B)

Figure 2.

7.1° (12.44Å)

Montmorillonite
(A)

Montmorillonite
Treated with Ethylene Glycol
(B)

Figure 3.

Significant physical properties of these liquids are given in Table 2. All these are polar liquids; this means that in their respective molecules the center of the positive charges does not coincide with the center of the negative charges. One differentiates between permanent dipoles, which are inherent in the molecules and are due to their normal structure, and induced dipoles, which are due to a deformation of the electron shell when placed in a strong electric field. Dipoles are characterized by the dipole moment which is the product of the electric charge and distance between the center of the charges and by the architecture of the molecule which determines how accessible the charge centers are and how close other ions or molecules can get to the respective centers.

Experiments Performed During the Investigation

Experimentation was concerned primarily with the consolidation test on the above-named mineral-liquid combinations. In addition it appeared worthwhile to determine the specific gravities and the Atterberg limits of the mineral materials with the various liquids.

1. Consolidation Tests. The consolidometers used were of standard type, taking a sample of approximately 2½ in. in diameter and 1 in. in height. A Federal dial, accurate to the nearest ten thousandth of an inch, was employed to measure the vertical movement (compression). On two of the consolidometers, the sealing ring was soldered to the sample barrel to aid in preventing the loss of liquid by leakage at this perimeter. On the other four consolidometers, sodium silicate with a cotton filler was put around this perimeter for the same purpose. This worked well when the organic liquids were used. White lead was employed in place of the cotton filler with the sodium silicate when water was used with the soils.

To prevent the volatile liquids from evaporating, a polyethelene cover was placed around the consolidometer. Also, a flask was placed above the apparatus with two flexible tubes feeding the liquid to the soil when the liquid level dropped below the desirable height. Aluminum foil was wrapped around the bottles to protect photosensitive liquids from sunlight.

The porous stones were soaked in the liquid to be used for at least one day and usually longer.

The soil-liquid mixture was placed in the consolidometer with a spatula. Care was taken to avoid the entrapment of air in the specimun as this would drastically affect the results.

The first load increment was 0.1 ton per square foot (TSF); each successive increment was double the last until one of 6.4 TSF was reached. The unloading decrements

TABLE 2

PHYSICAL CHARACTERISTICS OF LIQUIDS USED (36)

Liquids	Liquid Symbol	Formula	Mol. Wt.	Density[a] Gm/cc	Melting Point deg C.	Boiling Point deg C.	Latent Heat of Vapor. Gm-Cal/Gm	Latent Heat of Fusion Gm-Cal/Gm	Viscosity at 20 deg C. Centipoises (Cp.)	Dielectric Constant at 20 deg C.	Dipole Moment
Water	1	HOH	18	0.99823	0	100.0			1.000	81.07	1.8
Aniline	2	$C_6H_5NH_2$	93.12	1.022	- 6.2	184.4	103.68	20.95	4.40	7.25	1.55
Nitrobenzene	3	$C_6H_5NO_2$	123.11	1.19867	5.7	210.9	79.08	22.52	2.03	36.1	3.89
Methyl Alc.	4	CH_3OH	32.04	0.7917	- 97.8	64.65	262.79	16.39	0.597	33.1	1.68
Ethyl Alc.	5	C_2H_5OH	46.07	0.78934	-117.3	78.5	204.26	24.89	1.200	25.8	1.69
Butyl Alc.	6	C_4H_9OH	74.12	0.80978	- 89.2	117.71	141.26	29.93	2.948	7.8	1.67
Propyl Alc.	7	C_3H_7OH	60.09	0.8044	-127.0	97.19	164.36	21.02	2.256	22.2	1.65

[a] Densities refer to water at 4 deg C., the liquid being at 20 deg C.

were one quarter of the previous load; this unloaded the specimen in three decrements ending with the initial load.

For all the samples, one day was allowed between load stages except for the montmorillonite-water sample, which required two days to complete its primary consolidation and to establish a secondary compression rate. Two days were also allowed for expansion of this sample.

To derive the coefficients of consolidation from the laboratory data, a "fitting method" must be used which correlates the laboratory and the theoretical time-consolidation curves. The "square root of time" fitting method was employed for evaluating all results because of the rapidity of the compression rates (some reaching the ninety percent consolidation point within one minute).

Due to this rapid consolidation rate, the coefficient of consolidation and, therefore, the permeability values obtained were mainly of qualitative value, being important only in judging the order of magnitude of the coefficients involved. The permeability is often considered a material constant and the only liquid property affecting it is assumed to be its viscosity. It should be noted that the viscosities of several of the liquids were higher than that of water, but the permeabilities were also higher, not lower as would be the case if the assumed relationship were true. The cause of this is (a) the effect of liquid on the structural arrangement of the solids, making larger individual pores

$$\text{(for effect see Poisseuille } v = \frac{\pi r^4 \Delta p}{8 \eta \, \Delta l} \cdot t \text{);}$$

(b) the different thicknesses of the adsorbed or "restrained" liquid layers. (See Figs. 4, 5, and 6 which will indicate the permeability ranges of the three soils graphically.)

2. Specific Gravity. The specific gravity of any solid or liquid substance is the ratio of the unit weight of the substance to the unit weight of water at the same temperature. It is a measure of the heaviness of a material. The true average specific gravity of an actual soil is the weighted average of the specific gravities of all the mineral particles in the soil. A liquid that will not react with the soil in any way should be used to obtain this true specific gravity. E. W. Russell has shown that the specific gravity values obtained for a soil using various liquids will deviate from one another depending on the interaction between the liquid and the soil (19). He also found that "No evidence could be obtained of interaction between clays and non-polar liquids and interaction took place in all the polar liquids examined." To obtain the true specific gravity of the soil, decahydro-naphthalene (decalin), a non-polar liquid, was used.

If the test is run with entrapped air in the soil-liquid system, the apparent weight of the soil, liquid, and pycnometer is less than the true weight since the entrapped air is taking the place of water. Therefore, entrapped air will cause specific gravity values that are too low. A desiccator, provided with an interconnected flask filled with anhydrous calcium chloride attached to a Hyvac oil pump, was used to remove the entrapped air. The pump provided a suction of approximately 28 psi. The pycnometers with the soil-liquid mixture were left under this vacuum for at least one hour. The vacuum was released and the pycnometers were spun manually to aid the removal of entrapped air bubbles. This procedure was continued until, upon spinning, no more air bubbles appeared. The pycnometers were then replaced in the desiccator and remained under vacuum until the next day. This proved to be sufficient for the removal of entrapped air.

When liquids are employed that possess densities greater or smaller than that of water, the density of the dispersed minerals is obtained by using the volume rather than the weight of the liquid displaced by the mineral material. In the metric system, the density thus obtained is numerically equal to the specific gravity.

The density of liquids also varies with temperature changes. Therefore, temperatures were recorded during the test so that the unit weight of the liquid could be determined with regard to one standard temperature. All specific gravity results were standardized to 20 deg C.
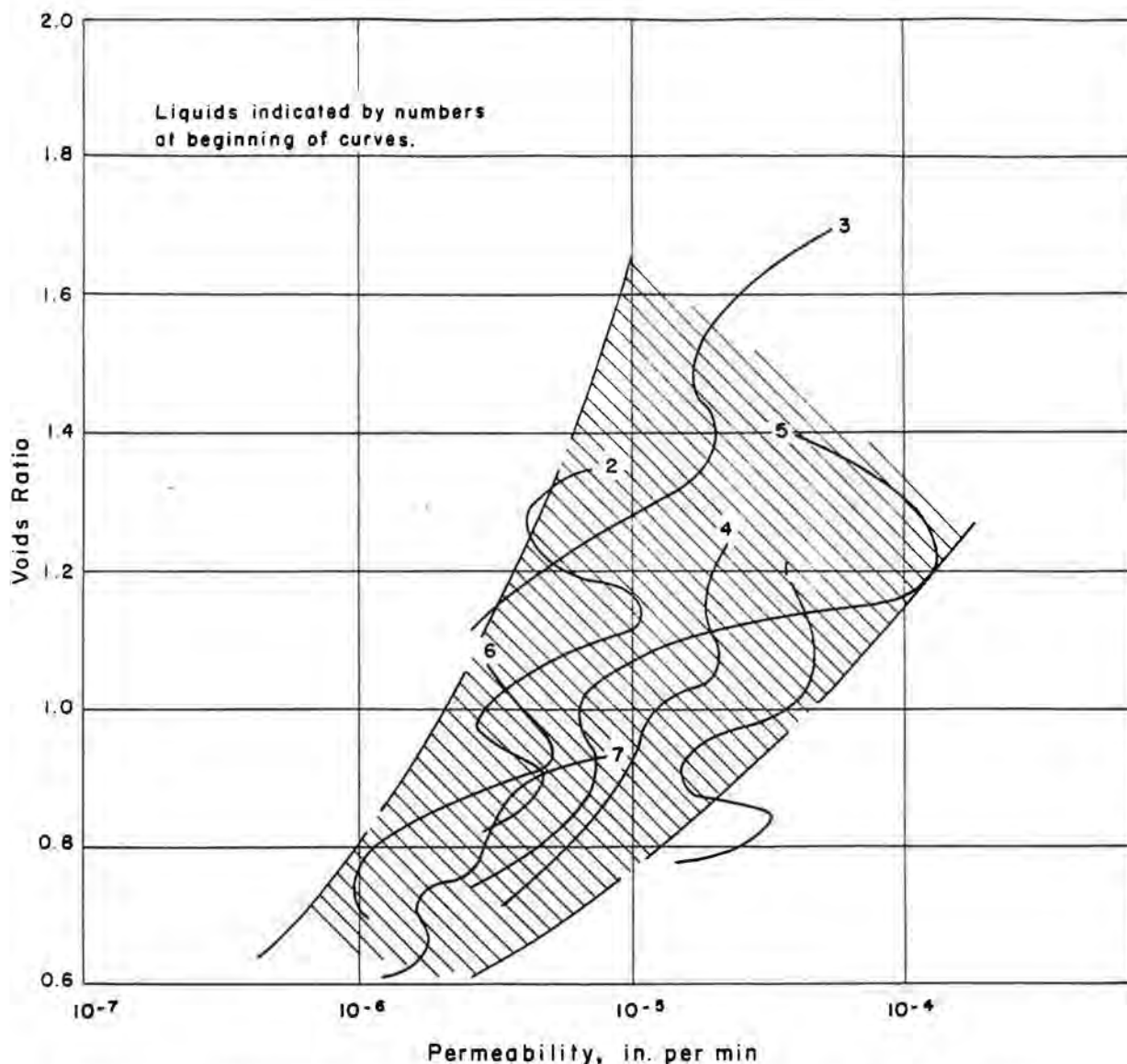
Figure 4. Permeability versus voids ratio using kaolinite with all liquids.

The test procedures with all liquids except water differed from the ASTM standard method (D854-52). The vapors of the various organic liquids had extremely annoying odors plus the fact that the inhaling of some of these vapors might prove harmful. Therefore, the test procedure used was as follows:

1. Weigh the pycnometer, clean and dry; (weighing device is a torsion balance; capacity 120 Gms.; $\pm$.01 Gms.)

2. Fill the pycnometer with liquid and place in desiccator with a vacuum of 28 psi applied to it to remove the dissolved gases the liquid may be holding. One hour seemed to be sufficient to remove these gases. The pycnometer was then filled to the mark with the liquid and the combined weight determined.

3. The pycnometer was then emptied and the little liquid remaining was evaporated by heating.

4. After the pycnometer was dry, it was allowed to cool.

5. The clay sample was placed in the pycnometer and the combined weight determined.

TABLE 3

RESULTS OF THE SPECIFIC GRAVITY TESTS

Liquid Soil	Water	Aniline	Nitro-Benzene	Methyl Alcohol	Ethyl Alcohol	Butyl Alcohol	Propyl Alcohol	Decolin
Kaolinite	2.560	2.481	2.577	2.585	2.569	2.628	2.588	2.530
White Clay	2.324	2.170	2.230	2.289	2.244	2.247	2.228	2.191
Bentonite	2.394	2.247	2.261	2.360	2.359	2.298	2.332	2.167

6. The liquid was then added; subsequently, the entrapped air was removed as previously explained, and the weight of the combined mixture taken.

The time interval that the liquid spent in the desiccator aided it to adjust itself to room temperature. The temperature of the main supply of the liquid, of the liquid in the pycnometer, and the room were within one degree of each other at all times, and did not vary more than one degree during a test run.

The results of the specific gravity tests are given in Table 3.
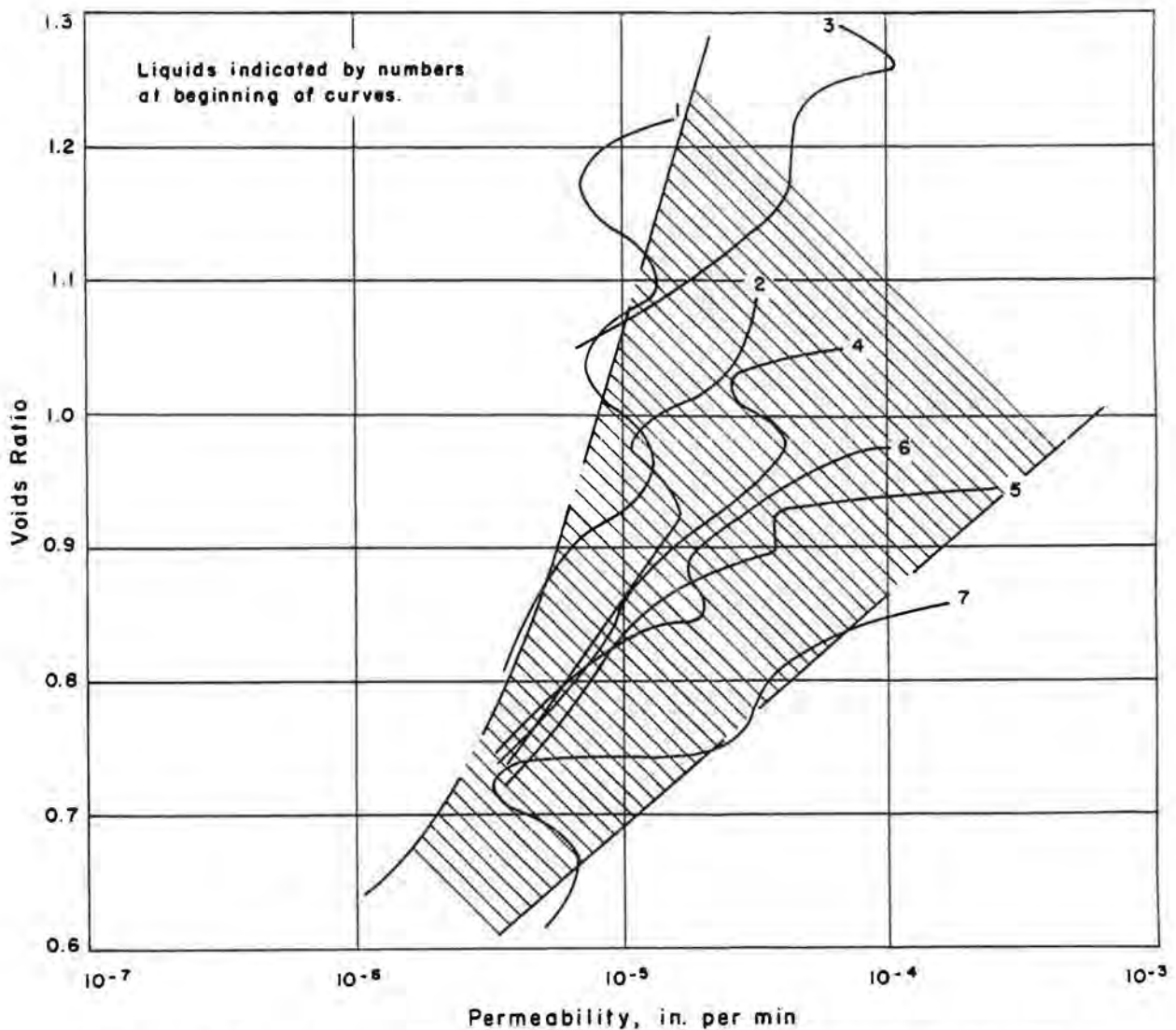
Figure 5. Permeability versus voids ratio with White Clay and all liquids.

Permeability for Curve I Only
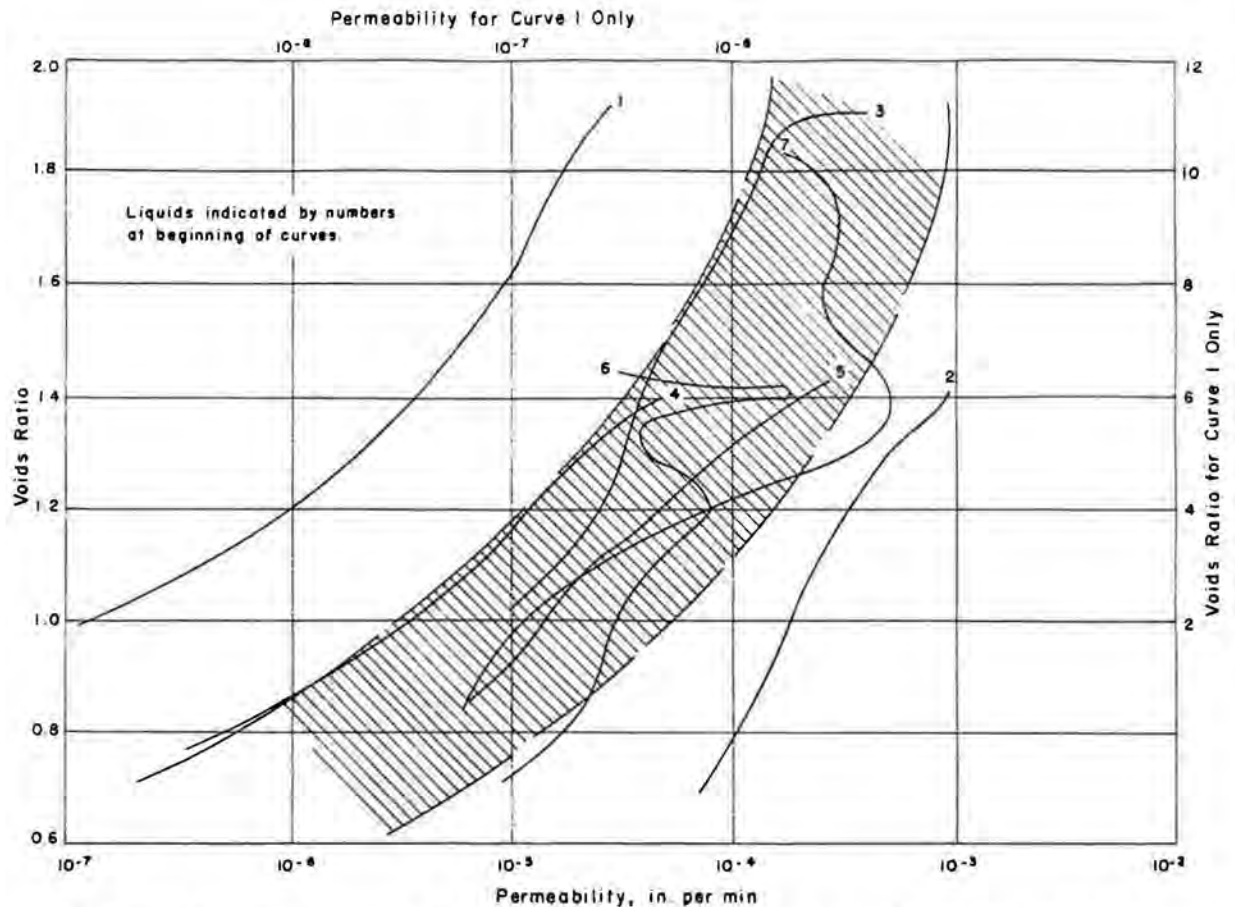
Figure 6. Permeability versus voids ratio using bentonite with all liquids.

3. **Atterberg Limits Tests.** The Atterberg tests determine the moisture content at the upper and lower limits of the moisture range within which soils exhibit plastic properties. The tests for the liquid and plastic limits are widely used to identify soils and to give an indication of certain properties, such as plasticity, cohesiveness, and bonding characteristics. Also, all soils have the same values of shear strength at their particular liquid limits. This is true because the liquid limit is really defined on a constant strength basis, and represents the moisture content at which all clays and organic soils have the same shear strength.

The Atterberg limits provide a good basis for positively identifying clay soils and differentiating them from silts. In clays, plasticity is the primary factor not found in silts.

The inherent characteristics of clays are plasticity, high affinity for water and other polar liquids, and base exchange capacity. Clays also are sticky, smooth or slippery, and have swelling and shrinking capacities.

The liquid limit is the point where soil passes from the liquid state to the plastic state. The plastic limit is the point where a soil is about to change from the plastic state to a solid state or vice versa. The flow index is the rate at which a soil changes from the plastic state to the liquid state. The toughness index is the rate at which the soil moves through the plastic index range due to moisture content change. The respective values obtained in this investigation are shown in Table 4.

The test procedures employed in the case of the various liquids were similar to the ASTM standards (D423-54T and D424-54T) but modifications of the laboratory equipment had to be made.

The soil in the liquid limit dish is supposed to flow into the groove cut in the soil due to the shocks administered to the soil sample (14). The White Clay slipped along the surface of the dish rather than flowing independent of the dish. Therefore, grooves

were cut into the brass dish, perpendicular to the direction of sliding. It was hoped that these grooves would provide a gripping surface for the soil. The grooves did not affect the liquid values of the kaolinite samples but did aid in obtaining better experimental data for the White Clay. Occasionally, the White Clay would slip along the spherical surface of the dish, thus losing the advantage of the grooves. Accordingly, the results of the Atterberg limits using White Clay with all the organic liquids were erratic and must be interpreted with care.

The temperature used to dry the soil samples was 110 deg C. This proved sufficient in all cases even though the boiling point of some of the liquids was well above this figure.

RESULTS

Consolidation Tests

Consolidation tests were run with the three clays and the seven liquids. The compression and expansion indices were obtained from the slopes of the log pressure versus voids ratio curves. Seven curves for each of the three soils are plotted on four graphs (Figs. 7, 8, 9, and 10); the compression and expansion indices are given in Table 5. The data in this table show that the respective indices for the clays with non-expanding lattices (kaolinite and White Clay) vary with the dipole moment. For the kaolinite, the larger the dipole moment of the liquid used, the larger is the slope of the compression curve (compression index). For the White Clay, however, the larger is the dipole moment of the liquid used, the smaller is the slope of the compression curve. This is in

TABLE 4

ATTERBERG LIMITS OF SOILS USED [a]

Soil	Liquid Limit	Plastic Limit	Plastic Index	Flow Index	Toughness Index
1-A	41.1	29.7	11.4	10.0	1.14
1-B	50.2	38.3	11.9	3.9	3.05
1-C	490.0	46.6	443.4	107.0	4.14
2-A	47.0			16.5	
2-B					
2-C					
3-A	67.5			17.0	
3-B					
3-C					
4-A	40.0	33.9	6.1	15.0	4.06
4-B	41.6			7.6	
4-C					
5-A	41.75	34.6	7.2	9.3	0.77
5-B	39.20			7.0	
5-C					
6-A	35.50	21.5	14.0	8.0	1.75
6-B	38.2			4.6	
6-C					
7-A	40.0	25.7	14.3	10.0	1.43
7-B	38.2			4.8	
7-C					

[a] Missing values could not be gotten due to soil structure.
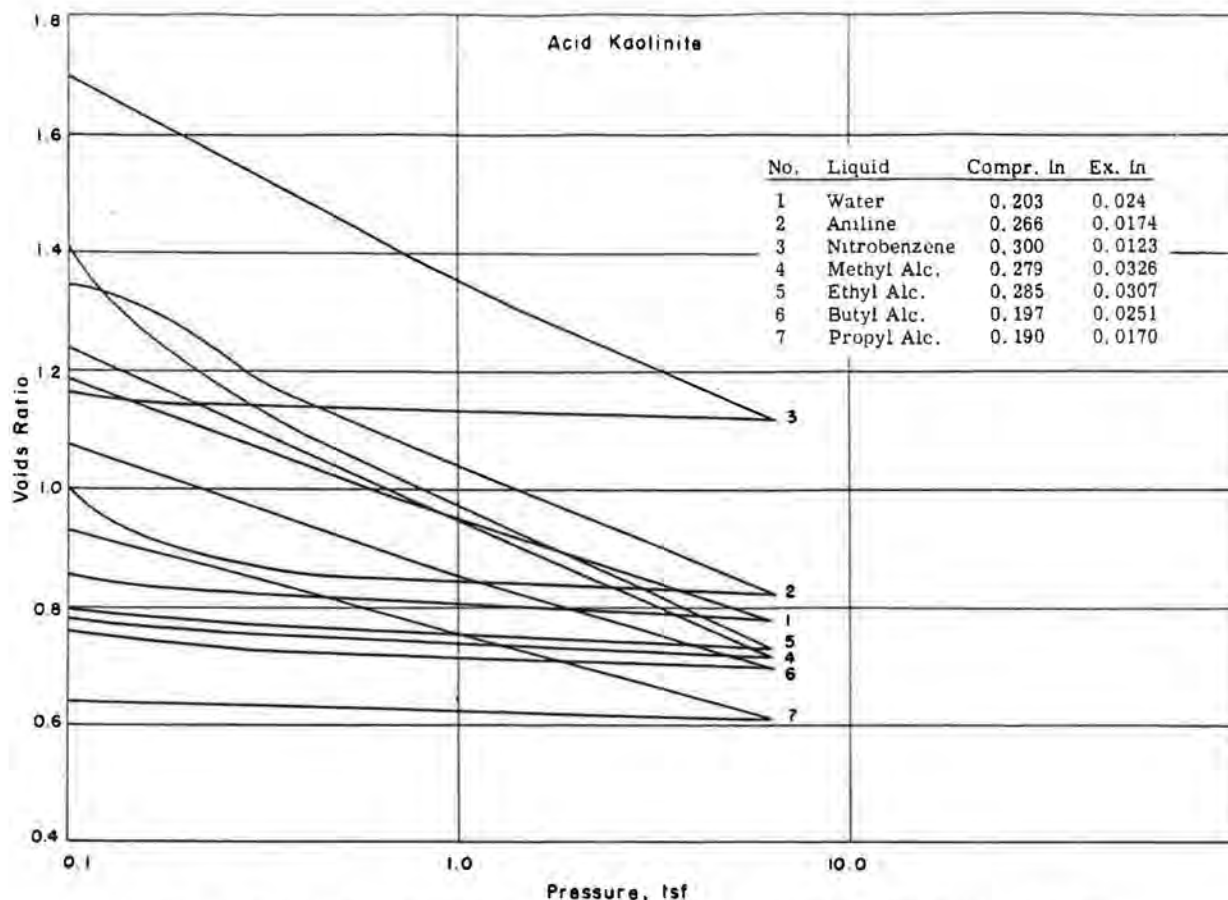
Figure 7. Pressure versus voids ratio for kaolinite with all liquids.

line with previous observations on absorption of organic liquids on lateritic clays that have SiO_2/R_2O_3 ratios smaller than two.

The liquids aniline and water are two exceptions common to both soils. It is possible that the aniline engaged in base exchange with the two non-expanding soils causing the formation of anilinium soils.

Water is the other exception to the observation. Water is one of the most common liquids, and yet, very little is really known about it. Its oddities are apparent but few are completely explainable. Methyl alcohol is another exception in the case of the White Clay. This liquid, having a molecular structure closely resembling water, acts similar to water on occasions.

TABLE 5

EXPERIMENTAL RESULTS TABULATED AGAINST THE DIPOLE MOMENT

Dipole Moment	Liquid	Kaolinite			White Clay			Bentonite		
		Compr. Index	Expan. Index	Sp. Gr.	Compr. Index	Expan. Index	Sp. Gr.	Compr. Index	Expan. Index	Sp. Gr.
3.89	Nitrobenzene	0.300	0.0125	2.577	0.195	0.0111	2.230	0.660	0.0216	2.261
1.8	Water	0.203	0.0240	2.560	0.246	0.0025	2.324	4.480	1.8320	2.394
1.69	Ethyl Alc.	0.285	0.0307	2.569	0.154	0.0072	2.244	0.326	0.0286	2.359
1.68	Methyl Alc.	0.279	0.0326	2.585	0.218	0.0115	2.289	0.398	0.0390	2.360
1.67	Butyl Alc.	0.197	0.0251	2.628	0.172	0.0083	2.247	0.534	0.0194	2.298
1.65	Propyl Alc.	0.190	0.0170	2.588	0.182	0.0106	2.228	0.614	0.0148	2.332
1.55	Aniline	0.266	0.0174	2.481	0.226	0.0028	2.170	0.610	0.0296	2.247

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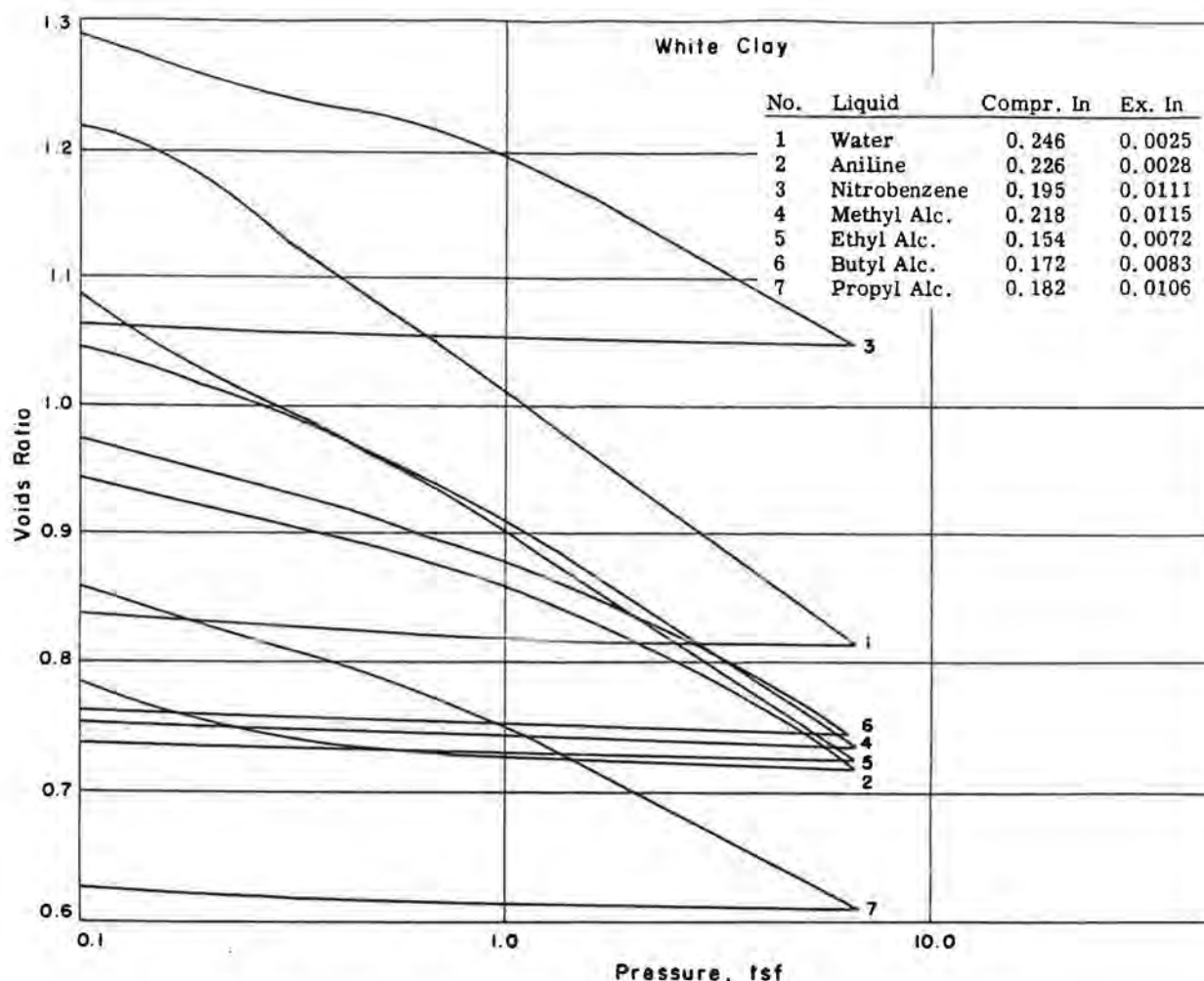
Figure 8. Pressure versus voids ratio for White Clay with all liquids.

No.	Liquid	Compr. In	Ex. In
1	Water	0.246	0.0025
2	Aniline	0.226	0.0028
3	Nitrobenzene	0.195	0.0111
4	Methyl Alc.	0.218	0.0115
5	Ethyl Alc.	0.154	0.0072
6	Butyl Alc.	0.172	0.0083
7	Propyl Alc.	0.182	0.0106

At this point, it should be mentioned that the molecular size and structure of the liquid in addition to the dipole moment influences the rate of consolidation and, therefore, the compression index. If the alcohols and water are considered as a separate group, better correlation of the data for the non-expanding clays is obtained. Nitrobenzene, having an exceptionally large dipole moment and exposed oxygen atoms, should be considered individually.

From the previous definition, the dipole moment can be seen to be a localized force couple within the molecule itself. The particles of a non-expanding clay do not absorb liquids within the lattice as an expanding clay will.

Montmorillonite clay, which possesses an expanding lattice, is affected by the dipole moment to a lesser extent than the clays with a non-expanding lattice. Rather, the dielectric constant, which is an integral function of the dipole moment and molecular structure, seems to have a more dominating influence on this type of clay mineral (Table 6).

To explain the effect of the dielectric constant, an example will here be given. The dielectric constant of liquid water at room temperature is approximately 80. This means that two opposite electrical charges in water will attract each other with a force that is $\frac{1}{80}$ as strong as in a vacuum. With this great reduction of the attraction forces, the inherent kinetic energy of the exchange ions is sufficient to overcome the attraction forces and cause an ionic atmosphere to be formed around the clay particles and between the expanding layers. Clays with expanding lattices possess high base exchange capacities or a high surface concentration of adsorbed ions. The higher the dielectric constant
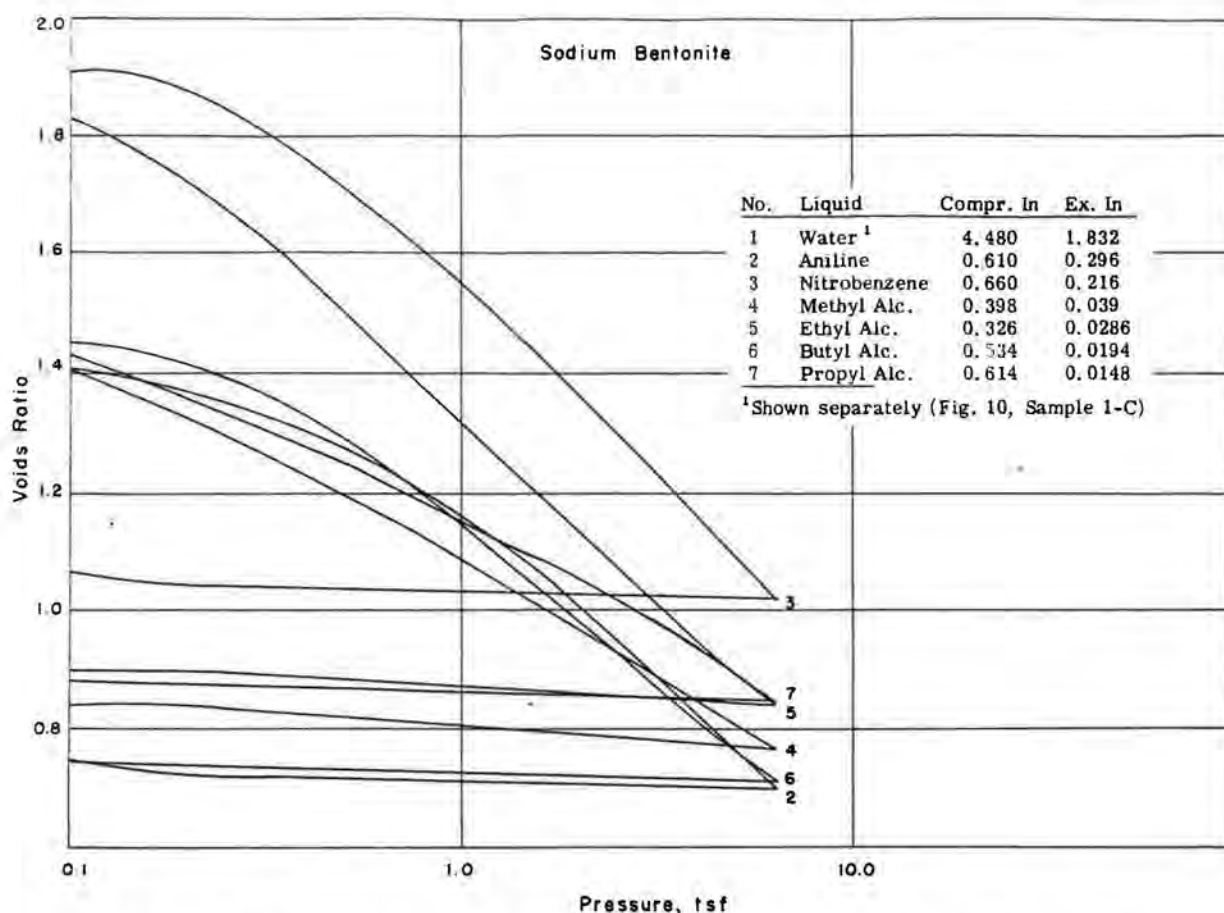
Figure 9. Pressure versus voids ratio for bentonite with all liquids.

Within the figure:

Sodium Bentonite

No.	Liquid	Compr. In	Ex. In
1	Water [1]	4.480	1.832
2	Aniline	0.610	0.296
3	Nitrobenzene	0.660	0.216
4	Methyl Alc.	0.398	0.039
5	Ethyl Alc.	0.326	0.0286
6	Butyl Alc.	0.534	0.0194
7	Propyl Alc.	0.614	0.0148

[1] Shown separately (Fig. 10, Sample 1-C)

Voids Ratio (vertical axis): 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0

Pressure, tsf (horizontal axis): 0.1, 1.0, 10.0

of the liquid, the more exchangeable ions will enter the liquid resulting in a swarm of positive ions surrounding negatively charged clay particles. As Winterkorn has shown in 1932, the swelling of such systems is directly proportional to the dielectric constant of liquids having molecules of similar architecture. This is exemplified by the water-alcohol series with montmorillonite. However, when lower dielectric constants are accompanied by larger molecular size (propanol and butanol), deviations from the proportionality occur. As the dielectric constant gets smaller, the ion concentration and the distance over which the electric field of the particles acts is reduced. Therefore,

TABLE 6

EXPERIMENTAL RESULTS TABULATED AGAINST THE DIELECTRIC CONSTANT

Dielectric Constant	Liquid	Kaolinite			White Clay			Bentonite		
		Compr. Index	Expan. Index	Sp. Gr.	Compr. Index	Expan. Index	Sp. Gr.	Compr. Index	Expan. Index	Sp. Gr.
81.07	Water	0.203	0.0240	2.560	0.246	0.0025	2.324	4.480	1.8320	2.394
36.1	Nitrobenzene	0.300	0.0125	2.577	0.195	0.0111	2.230	0.660	0.0216	2.261
33.1	Methyl Alc.	0.279	0.0326	2.585	0.218	0.0115	2.289	0.398	0.0390	2.360
25.8	Ethyl Alc.	0.285	0.0307	2.569	0.154	0.0072	2.244	0.326	0.0286	2.359
22.2	Propyl Alc.	0.190	0.0170	2.588	0.182	0.0106	2.228	0.614	0.0148	2.332
7.8	Butyl Alc.	0.197	0.0251	2.628	0.172	0.0083	2.247	0.534	0.0194	2.298
7.25	Aniline	0.266	0.0174	2.481	0.226	0.0028	2.170	0.610	0.0296	2.247
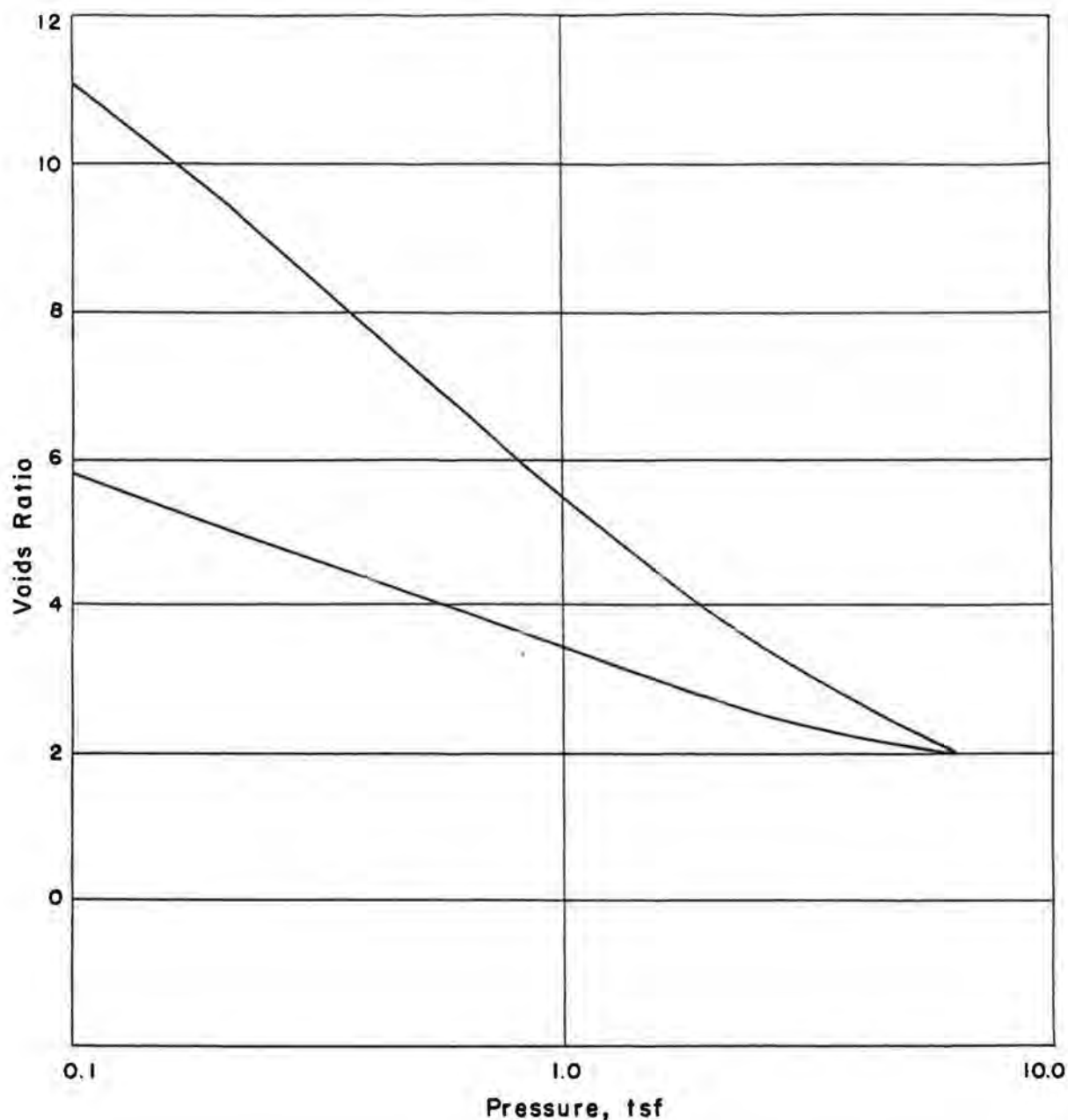
Figure 10.

the clay flakes can be forced closer together, permitting the size of the liquid molecules to influence the extent to which the clay flakes can be compressed. Flocculation phenomena may further complicate the picture.

Again, the results obtained with the aniline are of a different character, first because of the possible occurrence of base exchange phenomena, and second because of the specific polar character of the -NH₂ group.

The expansion indices of the various soil-liquid mixtures are influenced by factors similar to those that affect the compression indices. The major factors that have a pronounced affect on the expansion properties of a soil-liquid mixture are (a) the dipole moment, (b) the dielectric constant, (c) the effect of the sorbed liquid on the elastic rebound properties of the soil flakes, and (d) the size and structure of the liquid molecules. Of course, the four factors mentioned are not the only ones affecting the expansion. The above factors will vary with each liquid and with each soil and, therefore, it is difficult to state exactly what part each factor will play in influencing soil expansion.

Therefore, the correlation between the expansion indices and the dipole moment for the non-expanding lattice clays, and the dielectric constant for the expanding lattice clays are not as apparent as for the compression indices.

One of the factors mentioned above seems to affect particularly the rate of secondary compression. That is, the size of the liquid molecule and also another factor not mentioned previously, the viscosity of the liquid, appears to have an effect on the amount and rate of secondary consolidation. A number of other rheological factors are undoubtedly involved in this phenomenon; however, the type of apparatus used precluded a study of these factors in the present investigation.

Upon removing and drying the compressed soil-liquid samples from the consolidometer, it was noticed that occasionally the samples went through a color change (Table 7). It was also apparent that the structure of the bentonite samples was affected to different extents by the various liquids.

Specific Gravity

About 25 years ago E. W. Russell showed that the specific gravity of clay varied with the character of the liquid employed in the respective tests. Depending upon the electric surface structure of the clay minerals and the polar and structural characteristics of the liquids, the molecules of the latter can make structural arrangements on the solid-liquid interfaces which differ from the arrangements in the bulk of the liquid. Because of this, the adsorbed layers may have densities either larger or smaller than that of the bulk liquid. Since the latter density is used for calculation of the volume displaced by the clay particles, the specific gravity of the clays will be calculated either too large or too small. Thus the specific gravities determined for different clays using different liquids can serve as indicators of the degree of interaction between the mineral surfaces and the liquids involved. For this reason the specific gravities of the three clays investigated were determined in each of the liquids used in the consolidation study. The results are given in Table 8. From the data on the specific gravity of the clays using various liquids, it is apparent that the dipole moment has a noticeable effect on the variation of the specific gravity of the non-expanding clays and the dielectric constant has a noticeable effect on the variation of the specific gravity of the expanding clays. However, the size and structure of the liquid molecule is seen also to have a major effect on the specific gravity (Table 8). If water and the alcohols are listed in order of their molecular weights, it is apparent that the larger is the molecular weight, the larger is the specific gravity for the kaolinite, but the specific gravity decreases with increasing molecular weight of

TABLE 7

COLORS AND VISUAL STRUCTURE OF DRIED CONSOLIDATED SOIL

Soils	Liquids						
	Water	Aniline	Nitro-benzene	Methyl Alcohol	Ethyl Alcohol	Butyl Alcohol	Propyl Alcohol
Kaolinite	White (crumbled) Fine [a]	Light Violet Fine	Beige Fine	White (crumbled) Fine	White Fine	White Fine	White Fine
White Clay	Orange Yellow Fine	Dark Brown Fine	Brown Fine	Orange Fine	Beige Fine	Green Orange Fine	Brown Orange Fine
Bentonite	Green Very Fine	Dark Brown Coarse	Yellow Green Coarse	Green Fine	Yellow Medium	Green Coarse	Pale Yellow Coarse

[a] Indicates visual soil particle size.

TABLE 8
SPECIFIC GRAVITY TABULATED AGAINST MOLECULAR WEIGHT

Molecular Weights	Liquid	Kaolinite	White Clay	Bentonite
123.11	Nitrobenzene	2.577	2.230	2.261
93.12	Aniline	2.481	2.170	2.247
74.12	Butyl Alc.	2.628	2.247	2.298
60.09	Propyl Alc.	2.588	2.228	2.332
46.07	Ethyl Alc.	2.569	2.244	2.359
32.04	Methyl Alc.	2.585	2.289	2.360
18	Water	2.560	2.324	2.394

the liquid in the case of White Clay and the montmorillonite. It should be noticed that this same reversal took place previously in the case of the compression and expansion indices.

Nitrobenzene and aniline have a different molecular structure than the previously mentioned liquids and, therefore, should be considered separately. The nitrobenzene gives greater specific gravities than the aniline indicating a different type of reaction of the $-NO_2$ group as compared with that of the $-NH_2$ group on the benzene ring. In the case of the aniline there is probably an additional effect due to the formation of anilinium clays.

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Mechanism of Moisture Equilibrium and Migration in Soils

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Introductory Remarks by the Chairman

In dealing with phenomena of marked complexity, the temptation is great and ever present either to give up on theory and trust only observational evidence or to distrust the evidence of our senses and become armchair theorists. It is difficult to hold to the middle course and to cultivate in equal measure both experiment and theory. We should be grateful to those that can do this, but too often their only reward seems to be that they serve as favorite targets to the extremists on both sides, the pure empiricists and the pure theorists. However, their path is that of the truly great and sincere explorer of the unknown. Dr. Derjaguin and Mrs. Melnikova are such intrepid explorers and we are grateful for their valuable contribution to this symposium. In this paper, the authors examine the physical causes underlying observed phenomena of moisture equilibrium and migration in soils. They point out and prove the importance of geometrical and structural characteristics of the soil pores and of the water films in natural soil systems, and by recognizing in the water films such cohesive properties as may logically be expected from knowledge of the properties of the water substance and its interaction with different types of surfaces, they arrive at very plausible pictures on how and why water moves in soil under various potentials.

● THE CONDITIONS of moisture equilibrium in soils and the causes leading to its disturbance and giving rise to moisture "flows" in soils are among the most interesting questions of soil science from both a theoretical and a practical standpoint. Constructors and road builders are well acquainted with the frequently unexpected local accumulations of moisture in the soil which result in pavement swelling, in the destruction of foundations, in settling, and in other sometimes disastrous phenomena.

Questions of moisture migration through soils have been the subject of numerous and diverse studies. Attempts have been made repeatedly to estimate quantitatively and to forecast the migration of moisture through the soil. However, most of these studies were based on phenomenological (for instance, hydrodynamic) treatment (1) which passes over elucidation of the physical picture and the mechanism of moisture equilibrium and migration in soils.

The physical causes underlying these phenomena were examined in an effort to find a geometrical characteristic of soils which would enable quantitative estimation of the flow of moisture in the soil. The use of a cylindrical capillary model for this purpose is fairly out of the question, as such models do not by any means correspond to the true structure of soils and therefore do not give positive results.

Under natural conditions, one of the characteristic features of the water-soil-air system, due to the dispersion of the solid phase, is the distribution of the moisture between the relatively large volumes of ordinary bulk liquid water and the thin aqueous films. The latter possess specific physical-chemical properties, including a reduced capacity for dissolving substances, elevated viscosity, anomalous freezing temperature, and presence of a disjoining pressure.

The disjoining pressure of thin liquid layers, a result of the action of molecular

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surface forces in the thin layer, was discovered more than 20 years ago (2). It manifests itself upon attempts to thin a layer of water bounded by two phase interfaces; say, two solid surfaces, or a solid surface and air (in the case of a wetting film). Such a thinning could be counteracted by the viscosity of the liquid, the influence of which increases as the film grows thinner in the same way as the resistance to flow of a liquid through a capillary tube grows with decreasing radius of the latter. However, the influence of viscosity can be excluded by stopping the thinning of the liquid layer; this makes it possible to study the forces needed to keep the attained layer thickness from changing. It was found that to secure such an equilibrium, characterized by invariability of the thickness of the liquid layer, a certain pressure, differing from the pressure in the bulk liquid phase of which the thin layer was formed, must be applied. This excess pressure, which is a function of the film thickness, was termed "disjoining" pressure.

The disjoining pressure equals the pressure, P, exerted (in addition to the "normal" hydrostatic pressure in the layer) by a liquid layer in a condition of equilibrium, on the bodies bounding it, tending to move them apart and thicken the liquid interlayer separating them.

Here is a thermodynamic equilibrium which is due to the action of surface forces depending on the layer thickness; that is, on the distance between the phase surfaces limiting it. The mechanical properties of thin liquid layers—viscosity, plasticity, etc. —have no direct relation to the existence or to the magnitude of the disjoining pressure.

An important question is that of the nature of the forces of disjoining pressure. Its most important and commonest component, almost always manifest in such liquids as water, which contain ions, are the forces of repulsion arising from the overlapping of the ionic atmospheres forming in the thin layers on its two phase interfaces. When the thin layer is enclosed between two surfaces of identical nature, they both bear a double ion layer of identical sign and structure. As the layer grows thinner the peripheral parts of the ionic layers begin to overlap, giving rise to forces of electrical repulsion. A method of calculating these forces was developed 20 years ago (3).

The disjoining pressure between two solid bodies (say, between two soil particles) can be expressed by the force with which the particles must be pressed against each other to maintain the existing equilibrium thickness of the liquid layer between them.

In the case of a thin wetting film bounded on one side by a gaseous phase, the disjoining pressure equals the drop between the hydrostatic pressure in the layer itself and the pressure in the bulk of the adjacent gaseous phase, taken with the opposite sign. Thus, in equilibrium the hydrostatic pressure of a thin wetting film of liquid is somewhat lower than the hydrostatic pressure in the neighboring points of the bulk of the gaseous phase adjacent to it. This is very important for the water-soil-air system.

The disjoining pressure balancing the jump of hydrostatic pressures is applied to the phase interface and not to the volume elements of the thin layer itself. The disjoining pressure permits explanation of the existence of an equilibrium between thin water films and contact-zone accumulations of water in the soil, under conditions of partial filling of the pores with water.

MOISTURE EQUILIBRIUM IN SOILS

When present in a quantity insufficient to fill all the pores, the water is distributed between the contact-zone necks and the water films connecting them, much as in model systems (Fig. 1). In accumulations of contact-zone moisture the pressure is lower than in the surrounding
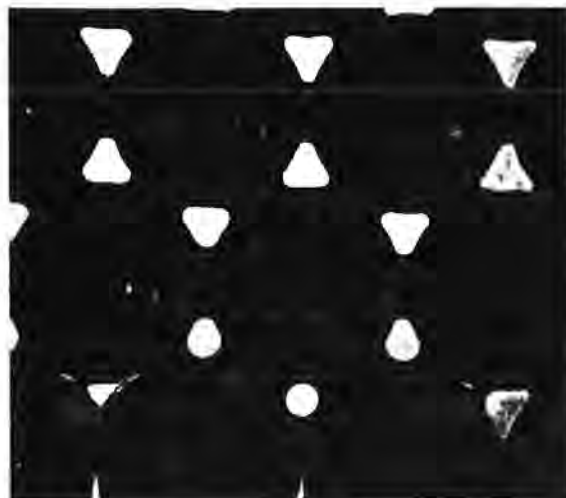
Figure 1. Photomicrograph of soil model at moment of drainage of water.

gaseous phase. According to the Laplace formula, this pressure drop due to capillary pressure is

$$\Delta P_r = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{1}$$

in which σ is the surface tension at the water-air interface, and r_1 and r_2 are the main curvature radii of the meniscus surface.

Nevertheless, the films do not drain under the neck menisci and can stay in equilibrium with them indefinitely. These two facts were proved experimentally (4).

Mechanical equilibrium between contact-zone accumulations and water films with identical gravitation field potentials can exist only if the pressure in the film moisture P_F (under the condition that it obeys Pascal's law) is the same as in the neck moisture P_M.

For this to be so, however, the pressure drops ΔP_M and ΔP_F on passing through the interface from the contact-zone moisture to the gas and from the film to the gas, must be equal; or

$$\Delta P_M = \Delta P_F \tag{2}$$

Inasmuch as the surface of the water film has an entirely different curvature (close to that of the wetted surface of a soil particle), mostly even of the opposite sign (convex), to satisfy Eq. 2 in the presence of an equilibrium film the pressure jump on its surface must differ from the Laplace jump, $\Delta P'_F$, by a certain value, P. Hence,

$$\Delta P_F = \Delta P'_F + P \tag{3}$$

in which

$$\Delta P'_F = - \sigma \left(\frac{1}{r'_1} + \frac{1}{r'_2}\right) \tag{4}$$

and r'_1 and r'_2 are the curvature radii (usually negative curvature) of the normal sections of the film surface, while P is precisely the "disjoining pressure" of the thin film $P(h)$. The relation between the disjoining pressure and the pressure jump on the surface of a thin film was indicated by Nerpin (5). From Eq. 3 it follows that:

$$P = P(h) = \Delta P_M - \Delta P'_F \tag{5}$$

Thus, knowing the curvature of the contact-zone meniscus and of the adjoining film (soil particle, $P(h)$ can be found and also h, the equilibrium thickness of the film. The thickness of the film as is adapts itself to the changing conditions.

In soil science the questions of the equilibrium and migration of moisture are often treated with the aid of the capillary potential or moisture content potential concept, Ψ, related to the concept of the chemical or the moisture potential. The relation between P, Ψ and μ can be examined for the part of the soil where the gaseous phase communicates with the atmosphere. Since in a state of equilibrium the hydrostatic pressure P_H, not only in the necks but also in the films, obeys the law of hydrostatic pressure, whereas in the gaseous phase it may be considered constant and equal to the atmospheric pressure, P_0,

$$P_H = P_0 - d g H$$

in which d is the density of the liquid, g is the acceleration due to gravity, and H is the height above the datum or "zero" level. But according to the definitions of Ψ, μ, and P,

$$\mu + g H = \text{Constant} = \mu_0$$

$$\Psi + d g H = \text{Constant} = \Psi_0 = 0$$

and

$$P = \Delta P_M - \Delta P'_F = d g M - \Delta P'_F$$

From these equations it follows that

$$P = - \Psi - \Delta P'_F = - \Psi - \sigma \left(\frac{1}{r'_1} + \frac{1}{r'_2}\right) \tag{6}$$

$$P = d(\mu_0 - \mu) - \sigma\left(\frac{1}{r'_1} - \frac{1}{r'_2}\right) \tag{7}$$

It can be seen that P differs from $-\Psi$ and $-d\mu$ by a value which depends little on the moisture, but depends on the dispersion of the ground particles. The mean value of P for soil particles may be considered in the first approximation to be

$$\bar{P} = -\Psi + \frac{2\sigma}{\bar{r}'} = -\Psi + \frac{2}{3}\sigma S \tag{8}$$

in which S is the specific surface of the soil particles with a mean radius r', related to unit volume.

The advantage of the $\bar{P}$ concept over the Ψ concept is that the former is single-valuedly related to h, the mean thickness of the water films.

For simplicity and convenience of examination of the conditions of equilibrium between neck and film moisture, the geometrical relations for schematized particles may be employed. This makes it possible to carry out calculations that can be compared with experimental data as a means of verification of theory.

Such experimentally verified calculations were carried out by Melnikova and Nerpin (6) for model systems of hexagonal packing of small uniform spheres. They showed that equilibrium existed between the film and the contact-zone moisture if

$$P = \frac{12\sigma}{d'}$$

that is, if the film developed a definite "positive" disjoining pressure (here σ is the surface tension and d' is the particle size).

The limit moisture content at which coexistence of contact-zone, moisture accumulations, and films, is possible corresponds to the moment when the neck menisci close up. The air gap of the pore thereupon becomes round in shape. The soil moisture potential corresponding to this moment has been called (5, 6, 7) the "critical" moisture potential $\bar{\Psi}_K$.

If the moisture potential of the system increases, when Ψ_K is reached the pores should fill up suddenly (5, 6) insofar as this is not impeded by entrapped air. But if the moisture potential decreases, a break in the continuity of the pore filling should take place in the parts of the system where Ψ_K is reached. This process can be seen on the photomicrograph of a model system (Fig. 1) taken at the moment of drainage of the water. Figure 1 also shows completely filled pores, triangular pores characteristic of sections where $\Psi < \Psi_K$, as well as round pores in which the neck menisci are still closed
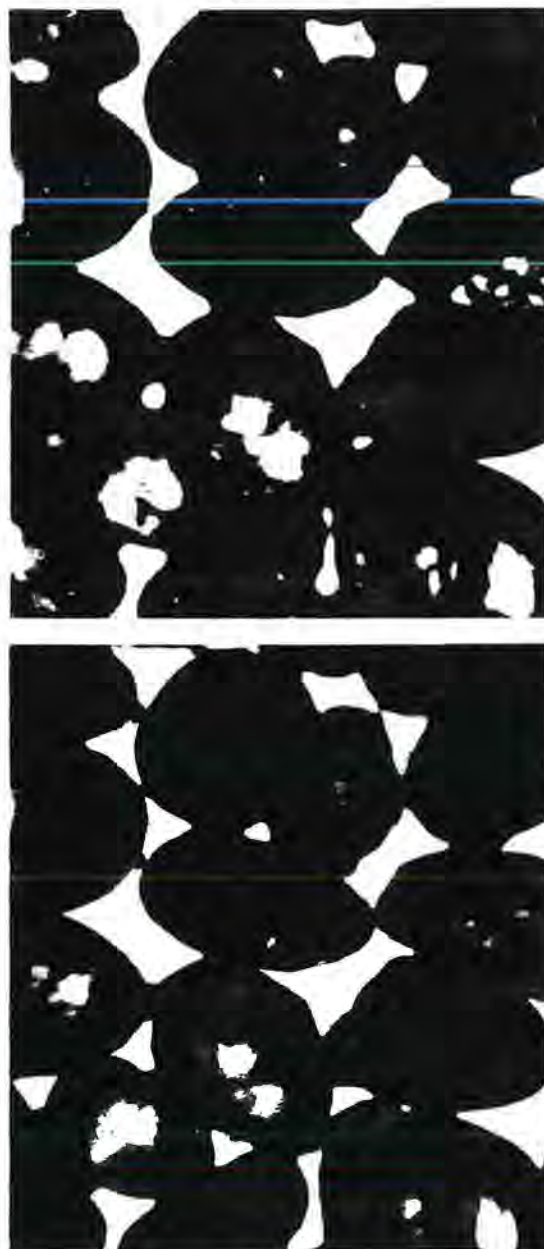
Figure 2. Photomicrographs of moisture distribution in sand after drainage of excess moisture.

($\Psi = \Psi_K$). A similar picture is observed in natural soils. Figure 2 shows photomicrographs of a sand layer with water draining from it. In the middle of the photograph three particles can be seen between which hang water necks bounding a small round pore. Its shape remains intact several hours after the main excess of moisture has drained off; then the gap suddenly acquires a triangular shape.

The critical moisture potential concept enables calculation of the capillary rise of the liquid through the dispersed medium; say of water through soil. This rise should cease at the height where the moisture content value reaches that corresponding to Ψ_K; that is,

$$h_c = - \Psi_K / g\,d \tag{9}$$

This dependency was verified experimentally and confirmed for model systems and sand (7).

The idea of the critical potential also enables estimation of the height of the water colume maintained in the bulk of a finely dispersed soil bedded on another soil of coarser mechanical composition. The height of the column of such "suspended" water can be determined by

$$h_S = - \frac{\Psi_1 - \Psi_2}{g\,d} \tag{10}$$

in which the subscripts 1 and 2 refer to the fine-pore and coarse-pore soils, respectively. Substituting h_c for Ψ_1 according to Eq. 9 gives

$$h_S = h_{c,1} - h_{c,2} \tag{11}$$

which holds well for model systems and sands (7).

MOISTURE MIGRATION IN SOILS

The moisture equilibrium in soils is disturbed, and the moisture goes into motion, when physical forces arise in the soil capable of making the water migrate. Such forces may be caused by the appearance of gradients of hydrostatic pressure, capillary pressure, disjoining pressure of aqueous films, chemical potential, and/or temperature.

Like the hydrostatic pressure gradient and gravity, mechanical forces are of predominant importance in water-saturated coarse soils. They cause water filtration, in many soils obeying the classical Darcy law. The Cozeny-Carman formula expresses the proportionality factor in this law through the viscosity and specific surface of the particles, making it possible to calculate the filtration flow:

$$Q = \frac{k}{\eta S^2}\,\delta^3\,\frac{\Delta P}{\Delta x} \tag{12}$$

Here Q is the bulk velocity of the flow per square centimeter of filtering layer cross-section, η is the viscosity of the liquid, S is the specific surface of the particles per cubic centimeter of soil, δ is the porosity, $\frac{\Delta P}{\Delta x}$ is the pressure gradient, and k is a numerical coefficient, usually about 1/5.

As has been shown (8), to obtain a correct idea of filtration and of the flow of moisture through soil in general, the outer specific surface of the particles, to which the moving water and air have access, should be introduced into the formula instead of the total specific surface of the soil, usually determined from the equilibrium adsorption, say, of nitrogen. The outer specific surface can be found by the method of rarified gas filtration (8, 9) or by the rate of capillary soaking (10).

The Cozeny-Carman formula is not applicable to clayey soils. The high specific surface of clays makes the aqueous interlayers within the zone of the radius of action of the surface forces very extensive. Therefore, in clayey soils the influence of the specific mechanical properties of thin aqueous films is particularly pronounced. This influence results in a reduced rate of filtration compared with that calculated by the Cozeny-Carman formula and in an initial gradient.

The elevated viscosity of thin water layers and the existence of an initial filtration gradient in them were proved experimentally (11) for the filtration of water through rigid-pore ceramic and charcoal filters with pores 10^{-5} cm and less in diameter. The role of the surface forces in this effect was proved by coating the pore walls of the ceramic filters with a monolayer of oleic acid. This increased the coefficient of filtration by approximately one order of magnitude.

The viscosity rise in thin layers may be attributed, but only partially (24), to "electroviscosity," which is the influence of the double ionic layers and their electrokinetic properties on the flow of the liquid through thin pores. The flow potential arising when the liquid flows through a porous system tends to cause an electroosmotic flow in a direction opposite to that of the initial liquid current. The resulting decrease in filtration rate will be considerable in gaps of the same order as the thickness of the ionic atmosphere; it will increase as the pore width decreases (for pores which are not too fine), approximately in inverse proportion to the square of the pore width. Reducing the thickness of the ionic atmosphere (by adding an electrolyte, for instance) decreases the "electroviscosity" effect and increases the rate of filtration.

In soils not completely saturated with moisture and containing contact-zone menisci which are separated, or rather connected, by thin wetting films, the hydrostatic pressure gradient is inevitably linked with the capillary potential gradients, the latter being related to the moisture content (per cubic centimeter of soil) gradients by the expression:

$$\text{grad } \Psi = \frac{d\Psi(W)}{dW} \text{ grad } W$$

in which $\Psi(W)$ is a function for which several methods of measurement have been developed.

Thus, to determine the moisture flow Q in this case, and therefore to determine the coefficient of moisture conductivity, it is necessary to establish the relation between Q and grad W, or -grad P.

In the general case this is a very complex problem, because when there is a moisture gradient the volume and the curvature of the contact-zone necks will be different in different parts of the soil, just like the disjoining pressure and the thickness of the films connecting the necks. The problem can be simplified, however, by examining the case where the films separating the menisci become so extensive that almost the entire drop of moisture potential and disjoining pressure occurs in them, and not in the contact-zone menisci, which for the most part affect only the moisture content. Under this assumption it can easily be proved that the bulk rate of flow of the liquid across unit perimeter of the wetting film amounts to $\frac{1}{3}\frac{h^3}{\eta}$ grad P, where η is the viscosity of the film moisture. At a low moisture content, when the number of contact-zone moisture accumulations is small, the total perimeter per unit area of soil cross-section will be $\frac{1}{2}$ S. Hence, the flow through the soil in the direction Z will be

$$Q = a S \frac{h^3}{\eta} \frac{\delta P}{\delta Z} \tag{13}$$

where a is a numerical coefficient. In the case where the thickness of the film is considerably smaller than that of the ionic atmospheres

$$Q = -3 a S \frac{A}{h} \frac{\delta h}{\delta Z} - 2 a S \frac{B}{\eta} \frac{\delta h}{\delta Z} \tag{13a}$$

where A and B are constants.

In the stationary flow examined by Hallaire (12), integration gives

$$3 a A \ln h + 2 a B h = \frac{\eta Q}{S} (Z - Z_0) \tag{14}$$

provided the volume of moisture in the contact-zone accumulations can be neglected, so that $h \cong \frac{W}{S}$.

If W is sufficiently small, it can be assumed approximately that $P = Ah^{-3}$ and instead of Eq. 14, Eq. 13 can be transformed to

$$\ln P = \frac{\eta Q}{a\,S\,A}\,(Z - Z_0)$$

which is close to the formula found empirically by Hallaire.

In the cases of moisture movement, the motive force (the pressure drop or gradient) was of a mechanical nature and, speaking of the drop in disjoining pressure, can even be determined mechanically through the hydrostatic pressure jump.

However, there are substantially different forces or factors capable of causing the migration of moisture through soils. These are:

1. Electric fields or potential gradients causing migration of liquids (electroosmosis).

2. Temperature gradients, which under certain conditions of moisture content may cause migration of the liquid at a rate proportional to the temperature gradient. The theory of this "thermoosmotic" slippage has been developed (13) and verified experimentally (14).

3. Solute concentration gradients; the slippage and the moisture migration (capillary osmosis) it causes were deduced theoretically and have been experimentally proved (15).

The common factor of the mechanism of moisture migration in all three cases is that the origination of the flow is connected with the appearance, in the thin liquid layers at the particle surfaces, of unbalanced tangential surface forces which cause a sort of slippage of the liquid along the surfaces of the soil particles. As a result, the liquid moves inside the pores as an integral whole and the entire velocity gradient is concentrated in a very thin layer adjacent to the wall where the surface forces are unbalanced.

When the liquid moves under the influence of mechanical factors, on the other hand, the particle surfaces only impede its movement and a characteristic Poiseuille velocity profile forms.

The foregoing analogy of the mechanism of moisture transfer makes it possible to speak of quasiosmotic transfer phenomena (21), the more so since the term "electroosmosis" has been used for a long time, "thermoosmosis" is a rather widely used term, and "capillary osmosis" seems quite rational.

In this connection the water transfer through a water-saturated soil obeys the same law in all cases of quasiosmotic transfer:

$$Q = \epsilon\,\underline{C}\,\frac{\Delta\Psi}{\Delta x} \tag{15}$$

where Ψ is one of the three factors previously mentioned; namely, the electric potential, the temperature, or the chemical potential of the solute. The influence of the pore geometry reflected in the coefficient ϵ is the same in all three cases. The difference between them is that the acting forces causing the slippage are different, which accounts for the different values of the proportionality factor in each case. But the moisture flow rate does not depend on the specific surface and does not fall off with decreasing pore size, as during filtration. Therefore, in finely dispersed soils the role of the three factors causing slippage may considerably exceed the influence of the mechanical forces determining the rate of filtration.

Electroosmosis is a widely known phenomenon. Attention is called to the fact that it is employed for drying clayey soils by introducing electrodes and applying a direct current; in clayey soils the water usually moves towards the negative pole. The electroosmotic effect is employed also to eliminate sticking of clayey soils to construction and transport machines. A short passage of current gives rise to electroosmotic phenomena in the aqueous film on the cathode, the film acting as a lubricant along which the soil slips off.

Capillary osmosis arises when the solute concentration near the solid surface—at a
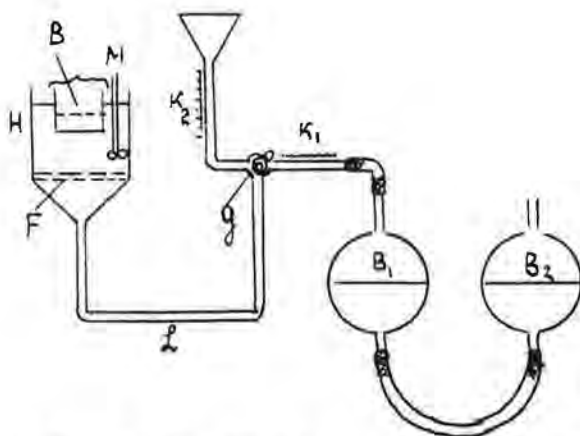
Figure 3. Apparatus for studying capillary osmosis.

Figure 4. Movement of meniscus in horizontal capillary tube during capillary osmosis.

distance of several molecular layers—differs from the concentration in the bulk of the liquid. Capillary osmosis is accompanied by a disturbance of the hydrostatic equilibrium under the influence of the chemical potential gradient or concentration gradients parallel to the solid surface. The result is slippage of a thin liquid layer along the solid wall at the boundary with the solid phase, this layer carrying the bulk phase along with it. The linear slippage velocity, q, depends on the structure of the mobile part of the adsorption layer and can be expressed by

$$q = \frac{1}{\eta} \underset{=}{C_0} \frac{\Delta \mu}{\Delta l} \xi \tag{16}$$

in which η is the viscosity, $\underset{=}{C_0}$ is the molar concentration of the solution, $\frac{\Delta \mu}{\Delta l}$ is the chemical potential gradient along the wall, and ξ is a constant characterizing the degree of diffuseness of the mobile part of the adsorption layer. (In order of value, ξ equals the square of its thickness.)

An experimental investigation of capillary osmosis was made with the apparatus shown in Figure 3. A concentration gradient was set up in a cylinder (H) with a porous membrane (F) by overturning vessel (B) containing the test solution and floating in the cylinder. Observations were made of the movement of the liquid meniscus in the capillary tube (K₂) the rate of which was measurable (4). The upper curve of Figure 4 refers to capillary osmosis in a solution of ethyl alcohol; the lower, to a solution of acetic acid. The difference in direction of motion of the liquids, in conformance with theory, is due to the different nature of adsorption on the glass: positive in the case of alcohol, negative in the case of acetic acid.

Figure 5. Movement, due to thermoosmosis, of air bubble in fused capillary tube filled with water.

In clayey soils the rate of osmotic filtration, depending on the concentration gradient, may exceed the rate of gravitational filtration manyfold, and the head due to quasi-osmotic pressure may rise as high as 20 meters (16).

The thermoosmotic effect caused by the different heat contents in the liquid layer adjacent to the solid phase and in the bulk phase of the liquid, results in a flow in the direction of rising temperatures. The thermoosmotic flux, Q, depends on the nature of the liquid and the pore walls and is proportional to the total pore section area, m, the temperature gradient, $\frac{\Delta T}{\Delta l}$, and the thermoosmotic coefficient, β, as follows:

$$Q = \beta \, m \, \frac{\Delta T}{\Delta l} \tag{17}$$

Experiments in sealed glass capillary tubes (14) revealed a picture of slow steady movement of the liquid towards the heated end of the capillary (Fig. 5). Under relatively high temperature gradients (about 2 or 3 C per cm) the rate of migration of the meniscus did not exceed 20 microns per hour.

Under natural conditions thermoosmosis in its pure form can be observed in soils in two cases; namely, with very low moisture contents and upon complete fill-up of the pores (that is, in the absence of contact-zone moisture accumulations). However, the conditions necessary for a perceptible thermoosmotic effect to appear in soils occur comparatively rarely: at low moisture contents the flow is so insignificant that it little affects the moisture content of the soil, whereas continuous complete fill-up of the pores can last (in the absence of connections with ground waters) only for a short time. A characteristic feature of soils under natural conditions is distribution of the moisture between the contact-zone accumulations and the films. But under the influence of the temperature gradient the presence of a water-air interface results in another mechanism of moisture migration, causing its transfer towards decreasing temperatures.

The migration of liquid moisture in soils from higher to lower temperatures has long been known to soil scientists, who have noticed that each soil has its own optimal moisture content for water transfer. In very moist and very dry soils the transfer is low. Various hypotheses have been advanced to account for the thermomigration of liquid moisture.

As far back as 1915 Bouyoucos (17) published a paper on the influence of the temperature on the movement of water vapor and capillary moisture, in which he attributed the movement of liquid moisture to changes in the soil moisture tension (the suction force of the soil) depending on the temperature. Smith (18), as well as Maclean and Gwatkin (19), held that water transfer was caused by the convection of water vapor; later Smith (20) gave up this point of view and attributed the transfer of liquid moisture to the formation of condensate in capillary pores. Not long ago Winterkorn (21) developed a theory of film flow of liquid moisture from the hot to the cold end, along the inner surface of a pore system, as a result of the change in the adsorption energy of the soil particles as a function of temperature change. Winterkorn also observed the appearance of a difference of electrical potentials in the soil in the presence of a temperature gradient and suggested that the thermo-migration of moisture might be a specific case of electroosmosis.

It is believed that even in the presence of a thermoelectromotive force the effect cannot be calculated only on the basis of electroosmosis equations, but requires strict application of the general principles of the physical kinetics and thermodynamics of non-equilibrium processes. This belief is shared by Winterkorn (21). Owing to the complexity of these calculations, they are not detailed here.

Gurr, Marshall and Hötten (22), who studied the thermomigration of moisture and dissolved salts through soil in fused cylinders, came to the conclusion that the water evaporating from the warmer soil as steam moves towards the colder layers, where it condenses, raising the moisture content of the soil. As a result of the moisture gradient thus set up, the water flows back, now in the liquid form, carrying dissolved salts with it.

In carrying out laboratory experiments in closed soil columns all the facts described in the literature were encountered. In all cases where there was a water-air
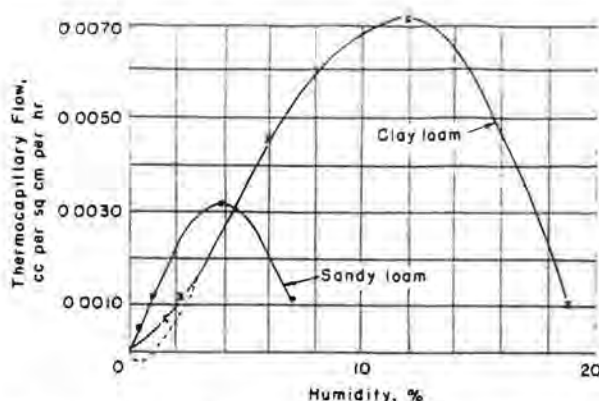
Figure 6. Thermo-capillary transfer of water in soils.

TABLE 1

ACCUMULATION OF WATER[a] AT COLD END[b] OF SOIL COLUMN, DEPENDING ON MECHANICAL COMPOSITION AND MOISTURE CONTENT OF THE SOIL

Moisture Condition of Soil	Heavy Loamy Soil		Sandy Loamy Soil	
	Calc.[c]	Obs.	Calc.[c]	Obs.
Air-dry	0.0017	0.0011	0.0011	0.0004
Maximum hygroscopic	0.0017	0.0045	-	-
Withering moisture content	0.0017	0.0071	0.0011	0.0031
Moisture content of plant growth retardation	0.0017	0.0100	0.0011	-

[a] In cubic centimeter per square centimeter per hour.
[b] Temperature gradient 2.5 C per cm.
[c] Calculated by Fick's diffusion law.

interface in the pores, the water migrated in the "cold" direction. The amount of water that migrated depended on the specific surface, $\underline{S}$, (mechanical composition) of the soil and on the initial moisture content.

It was greater in heavy soil, and increased from a moisture content equal to the maximum hygroscopic to the moisture content of plant growth retardation, after which it again began to drop (Fig. 6).

The accumulation of moisture at the cold end of the column caused it to flow backwards to the hot end because of the resulting moisture gradient.

The data obtained led to the conclusion that the migration of liquid water under the influence of a temperature gradient should be of much greater importance in natural conditions than is usually thought. Therefore, field experiments were undertaken. Thermo-migration of moisture may be expected in the winter season, when considerable temperature gradients often arise in the soil between the deeper, moister and warmer layers of the soil and the rapidly cooling surface. Under such conditions there should be a flow of liquid moisture (greater with higher temperature gradient) towards the surface of the soil. Observations of the winter conditions of soil moisture content by Rozhanskaya and Godun (22) actually revealed a considerable upflow of moisture in winter months. An analysis of the results of laboratory experiments and field observations showed that the upflow of moisture is many times higher than the vapor transfer possible under experimental conditions by diffusion, with allowance for the saturating vapor pressure gradient (Table 1).

The thermo-transfer of moisture under conditions of incomplete saturation of the soil is believed to be caused by the surface tension gradient, as pointed out much earlier by Lebedev (23); such a moisture transfer can be conveniently called thermo-capillary transfer. The temperature gradient gives rise to a surface tension gradient in the menisci, under the action of which the thermo-capillary migration of liquid water begins in the direction of higher surface tension; that is, in the direction of decreasing temperatures. In the case of capillary migration the unbalanced resultant due to surface tension and the temperature gradient, is applied to the outer surface of the film. The shear stress τ arising therefrom is transmitted without dissipation to all the layers of the wetting film as far as the surface of the solid wall, where it is balanced by the resistance of the latter. The stress $\tau = \dfrac{\delta \sigma}{\delta l}$, constant within the film, causes a current with a constant velocity gradient:

$$\frac{\delta v}{\delta y} = \tau / \eta$$

The profile of this flow is represented in Figure 7. The surface tension resultant is directed toward the cold end and has the value

$$\tau = \frac{d\sigma}{dT} \frac{dT}{dl}$$
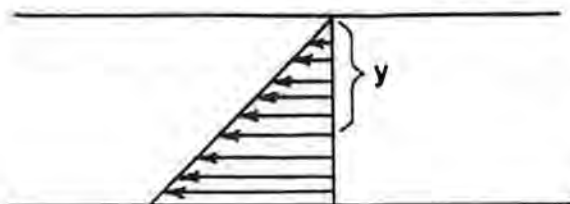
Figure 7. Velocity profile in liquid film during thermo-capillary transfer.

In accordance with the shape of the velocity profile, the thermo-capillary flow may be expressed by

$$Q = \frac{1}{2} \frac{\delta v}{\delta y} h^2 = \frac{1}{2\eta} \frac{\delta \sigma}{\delta l} h^2 = \frac{1}{2\eta} \frac{d\sigma}{dT} \frac{dT}{dl} h^2 \qquad (18)$$

in which Q is the discharge of liquid per unit perimeter and h is the film thickness.

It can easily be shown that the average linear velocity of the water carried by the thermo-capillary flow towards the "cold" end is proportional to the average thickness of the films, and therefore to the moisture content in the soil, and is inversely proportional to their specific surface.

Calculation shows that the resultant of two simultaneous moisture flows in opposite directions—the thermoosmotic and the thermo-capillary—may be expressed by

$$Q = W(\alpha - \gamma \frac{W}{S}) \frac{dT}{dl} \qquad (19)$$

in which $\alpha(= \frac{2}{3}\beta)$ and $\gamma(= \frac{1}{3}\eta\frac{d\sigma}{dT})$ are constants, W is the moisture content, and S is the specific surface (outer).

Calculation of the flow which should move towards the soil surface by substituting the field data of Rozhanskaya and Godun in Eq. 19 gave a value very close to that actually measured in the field, as follows:

Item	Flow (mm)	
	Actual	Calculated
Total flow between Dec. 16 and Feb. 25	112	102
Daily flow, December	2.3	2.0
Daily flow, January	1.5	1.3
Daily flow, February	1.1	0.8

Thus, the film movement of moisture is capable of causing the migration of considerable quantities of water through the soil. This may occur even in the absence of a temperature gradient, if there is only a moisture content gradient, due to the disjoining pressure in films of unequal thickness. If the disjoining pressure gradient is not balanced by the system of normal pressures in the adjoining gaseous phase, a flow will spring up spontaneously in the thin film without the action of outer forces except those of interaction with the solid phase. The liquid will flow in the direction of thinner layers if $\frac{dP}{dh} < 0$, and in the direction of thicker layers if $\frac{dP}{dh} > 0$. In the first case the disjoining pressure acts as a stabilizer; in the second it makes the film unstable, resulting in a tendency for it to divide up into thinner and thicker sections.

If the equilibrium moisture distribution in the soil is disturbed (for instance, due to the appearance of a moisture gradient), the water begins to migrate at rate which, with open contact-zone accumulation menisci, depends on the thickness and the viscosity of the wetting films. In such a case, as experimental data have shown, vapor diffusion always plays but a minor role in the moisture transfer.

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Movement and Equilibrium of Water in Soil Systems as Affected by Soil-Water Forces

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Introductory Remarks by Chairman

It is always a special pleasure to peruse a paper in which theory and experimental data are well balanced and combine to form a lucid picture of the phenomena under investigation. Grateful acknowledgment is given to Professor Low for contributing a paper of this quality to this Symposium. Of particular interest is the experimental proof of the lesser density of water held on the planar surfaces of montmorillonite clay particles. This finding falls well in line with the evidence on "icebergs" available on other including biologic systems. It is hoped that Professor Low will extend his investigations to systems involving other clay minerals. It would be of particular theoretical and practical interest to find out to what extent in a clay-water suspension the lesser density of the water layers around planar surfaces may be offset by the known electrostriction effect of the exchangeable cations.

● THE INTERACTION between water and soil minerals is an intriguing problem of fundamental significance. The solution of this problem must be obtained before many practical problems in agriculture, soil engineering and related fields can be solved. Therefore, the author and his colleagues have studied the forces between water and soil minerals, especially the clays, and their influence on water movement and equilibrium. This paper summarizes the results and conclusions to date.

Following the thermodynamic methods of Willard Gibbs, it is possible to show (5) that Φ, the total potential of a constituent,[1] can be divided into μ, the chemical potential, and θ, the positional potential; thus,

$$\Phi = \mu + \theta \qquad (1)$$

The chemical potential is the chemical free energy per mole and depends on the intrinsic nature and state of the constituent; whereas, the positional potential is the potential free energy per mole and depends on the position of the constituent in an external force field or force fields. Obviously, the distinction between internal force fields, which influence the chemical potential, and external force fields, which influence the positional potential, is arbitrary. For this discussion an external force field will be any force field which extends over a region which is large compared to the size of a molecule.

WATER MOVEMENT

Since Φ is a measure of the escaping tendency of the constituent, assume that the gradient of Φ is the force tending to cause movement. If it is further assumed that the frictional forces are proportional to v, the steady-state velocity, can be written Equation 6.

$$v = -k \frac{d\Phi}{dx} \qquad (2)$$

where k is the transmission constant. When the right hand side of Equation 1 is sub-

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[1] The total potential is identical to $\overline{F}$, the partial molar free energy, but the former term will be used here because it is more descriptive.

stituted for Φ Equation 2 becomes

$$v = -k \left[\frac{d\mu}{dx} + \frac{d\theta}{dx} \right] \qquad (3)$$

But, in an ideal solution,

$$d\mu = \bar{v}\, dP - \bar{s}\, dT + \frac{RT}{N}\, dN \qquad (4)$$

where $\bar{v}$, $\bar{s}$ and N are the partial molar volume, partial molar entropy and mole fraction of the constituent respectively, P is the pressure, T is the absolute temperature and R is the molar gas constant. Therefore, showing

$$v = -k \left[\bar{v}\, \frac{dP}{dx} - \bar{s}\, \frac{dT}{dx} + \frac{RT}{N}\, \frac{dN}{dx} + \frac{d\theta}{dx} \right] \qquad (5)$$

In this equation each of the terms can be regarded as a force tending to cause water movement with respect to a particular frame of reference. If the frame of reference is not the same for the different forces they will not have the same transmission constant. In particular, the mole fraction term represents an "osmotic force" tending to cause water movement with respect to the dissolved solutes. Unless the dissolved solutes are stationary relative to the soil particles this term must be excluded from the brackets and assigned a different transmission constant. Of course, if the soil solution is homogeneous, $dN = 0$ and the term drops out.

From Equation 5 several equations applicable to the movement of water in soil may be obtained. If the temperature is uniform, free salts are absent or are uniformly distributed, and the only force field present is the gravitational field, $dT = o$, $dN = o$ and $d\Phi = Mg\, dh$ so that

$$v = -k\bar{v} \left[\frac{dP}{dx} + \rho g\, \frac{dh}{dx} \right] \qquad (6)$$

In these equations M is the molecular weight of water, g is the acceleration due to gravity, h is the height above datum and ρ is the density of the water. Since Q, the volume flow, is equal to vA, where A is the cross-sectional area of the pores, write

$$Q = -k\bar{v}A \left[\frac{dP}{dx} + \rho g\, \frac{dh}{dx} \right] \qquad (7)$$

which is a form of the Darcy equation.

If the soil water is moving in the vapor phase under conditions of uniform temperature and pressure and if the gravitational field is ignored, Equation 5 reduces to

$$v = -\frac{kRT}{N}\, \frac{dN}{dx} \qquad (8)$$

In this equation p, the partial pressure of the water vapor, can replace N because $p = NP$. Thus,

$$v = -\frac{kRT}{p}\, \frac{dp}{dx} \qquad (9)$$

The number of water molecules dn, crossing the area A in time dt is[2]

$$dn = \frac{p}{RT}\, vA\, dt \qquad (10)$$

When Equation 9 and 10 are combined the result is

$$\frac{dn}{dt} = -kA\, \frac{dp}{dx} \qquad (11)$$

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[2] Note that $p/RT = c$, where c is the concentration of water molecules.

This equation is a form of Fick's law for diffusion.

For water flow in soils it is often impossible to assess separately the contributions of the last two terms on the right hand side of Equation 5. This is especially true when the water moves in films along the solid-liquid interfaces where both microscopic concentration gradients and force field gradients exist. In this event there is no longer any advantage in separating Φ into its component parts. Instead, we use the expression

$$\Phi = \Phi^0 + RT \ln \bar{a} \qquad (12)$$

where Φ^0 is the total potential of the water in the standard state and $\bar{a}$ is the total activity (5) of the water. The value of Φ^0 depends on the pressure and temperature; whereas, the value of $\bar{a}$ depends on the concentration of the constituent, the degree of interaction with neighboring molecules or ions and the nature and magnitude of any force fields which are operative. When the right hand side of Equation 12 is substituted for Φ in Equation 2 and the temperature held constant, the following is obtained

$$v = -k\left[\bar{v} \frac{dP}{dx} + RT \frac{d(\ln \bar{a})}{dx}\right] \qquad (13)$$

But π, the osmotic pressure, can be related to $\bar{a}$ by the equation

$$\bar{v} \pi = -RT \ln \bar{a} \qquad (14)$$

As a result,

$$v = -k\bar{v}\left[\frac{dP}{dx} - \frac{d\pi}{dx}\right] \qquad (15)$$

This equation was tested experimentally and was found to be valid (7).

WATER EQUILIBRIUM

When equilibrium is attained the velocity of the water is zero and Equation 5 becomes

$$\bar{v} \, dP - \bar{s} \, dT + \frac{RT}{N} \, dN + d\theta = o \qquad (16)$$

which can be integrated between the reference phase, indicated by the zero superscript, and any other phase at the same temperature, to give

$$\bar{v} \, (P - P^0) = RT \ln \frac{N^0}{N} - (\theta - \theta^0) \qquad (17)$$

Now, the first term on the right hand side of this equation is related to the difference in the concentrations of solutes in the two phases. When the appropriate substitutions (6) are made Equation 17 can be written

$$P - P^0 = RT \Sigma (m_s - m_s^0) - \frac{(\theta - \theta^0)}{\bar{v}} \qquad (18)$$

where m is the molar concentration of any ionic or molecular species designated by the subscript s.

To apply Equation 18 to the swelling of clays, let the symbols without superscripts refer to the median plane between two parallel clay plates and the symbols with zero superscripts to the external solutions. Then, the pressure difference $(P - P^0)$ is equal to the hydrostatic replusive force which tends to separate the plates and cause swelling. From the equation it is evident that this force results, not only from the difference in ion concentration between the median plane and the external solution, but also from the difference in the potential energy of the water between these two phases. The question now arises as to whether clay-water forces exist which lower the potential energy of the water in the interfacial region relative to that in the external solution. The following paragraphs will be devoted to a discussion of the evidence in favor of such forces. Obviously, if they exist, they will influence water movement as well as water equilibrium.

An attempt was made by Hemwall and Low (4) to assess qualitatively the importance of the terms in Equation 18. It seemed reasonable to assess the importance of the first term by altering the number and dissociation of the adsorbed cations and by measuring the resultant change in swelling. These cations are responsible for the difference in ion concentration between the interplate and external solutions. It seemed reasonable also to assess the importance of the second term by altering the adsorptive forces between clay and water and measuring the resultant change in swelling. These adsorptive forces would account for any difference in the potential energy of water between the two regions. Treatments were designed, therefore, to alter or eliminate separately the degree of cation dissociation and the adsorptive forces between clay and water. Swelling measurements were made before and after the treatments. In addition, water in the clay which remained unfrozen at - 5 C was determined. Unfrozen water and clay swelling should be related since the same forces are probably responsible for both.

Wyoming bentonite clays were prepared which were saturated with Na, with a mixture of Na and Th and with Th only. Thorium was used because each tetravalent Th ion would replace four monovalent Na ions and would likely be dissociated less than the Na ions. Therefore, the number of osmotically active, adsorbed ions should be greatest on the Na-clay, less on the Na-Th-clay and least on the Th-clay. Electrophoretic measurements and potentiometric and conductometric titrations indicated that such was the case. An X-ray pattern of a rehydrated sample of the Th-clay showed that the individual layers of the clay were only partially expanded.

A portion of the Na-clay was treated with dimethyldichlorosilane which, according to Rochow (10), reacts with the adsorbed water on the clay to form a polymerized monolayer in which methyl groups are exposed at the new surface formed. Since any surface made up of methyl groups is hydrophobic, it was felt that this treatment would eliminate any clay-water forces which might exist. The Na-clay adsorbed 0.253 gm of silane per gm of clay. A subsequent X-ray analysis disclosed, however, that no interlayer adsorption of silane occurred. Consequently, clay-water forces were eliminated at external surfaces only. Ion dissociation was also eliminated at these surfaces because the electrophoretic mobility of the silaned clay was zero and the cation exchange capacity was reduced

O   Na-clay in 0.001N NaCl
□   Na-clay in 0.001N NaCl and 0.1173M dioxane
Δ   Na-Th-clay in 0.001N NaCl
+   Na-clay (silaned) in 0.001N NaCl
X   Th-clay in 0.0001M ThCl₄

GRAMS OF WATER BOUND PER GRAM OF DRY CLAY

GRAMS OF WATER ADDED PER GRAM OF DRY CLAY
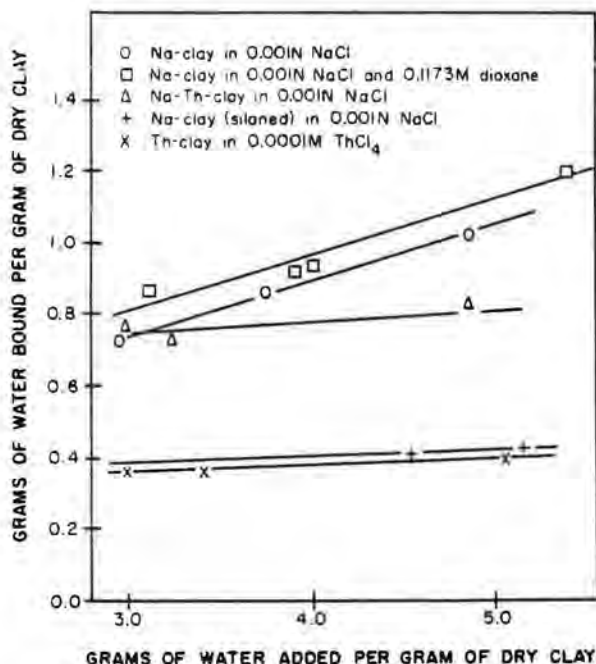
Figure 1.   Unfrozen water in clay.

from 1.05 me. per gm to 0.98 me. per gm.

The apparatus used for obtaining swelling pressures and the results obtained will not be discussed here except to say that the non-silaned clays swelled in the expected order, namely, Na-clay> Na-Th-clay > Th-clay. The dilatometer used to determine unfrozen water at -5.0 C was the same as that of Buehrer and Rose (2). It should be mentioned that, with the dilatometer method, unfrozen water is the water which does not exhibit the normal volume expansion associated with freezing. Consequently, any adsorbed water with a structure which is less dense than that of pure water might freeze, but still appear partly as unfrozen water. The experimental data are shown in Figure 1.

The data in Figure 1 have a direct bearing on the existence of clay-water forces. A calculation shows that, if all the exchangeable and free ions were concentrated in the unfrozen water on any of the clays, the ion concentration would not be sufficient to prevent freezing at -5 C. This would be true even if all the exchangeable ions were completely dissociated, which is unlikely. Therefore, it is safe to conclude that the un-

frozen water was due to clay-water forces and not to a depression of the freezing point by the dissolved solutes.

At the water contents used in the freezing studies the Na-clay was not at maximal swelling because the addition of more solution to the system formed a new gel of larger volume. This was true in the presence or absence of dioxane, which has an inhibitory effect on hydrogen bonding and was added to reduce any hydrogen bonding which might occur between clay and water. The addition of more solution not only increased swelling but, as shown in Figure 1, unfrozen water also. If the curve for Na-clay in 0.001 N NaCl is extrapolated to the water content at maximal swelling (7.6 gm of water per gm of clay) it can be seen that, at this water content, there would be approximately 1.4 gm of unfrozen water per gm of clay, representing a water layer about 16 A thick. In the presence of dioxane this layer would be a little thicker, a fact which indicates that this reagent did not interfere with clay-water forces but with the hydrogen bond formation in ice. Apparently, unfrozen water increases with swelling because the force fields become more effective with increasing interplate distance.

The silaned Na-clay, the Na-Th-clay and the Th-clay were at maximal swelling at all the water contents used in the freezing studies. A clear supernatant liquid was used as the criterion for maximal swelling. Note that, for these clays, increasing the water content had relatively little effect on the unfrozen water. Since, unfrozen water at -5.0 C increased with an increase in swelling but remained unchanged when swelling was at a maximum, it is evident that the amount of unfrozen water and the degree of swelling are related. Additional evidence for this relationship is provided by the fact that, for the non-silaned clays, the unfrozen water sequence was the same as that for the swelling sequence, i.e., Na-clay > Na-Th-clay > Th-clay. However, it should be observed that the silaned Na-clay, with only internal surfaces available for adsorption, and the Th-clay, with mostly external surfaces available for adsorption, contained the same amount of unfrozen water. Internal surface area far exceeds external surface area. Therefore, it appears that clay-water forces are more extensive at external surfaces than at internal surfaces.

If clay-water forces exist they should alter the structure of the adsorbed water and, thereby, change its density. Consequently, experiments were conducted on the density of water adsorbed on Wyoming bentonite saturated with either K, Na or Li ions. In the first of these experiments (8) $\bar{v}_w$, the partial specific volume of water (volume per gm of the last increment), was determined in different suspensions at 25 C by a pycnometer method. Suspension densities for K-, Na- and Li-clay in water were obtained at different clay concentrations. Then a graph of ρ, the suspension density, against c, the clay concentration, was made for each clay and the value for $\bar{v}_w$ at any concentration was calculated by the equation

$$\bar{v}_w = 1 \Big/ \left[\rho - c \, \frac{d\rho}{dc} \right] \tag{19}$$

All the terms in this equation were obtainable from the aforementioned graphs, one of which is shown in Figure 2.

From Figure 2 it is obvious that the plot of ρ against c produced a straight line. The equation for this line is

$$\rho = c \left(\frac{d\rho}{dc} \right) + \rho_0 \tag{20}$$

where ρ_0 is the density of pure water. Substituting the right hand side of Eq. 20 for ρ in Eq. 19 shows that the partial specific volume of the water is the same as that for pure water at all the clay concentrations employed. The same was true for the Na-clay and the Li-clay. Since the interplate distance at the highest clay concentration (the concentration at maximal swelling) was about 168 A, it can be concluded that, for these clays, water had its normal density at 84 A from the clay surface.

In the second experiment on adsorbed water density (1) pastes of K-, Na- and Li-clay were compressed between a column of mercury and a porous, stainless-steel filter. The mercury was confined in a capillary, as was the water which was forced through the filter. Thus, the change in volume of the clay paste and of the expressed

water could be observed simultaneously. From these observations, and from the weight of water in the paste at the termination of the experiment, it was possible to plot the volume of the clay paste against the weight of water in the paste. Since, the slope of the resulting line at any water content is equal to the partial specific volume of the water at that water content, and since density is the reciprocal of the partial specific volume, water densities could be obtained at several water contents for each of the three homoionic clays. The results are shown in Figure 3. In this figure distances from the clay surface were calculated by assuming a surface area of 8×10^6 cm^2 per gm and an average water density of unity.

From Figure 3 it is at once apparent that the water density decreased continuously from > 60 A to < 10 A from the surface. At a distance of about 10 A the density decrease is of the order of 2 to 3 percent. At all distances the water density was less than that of normal water which has a density of 0.9970 at 25 C and of 0.9999 at 1 C. Evidently, the nature of the adsorbed ion influences the water structure. At water contents below about 4.0 gm of water per gm of clay the clays decreased the water density in the order Na-clay > Li-clay > K-clay. At higher water contents the order is reversed for the Na- and Li-clay. In addition, there was a more rapid decrease of water density with proximity to the surface at 1 C than at 25 C.

An explanation for the observations made in Figure 3 can be based on the current ideas of the structure of water and ionic solutions. Water can be regarded as

Figure 2. Plot of suspension density against clay concentration for K-bentonite at 25 C.

a "broken down ice structure" in which there is a tendency for each water molecule to bond itself tetrahedrally to four neighboring water molecules. The bonds are continually breaking and reforming so that, on the average, each molecule is bonded to less than four neighbors and has other neighbors at various distances. When ions are added to water its loosely co-ordinated structure is disrupted and a closer packing (increase in density) of water molecules results. In general, the disrupting effect is least with small ions and greatest with large ones. Extending these ideas to the clay-water system, one is compelled to ascribe the observed decrease in density to the influence of the clay surface and not to the adsorbed ions. Therefore, it is

Figure 3. Effect of temperature and exchangeable cation on adsorbed water density.

proposed that the "broken down ice structure" of water is stabilized by the polarizing influence of the negatively charged clay surface or by hydrogen bonding to this surface. It is not to be inferred that the stabilized structure is rigid but only that a more regular ordering of the water molecules exists. In this structure, as in water, the ions exert a disrupting influence, probably by decreasing the extent of hydrogen bonding. This influence appears to be in the order K > Li > Na. Hence the structural development of

the adsorbed water should be greatest on the Na-clay, less on the Li-clay and least on the K-clay. Support is given to the proposed order of structural development by evidence, which will be referred to later, that the activation energy for ionic movement in this water is greatest for Na, less for Li and least for K. Also, as in water, a decrease in temperature results in an increase in structural regularity. In the adsorbed water this is manifested by a density decrease.

The above results show that the density of the adsorbed water structure is less than that of pure water up to distances greater than 60 A but not exceeding 84 A. A reasonable conclusion, therefore, is that the clay-water forces responsible for this structure extend 60 to 84 A from the surface. For these clays 84 A was the half-distance between adjacent clay layers at maximal swelling. When one realizes that a very large force is required to sensibly alter the structure of water (e.g., a pressure of 200 atmospheres increases the density of water by only 1 percent) it becomes evident that the forces referred to may be of considerable magnitude.

The experiments of the preceding sections throw light on experiments conducted in this laboratory several years ago[3], and vice versa. In the earlier experiments, samples of K-, Na-and Li-clay were suspended in solutions of different salt concentration. In each case, the salt was the chloride of the cation with which the suspended clay was saturated. The resulting suspensions were put in centrifuge tubes and immersed in a constant temperature bath at -50 C for 12 hours. At the end of this time if the suspensions were not frozen they were diluted slightly with the appropriate chloride solution and returned to the bath for another 12-hour period. This process was continued until freezing occurred. The clay concentration was recorded for each suspension which froze. In addition, the zeta potential of each clay was determined at each salt concentration. The results for the Na-clay are shown in Figure 4. Analogous results were obtained for the K-clay and Li-clay.

From Figure 4 it is clear that the concentration of clay in suspension at freezing was related to the zeta potential of the suspended particles; as the zeta potential increased, indicating an increase in cation dissociation, the clay concentration at freezing decreased, and vice versa. But the observed clay concentrations at freezing were not the equilibrium values be-

Figure 4. Zeta potential and freezing concentration of Wyoming bentonite as a function of sodium chloride concentration.

cause none of the suspensions contained enough exchangeable ions and free salt to lower the freezing point more than a fraction of a degree. In addition, there was very little unfrozen water in the frozen suspensions. Apparently, the particles in suspension affected the supercooling of the suspension; the degree of supercooling being a function of the concentration and zeta potential of the suspended particles. Supercooling was enhanced by the particles because particle-free solutions of the same salt concentrations froze with little or no supercooling under the same conditions. Also, in most suspensions the particle concentration had to be reduced before freezing occurred.

The contribution of the clay particles to supercooling cannot be attributed to the

[3] Deming, John M. Forces involved in the swelling of clays. Unpublished Ph.D. Thesis Purdue University. 1951.
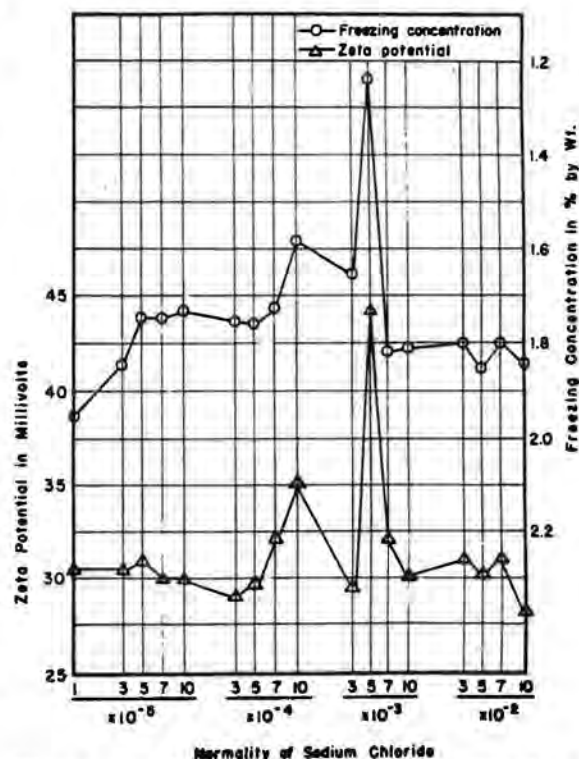
influence of the exchangeable ions because supercooling was not affected directly by the addition of electrolytes. Further, Dorsey (3) has shown that electrolytes have a negligible effect on supercooling. Consequently, the observations reported here can be attributed to clay-water forces which promote supercooling and become more effective as the zeta potential goes up. These facts elicit the following proposals: (a) the water structure formed as a result of the clay-water forces is not identical with that of ice; otherwise, there would be no supercooling, (b) an increased dissociation of ions from the clay surface is conducive to the structural development of the adsorbed water; either the disruptive effect of the ions is lessened or the intensity of the clay-water interaction is increased as the ions become distributed through a larger volume. Clay-water interaction would be increased by increased ionic dissociation if this interaction was due to the polarizing effect of the electric field at the particle surfaces. Support is given to proposal (1) by the fact that, in the dilatometer work, it was difficult to supercool suspensions of the silane-treated clays. Recall that the silane treatment eliminated clay-water forces at external surfaces. Now let us examine additional evidence for proposal (2).

In the dilatometer work on unfrozen water in clay systems, the Th-clay was not only undissociated but adsorbed Th ions in excess of its inherent exchange capacity (zeta potential =+53.8 mv.); it contained relatively little unfrozen water.[4] The Na-Th-clay was slightly dissociated (zeta potential = - 17.6 mv.) and contained more unfrozen water. The Na-clay was largely dissociated (zeta potential = - 35.0 mv.) and contained the most unfrozen water. In addition, external surfaces accounted for more unfrozen water than did internal surfaces. Ionic dissociation should extend farther, i.e., the ionic atmosphere should be more diffuse, at external surfaces. Hence, the dilatometer work supports proposal (2).

Recently, the author (9) used the same clays as those employed in the water density research to obtain the mobilities and activation energies for movement of the adsorbed ions. A Na-clay, which was saved from another experiment, was also used. The results are shown in Table 1.

TABLE 1

NATURE OF WATER ADSORBED ON CLAYS IN RELATION TO THE
ELECTROCHEMICAL PROPERTIES OF THE EXCHANGEABLE IONS

Clay[a]	Ionic Mobility at 25 C.	Ionic Activation Energy	Ionic Dissociation	Density of Adsorbed Water at 25 C.	Structural Development of Water
	sq. cm./ volt/sec.	cal./ gm. ion	(relative)	gm./cc.	(relative)
K-clay	0.000051	4037	++	0.981[b]	+
Na-clay	0.000069	4486	+++	0.972	+++
Li-clay	0.000057	4358	++	0.975	++
Na-clay	0.000132	5157	++++	—	—

[a]The first three clays were prepared from <2.0 μ, columnated Wyoming bentonite by titration. The last clay was prepared from <0.2 μ, electrodialyzed Wyoming bentonite by titration.

[b] These values are for a distance of 10 A. from the clay surface.

In Table 1, the data in columns 2, 3 and 5 were obtained experimentally. The data in column 4 were obtained by using the following relationship between U, the ionic mobility, and E, the activation energy, $U = \alpha \beta B e^{-E/RT}$ (21)

[4] The relatively small amount of unfrozen water on this clay was due partly to its lack of interlayer expansion.

where α is the degree of ionic dissociation, β is a geometry factor for movement in the porous clay-water system, B is a constant which is dependent on the distance between successive equilibrium positions of the ion, R is the molar gas constant and T is the absolute temperature. Values of B were assumed to be the same as those in solution, namely, 0.252 for K, 0.389 for Na and 0.484 for Li. The value of β was assumed to be the same for all systems since the clay was packed the same in each one. The data in column 6 were obtained by regarding the water density as a criterion of structural development, the less the density, the greater the structural development.[5]

The activation energy for ionic movement is equal to the sum of the energies expended by the ion in pushing back molecules to form a hole and in breaking bonds with the clay and neighboring water molecules so that it can move into the hole thus formed. Therefore, one would expect the activation energy to go up with an increase in the coherence of the water structure.[6] Evidently, this is what happened, as indicated by the data in the table. But, activation energies and the degree of ionic dissociation were in the same order. A reasonable conclusion is that the water structure became better developed as the degree of ionic dissociation increased. Here also, the evidence supports proposal (2).

The nature of the exchangeable cation should have an effect on the structural development of the adsorbed water. In solutions, ions disrupt the water structure in the order K > Na > Li. It would be expected that this order would obtain for clay-water systems as well. Apparently it does because, even though the K- and Li-clay were equally dissociated, there was less structural development in the adsorbed water on the former than on the latter. Structural development of water was greatest on the Na-clay because this clay was the most dissociated.

In summary, it appears that clay-water forces are responsible for the development of a water structure at the clay-water interface. This structure extends upwards of 60 A. from the clay surface and becomes less regular, and probably more fluid, with distance from the surface. This adsorbed water structure and that of ice are not identical but are similar in that both are less dense than normal water. Very likely, both owe their coherence to hydrogen bonds. Structural development in the adsorbed water is enhanced by ionic dissociation from the clay surface, possibly because the disruptive effect of the ions is less when they are distributed over a larger volume and not concentrated at the surface where the structure is "anchored." The disruptive effect of the ions is probably in the order K > Na > Li when they are equally dissociated.

If clay-water forces give rise to a more regular water structure in the vicinity of the clay mineral surfaces, they must also increase the viscosity of the water near these surfaces. Since water tends to move toward regions of low potential energy, it should accumulate in the interfacial regions between clay and water, the extent of the accumulation being proportional to the magnitude of the forces. For the same reason, these forces should affect such soil properties as swelling, aggregation and compaction. In addition, they should be effective in preventing the freezing of water. Thus, it is reasonable to believe that soil- and clay-water forces affect the movement and equilibrium of water in soil systems.

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[5] Note that if all the hydrogen bonds in water were broken and the water molecules became close-packed, the water density would be 1.84.

[6] For example, one would expect a much greater activation energy for ionic movement in ice than in water.

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Influence of Surface Forces on Flow of Fluids Through Capillary Systems

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Introductory Remarks by Chairman

The science of physics started and developed its laws by measuring and mathematically correlating phenomena in the world of normal dimensions. What these normal dimensions are is evident from the choice as most suitable measuring units of the cm, the gram and the second. From this base, physics has extended its realm both ways to tremendously large and exceedingly small dimensions. During this process, it soon became evident that most laws of the normal dimensions are of a statistical and approximate nature and that they represent special solutions for the particular dimensions of more general laws. While the search for the latter is still going on and since human activity cannot be stopped until the most general laws have been discovered and special solutions found for each world of different dimensions, it is useful and proper to find by experiment the laws ruling the areas of particular dimensions or sets of dimensions. Such experimental search will, of course, be guided by the knowledge of the searcher of either or both the laws governing areas of larger and of smaller dimensions than those of the particular area of interest. One such area has been called by Wolfgang Ostwald "The World of Neglected Dimensions". It is the world of colloid chemistry characterized by a range of dimension from the size of large molecules to the wavelength of light just visible to the human eye. There is no valid a priori reason why the laws governing the world of colloidal dimensions should not be derivable in their simplest and most useful form from proper experimentation within the realm of these dimensions.

Nor is there a good reason why the relationship between these laws with those of the macro-world, on one hand, and the atomic world, on the other, should not be fully explored and evaluated. Dr. Flood deserves special commendation for clearly defining the areas dominated by molecular and mass phenomena, respectively, in flow through capillary systems and for presenting a simple equation that correlates micropore flow rates with relevant adsorption isotherms.

● FLUID FLOW mechanisms may be classified broadly into two categories: (a) Mechanisms which are essentially mechanical in nature, the flow depending on the bulk properties of the fluids concerned and upon the mechanical forces exerted upon the fluid bodies. (b) Mechanisms which are essentially molecular in character, the flow depending largely on the thermal motion of the individual molecules, the molecular weight, the collision cross-section, the mean free path, etc., rather than upon the density, pressure, viscosity, etc., of the fluid in bulk.

The Bernoulli flow of the inviscid liquid of classical hydrodynamics may be taken as an example of the first category. In this type of flow, pressure potential is converted into velocity potential and vice versa. The flow thus resembles the motion of a frictionless pendulum, potential energy of fluid masses being converted into kinetic energy of mass motion and vice versa. This type of flow involves no loss of energy, no loss of

net potential. While all ordinary fluid flow involves some loss of potential due to friction and/or entropy production, nevertheless the ideal Bernoulli type of flow is approximated quite well in the case of the flow of large masses of water at fairly high net velocities in pipes of large diameter. Another example of "mechanical" flow is that of the viscous flow of nearly incompressible liquids where the flow is controlled by viscosity and hydrostatic pressure gradients.[1]

Molecular flow is exhibited in such phenomena as "tagged molecule" self diffusion and generally by the interdiffusion of components where concentration gradients exist.

The mechanism of gaseous flow in small pipes and channels is more or less intermediate between the purely mechanical and the purely molecular flow mechanisms.

Usually in the case of "mechanical" flow, work is done to initiate the flow and work must be done continuously to maintain the flow, but little or no change in entropy of the fluid is involved. In the case of molecular flow mechanisms, the flow is accompanied by considerable entropy changes of the fluid and may involve little or no energy change and little or no net performance of work

That the flow mechanism and even the direction of flow depends not only on the fluids concerned, not only on the thermodynamic potential differences that may be involved but also on the nature of the flow path may be illustrated by considering the flow between two equal volumes of an ideal gas where the pressures and temperatures of the two volumes differ. Let p_1, t_1, n_1, and p_2, t_2, n_2 be the pressures, temperatures, and concentrations of the two gases in the two volumes. We shall suppose that $T_1 > T_2$ and that p_1 lies between p_2 and $\sqrt{\dfrac{T_1}{T_2}} \cdot p_2$, and hence that n_1 lies between n_2 and $\sqrt{\dfrac{T_2}{T_1}} \cdot n_2$, thus $p_1 > p_2$, and $n_1 < n_2$.

In this case if the two reservoirs are connected by means of a pipe whose diameter is small compared with the mean free path of the gas, the flow will be toward the first reservoir, that is, in the direction of decreasing concentration but in the direction of increasing pressure, i.e., the gas flows toward the higher pressure and the higher temperature. If, however, the diameter of the pipe is large compared with the mean free path, the body forces will prevail and the flow is toward the lower pressure. In the former case the net flow is determined by the statistics of the individual molecules while in the latter case by the net forces acting on small volumes or laminae of the fluid which contain many molecules. The latter is, of course, mainly a viscous or laminar flow with slip, the slip being modified by the temperature gradient. The relevant equations (1) are:

1. Molecular effusion through a hole of area A into a vacuum $Qm = A\left(\dfrac{M}{2\pi RT}\right)^{1/2} p$

2. Effusion through a long circular capillary of radius r. The mean free path much greater than r $Qm = -\dfrac{8}{3} r^3 \left(\dfrac{\pi M}{2R}\right)^{1/2} \dfrac{d}{dz}\left(\dfrac{p}{\sqrt{T}}\right)$

3. Maxwell's equation for laminar flow with slip and thermal creep
$$Qm = -\dfrac{\pi r^4}{8\eta}\dfrac{M}{RT}p\dfrac{dp}{dz} - \dfrac{\pi r^3}{2}\left(\dfrac{\pi M}{2RT}\right)^{1/2}\left(\dfrac{2-f}{f}\right)\dfrac{dp}{dz} + \dfrac{3}{4}r^2\dfrac{\eta}{T}\dfrac{dT}{dz}$$

Qm = flow rate gr/sec, other quantities in c.g.s. units.

When the connecting pipe is of relative large diameter, and the mean flow velocity high there will usually be a contribution of the Bernoulli flow type, i.e., the kinetic energy of the flowing mass may be appreciable.[1]

Evidently the flow of gas through a pipe may be either largely mechanical or hydrodynamic in character or largely molecular or diffusive in character or of mixed character depending on the dimensions of the pipe, the mean free path, etc. In the case of liquids where the "mean free path" or mean "amplitude of vibration" is usually considerably less than a molecular diameter, the flow through pipes or capillary passages whose diameters are greater than only a few molecular diameters will be largely hydrodynamic in character. Thus even in the case of exceedingly small capillary spaces we

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[1]Viscosity itself is, of course, related to molecular diffusive properties, directly in the case of gases and more or less inversely in the case of liquids.

must know something concerning the density of the fluid before we can tell whether the flow mechanism is likely to be largely hydrodynamic or largely diffusive in character. When the capillary passages are of molecular dimensions or smaller, relatively large attractive and repulsive forces are involved, and large forces are required to force molecules through the repulsive regions, i.e., the flow is controlled by the "activation energies" corresponding to the potential energy barriers through which the molecules must flow. The flow mechanism in this case will be largely diffusive in character.(3)

Before discussing the influence of surface forces on the flow of fluids through capillary systems, the nature of the solid surface forces which are associated with adsorption and capillarity will be discussed briefly.

Just as flow mechanisms were divided into two broad categories, surface forces at room temperature can be divided into two distinct classes, namely: (4, 5) (a) Surface forces associated with definite isolated high energy sites, the whole volume of the energy field associated with the site being comparable with, or less than the volume of a single adsorbate molecule. The surface forces of such sites are large and lead to quantized energy states or to bond formation and chemi-sorption. In this case the adsorbate molecules become practically a part of the solid surface and, compared with molecules in a liquid or gas, such chemi-sorbed molecules are largely immobilized. (b) Surface forces associated with relatively large areas of the solid surface or with many "sites" the fields of which overlap so as to form a surface region or layer of considerable volume under the influence of an attractive force field. Energy states of molecules due to these fields only are not quantized but are continuous and behave classically. Thus molecules of adsorbate in such regions will have properties closely resembling the properties of the adsorbate in bulk at corresponding densities and temperatures. The thickness of the layer will depend on the size and nature of the adsorbate molecules and may be of the order of 10 A. For approximate calculations we may use overlapping Leonard-Jones six-twelve potentials taking the size of adsorbate molecules into consideration.

If molecules of a condensable gas are allowed to fall into such regions the equilibrium density of the gas molecules in the surface region may be much higher than that remote from the surface and hence at some critical density may condense to the corresponding liquid under the influence of their own attractive forces. Once the liquid is formed, the liquid vapour interface will have a surface potential peculiar to the particular adsorbate. In general, this potential will be of opposite sign to the potential of the solid surface. Thus the formation of liquid-vapour surfaces of tension will tend to reduce the net surface potential. Adsorption phenomena in such regions will be essentially Polanyi adsorption.

While in general any surface will have surface forces of both these extreme types as well as those of intermediate character, the behaviour of active adsorbents such as active carbon indicates that the bulk of the net adsorption phenomena is of the latter type, since the adsorption is readily reversible and strongly influenced by the condensability of the adsorbate. (6)

In the case of transient or non-steady state flow, if the total surface area is at all large, all of the different types of surface forces will influence the rate of adsorption and permeation of the capillary system. In the case of steady-state flow, however, surface forces of the first type will have a negligible influence in most cases since molecules once adsorbed will be largely immobilized. The number of such very high energy sites being comparatively small any effect on the dimensions of the capillary passages will be small in cases where the mean pore sizes are reasonably large (i.e., 10 A or more).

In what follows we will confine our discussion to cases where the surface forces are entirely of type (b), i.e., to cases where any effect of surface forces leads to a Polanyi type adsorption mechanism.

INFLUENCE OF SURFACE FORCES ON PRESSURE AND DENSITY OF FLUIDS IN CAPILLARY SPACES

In order that an equilibrium exist between the fluid within the capillary system and the fluid remote from surface forces their thermodynamic potentials must be the same,

i.e., $\mu_a = \mu$ where the subscript $\underline{a}$ refers as before to the fluid in the capillary system. As the pressure of the fluid remote from the surface is varied, the temperature being constant, the thermodynamic potentials must remain equal to preserve the equilibrium. Since $d\mu = -Sdt + vdp$, we have the following isothermal equilibrium condition equation:

$$\delta v_{ai} \cdot dp_{ai} = \delta v_i \cdot dp$$

where δv_{ai} is any element of volume of the fluid in the capillary region and dp_{ai} the pressure change in this element while δv_i is an element of volume of the reference fluid remote from the surface forces which contains the same matter as δv_{ai} and dp is the change in the uniform pressure of this reference fluid. Hence for the whole of the adsorbate:

$$\underset{v_a}{\Sigma} \; \delta v_{ai} \cdot dp_{ai} = \underset{v}{\Sigma} \; \delta v_i \cdot dp$$

or

$$v_a \cdot d\overline{p}_a = vdp$$

where $\overline{p}_a$ is the volumetric mean pressure of the adsorbate. Hence,

$$d\overline{p}_a = \rho_a / \rho \cdot dp$$

where ρ_a is the mean adsorbate density, and ρ the density of the reference fluid. On integrating:

$$\overline{p}_a = \int_{P=0}^{p=P} \rho_a / \rho \cdot dp = aP$$

where a as defined by the equation is the mean value of ρ_a / ρ over the pressure interval O-P. Thus the volumetric mean pressure of the adsorbate $\overline{p}_a$ is given by the integral of ρ_a / ρ from O to P, P being the pressure of the reference fluid or gas remote from the surface; ρ_a the mean adsorbate density will be given by the total weight of adsorbate divided by the void volume of the capillary system. Thus if X is the weight adsorbed per gram of capillary then (N.B.: the weight

$$\frac{X + \rho v_a}{v_a} = \rho_a \;.$$

adsorbed is usually taken to be the weight in excess of that which the void volume would contain in the absence of surface forces, i.e., in excess of ρv_a.) Since $\rho = \dfrac{pM}{RT}$ for an ideal gas,

$$\overline{p}_a = \int_O^P \left(\frac{XRT}{pMv_a} + 1 \right) dp$$

Thus when $X = O$, $\overline{p}_a = P$ and when X is much greater than pM/RT, $\overline{p}_a$ is much greater than P. $\overline{p}_a$ can be obtained graphically from the adsorption isotherm.[2]

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[2] It is of course much better to obtain this integral graphically from a known observed reversible isotherm than from an assumed adsorption isotherm equation. Equation 1 is exactly equivalent to Guggenheim's "spreading pressure" and like the spreading pressure is thermodynamically necessary regardless of any assumption concerning the mechanism of the adsorption. However, in the case of chemisorption the "spreading pressures" are not even approximately hydrostatic pressures of the adsorbate or of the adsorbate-adsorbent interface, but rather are analogous to osmotic pressures. In the general case the spreading pressure is measured by that external force which must be exerted (parallel with the surface) on a movable mechanical wall or barrier dividing the adsorbed layer from the clean surface, the height of barrier extending to the limit of the range of the surface forces. If such an equilibrium can exist then the external force divided by the area of the barrier is the spreading pressure. However, under the assumed conditions these mean adsorbate pressures are mean hydrostatic pressures and are closely analogous to the mean horizontal pressure exerted on the vertical walls of a tall water tank due to gravity or any other scalar force field.

If hysteresis occurs so that a second thermodynamically reversible path intersects the path along which p increases from O to P, and the pressure is reduced from P to say P', the mean adsorbate pressure is obtained from the equation,

$$\overline{p_a} = \int_O^P \rho_a/\rho \cdot dp - \int_{P'}^P \rho_a'/\rho \cdot dp \qquad (1)$$

where ρ_a' is the mean density along this second path. If ρ_a' greatly exceeds ρ_a, $\overline{p_a}$ may become negative. But along any reversible path of increasing equilibrium pressure $\overline{p_a}$ cannot become negative.

Evidently when a long porous body which adsorbs vapour appreciably is exposed at its extremities to two different pressures, the pressure gradient along its length within the porous body may be much greater than that corresponding to the pressure gradient that would subsist in the absence of surface forces, i.e., in the absence of adsorption or any other conditions which can maintain an appreciable density difference between the fluid within and that outside of the capillary system.

In pipes of diameters consistent with hydrodynamic or laminar viscous flow we might expect the flow rate in mass units to be proportional to the adsorbate density and to the adsorbate pressure gradient. Thus we might expect that we could write

$$Am = -A\rho_a \cdot \frac{dp_a}{dz}$$

where Qm is the flow rate in mass units, A a constant characteristic of the pipe, ρ_a the mean density of the fluid within the pipe, and dp_a/dz the pressure gradient within the pipe. However, it is immediately evident that if the "viscosity" is variable, near the wall approaching say liquid viscosity while remote from the wall approaching gas viscosity, A will not be by any means a constant but will be a complex function of ρ_a. The complete equation in this case is very complex and involves a number of unknown parameters. However, there are two special cases where the complete equation can be greatly simplified and leads to a useful equation. The simplest case is that where the fluid is well below the critical temperature and where the surface forces condense the vapours to liquids or to thin liquid films on the surface of the capillary region and where $\rho_a \gg \rho$. Assuming now that the condensed liquid has the normal liquid viscosity it can be shown that for small pipes of circular cross-section the flow rate is given by

$$Qm = -\frac{\pi r^4}{8\eta_l} \cdot \rho_a \frac{dp_a}{dz}$$

and since $dp_a = \rho_a/\rho \cdot dp$,

$$Qm = -\frac{\pi r^4}{8\eta_l} \cdot \frac{\rho a^2}{\rho} \cdot \frac{dp}{dz} = \frac{\pi r^4}{8\eta_l} L \cdot \int_{P_1}^{P_2} \frac{\rho a^2}{\rho} \cdot dp$$

where L is the length of the pipe and P_1, P_2 the input and output pressures respectively.

This equation is applicable only when the relative contribution from the simultaneous gaseous flow is negligible. It is to be emphasized that the equation is a simplification of a much more complex equation. (7) Even the shape of the pipe will modify the form of the integrand. However, with suitable numerical coefficients the equation should be approximately valid for pipes of more or less square or circular cross-section where the range of the surface forces or the thickness of the dense surface layer is comparable with the dimensions of the pipe.

Where the equation is applicable to a single capillary a similar equation will of course be applicable to bundles of parallel capillaries of the same dimensions and having the same film thicknesses. The equation will be approximately valid for bundles of parallel capillaries whose radii vary a little provided that corresponding variations in film thickness are roughly inversely proportional to r, i.e., that the fields are somewhat higher in the smaller capillaries (r^4 is of course replaced by $\overline{Nr^4}$ in such cases).

In the case of large pores, where the density of the fluid in the capillary system under static equilibrium conditions is practically the same as that of the fluid outside of the capillary system, the flow rates for pipes of lengths comparable with their diameters will be given by the following classical equations:

For liquids:

$$Qm = \frac{\pi r^4}{8\eta_1} \, \rho_1 \, \frac{P_1 - P_2}{L}$$

where ρ_1 is the density of the liquid and η_1 its viscosity.

For ideal gases:

$$Qm = \frac{\pi r^4}{8\eta} \, \frac{M}{RT} \, \frac{P_1^2 - P_2^2}{L} + \frac{\pi r^3}{2} \left(\frac{\pi M}{2RT}\right)^{1/2} \left(\frac{2-f}{f}\right) \frac{P_1 - P_2}{L}$$

where η is the gas viscosity (more or less independent of density) and $f \approx 0.9$.

Gaseous flow rates are commonly expressed in K units, i.e., in pv units divided by ΔP. In these units,

$$K = \frac{Q_{pv}}{P_1 - P_2} = \frac{Qm}{P_1 - P_2} \, \frac{RT}{M}$$

$$= \frac{\pi r^4}{8\eta L} \, \frac{P_1 + P_2}{2} + \frac{\pi r^3}{2L} \left(\frac{\pi RT}{2M}\right)^{1/2} \left(\frac{2-f}{f}\right)$$

in which f is the fraction of the tangential momentum convected to the surface of the pipe per second by thermal motion which is actually transferred to the surface (i.e., f = O for specular reflection and f = 1 if every molecule striking the surface sticks to it).

Since $(P_1 + P_2)/2$ is the mean of the input and output pressures, when K is plotted against $\overline{P}$ we get a straight line, the slope of which is given by the first term of the right hand member of the equation and the intercept by the second.

This is Maxwell's equation with slip. At very low densities the flow mechanism becomes molecular effusion which is a different phenomenon. The flow rate is given by an expression which resembles the term in r^3 but is numerically different. In the case of long narrow capillaries the effusive or Knudsen flow in K units is given by

$$K = \frac{4\pi r^3}{3L} \left(\frac{2RT}{\pi M}\right)^{1/2} \frac{2-f}{f}$$

This term is larger than Maxwell's slip term, hence when K is plotted as a function of $\overline{P}$ the graph should show a minimum.

However, as shown by Clausing (8) in the case of short tubes the effusion flow becomes practically identical with the "slip flow". In more or less granular isotropic or porous bodies the "bottle necks" controlling the flow rates should have lengths comparable with their diameters. Accordingly, no minimum is to be expected in the case of gaseous flow through porous or granular beds when surface forces can be neglected.

In cases of complex capillary systems where there are both micropores and macropores, the micropore and macropore systems should be treated separately if at all possible. In the case of many active adsorbents the two pore systems are quite distinct, the micropore systems having nearly uniform pore diameters of the order of 10 to 20 A while the macropore systems have pore diameters showing a considerable variation from the mean, the mean being of the order of 10^3 or 10^4 A. If the volumes of these two pore systems are at all comparable it is evident that the permeability of the micropore system will be quite negligible compared with that of the macropore system in the absence of surface forces or some agency which profoundly modifies the flow mechanism. Since surface forces may easily increase fluid densities by factors of 10^4 and more, and accordingly increase pressure gradients by similar factors, flow rates may be increased a million fold even when the viscosity of the adsorbed material is increased a hundredfold. We have found experimentally that the flow rates of a number of vapours through both the macropores and micropores of some activated carbon rods may be described quite well by means of the following equation

$$Qm = -\frac{A}{\eta_1} \, \frac{\rho a^2}{p} \, \frac{dp}{dz} - \frac{\beta}{\eta} \, p \, \frac{dp}{dz} - c \, \frac{dp}{dz}$$

In the case of water vapor in adsorptive states of flow[3] the equation describes the results probably within the experimental error (see Fig. 1). The equation also describes the flow of rates of vapors of methanol, ethyl chloride, diethyl ether and benzene quite well. However, the experiments (9) indicate that the temperature coefficient of the viscosity of adsorbed water is somewhat higher than that of liquid water especially at temperatures below 0 C and hence that the viscosity itself is probably appreciably greater at room temperature than that of ordinary water. This might be expected if the surface forces fall off rapidly with distance so that the deformation accompanying the laminar flow state involves work against the surface forces.

Where ρ_a is relatively low and the adsorbed material largely gaseous in character the flow equation becomes more involved. However at very low equilibrium gas pressures where even the adsorbed material behaves largely as an ideal gas, if $\rho_a >> \rho$, the last two terms may vanish and the flow become virtually a molecular effusion or a "surface diffusion" through the micropore system alone. The terms B and C refer of course to the macropore system while A refers to the micropore system. If the distributions of pore sizes are known, as well as their shapes, etc., the equation can be used for estimating pore sizes of both micropores and macropores. For a macropore system of parallel capillary passages B contains $N\overline{r^4}$ while C contains $N\overline{r^3}$. When the frequency distribution of pore radii of the macropore system is of the form $N(r) = Nhe^{-hr}$, then $\overline{r^4} = 4\overline{r^3} = 24\overline{r^4}$.

STRESSES AND STRAINS

The basic thermodynamic equations enable one to estimate the solid stresses resulting from the adsorption reaction. The volumetric mean stress intensity of the solid is given by (10, 11, 12)

$$\overline{p}_c^{\,v} = \left[1 + \frac{v_a}{v_c}(1-a)\right]P$$

where v_a is the void volume and v_c the solid volume so that the total volume of the porous body is $v_a + v_c$ and as before, $\overline{p}_a = aP$. The linear mean stress intensity may be written

$$\overline{p}_c^{\,L} = \left[1 + K_p \cdot K_s \frac{v_a}{v_c}(1-a)\right]P$$

Figure 1. Flow rates of water vapour through the micropore system of an activated carbon rod; adsorption state. (By permission of the Canadian Journal of Chemistry).

where K_s is a numerical constant which is in general greater than unity (usually about 3) which measures the variation in solid cross-section of typical linear filaments of the solid. K_p is a statistical correlation factor which may be greater or less than unity (usually less) but which approaches unity at high adsorbate densities. Since the elongation accompanying an adsorption reaction is given by $\partial l/l = -\beta \partial \overline{p}_c^{\,L}$ where β is roughly $\frac{1}{3}$ of the bulk compressibility of the solid, the dimensional changes may be used as a rough measure of

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[3] Where hysteresis occurs there will be a difference in flow rates between adsorption and desorption states. Adsorption states are obtained by exposing the sample to gradually increasing gas pressures equilibrating at the desired output pressure, then increasing and maintaining constant the pressure on the input side until a steady state of flow is reached. The desorption state by decreasing the gas pressure from saturation to the input pressure equilibrating at the input pressure and then lowering the output pressure, etc.

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$\overline{p}_a$ and hence of the adsorption potential.[4] This might prove of value in cases where for practical reasons adsorption isotherms cannot be measured directly e.g., oils of very low vapour pressure.

It may be remarked that one must be careful in the use of spreading pressures such as $\overline{p}_a$ in estimating say the tendency of a paint film to be "lifted" from a porous body by moisture since the "spreading pressure" of the paint film may actually exceed that of the water. Where adsorbed layers of two different materials are completely immiscible everywhere in the surface region the tendency of one to displace the other will be measured by the difference of their spreading pressures.

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[4] Where the solid and fluid are practically incompressible the entropy of the system adsorbent-adsorbate (the adsorbent being completely filled with fluid) and the sum of the entropies of the two separately should be practically the same in many cases. In such cases the adsorption or surface potential will appear wholly as an energy and the heat of immersion will provide a measure of the adsorption potential. In general, the heat of immersion will vary for different fluids, i.e., the surface potential is not due wholly to the surface free energy of the solid alone by any means.

Mechanism of Soil Moisture Extraction from a Pressure-Membrane Apparatus

HITOSHI FUKUDA, Professor of Irrigation and Drainage, Faculty of Agriculture, University of Tokyo, Japan

Introductory Remarks by Chairman

Modern science is based on observations and measurements. To use the latter properly one must know what is measured, how reproducible the measurements are, what sources of deviations exist, and how to correct for known sources of deviations. This means that one must know as well as possible what is going on within the apparatus, whether the measurements really answer the requirements, what accuracy of measurement is obtained, and whether or not corrections of the raw data are called for. Professor Fukuda has made a significant contribution to the symposium by analyzing theoretically and experimentally what goes on when soil moisture is extracted in a pressure-membrane apparatus.

● FOR ONE of the fundamental studies of irrigation, soil moisture tension can be measured by a pressure-membrane apparatus developed by Richards.[1]

In the apparatus the soil from which moisture is to be removed is placed in a chamber in which nitrogen gas pressure is increased above atmospheric pressure.

The side of the chamber which supports the soil consists of a cellophane membrane supported on a brass screen and a brass plate in such a way that any moisture passing through the membrane is conducted away. Thus it is considered, that the moisture content of the soil in contact with the membrane will be reduced by the amount that would be necessary under normal atmospheric conditions to make the pressure deficiency of the soil water equal to the excess gas pressure in the extracted chamber.

This paper deals with a mechanism by which soil moisture is to be extracted through the cellophane membrane.

Conditions of Soil Moisture in a Pressure-Membrane Apparatus

As a quantity to express soil moisture content, an equivalent height h is used here, which means the height above the ground water level. At this height the soil moisture in equilibrium is assumed to be constant, hence instead of moisture content the height h is used to express this factor.

Taking out a part of such soil (Fig. 1), and considering p_w, and p as a pressure in meniscus and out of it respectively, gives:

Figure 1. Pressures p_w, p in meniscus and out of it, respectively.

$$p - p_w = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \qquad (1)$$

where R_1, R_2 are the principal radii of curvature, σ being surface tension or water.

At the ground water surface, water and air pressures are both one atmosphere (p_0). In Figure 1, when soil is at the height h above the ground water:
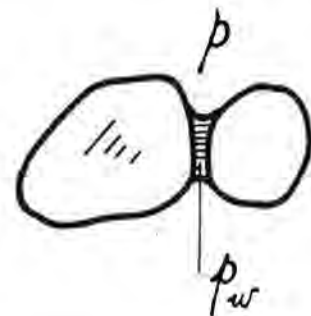
[1] Richards, L. A., "A Pressure-Membrane Extraction Apparatus for Soil Solution." Soil Sci., 51:2, (1941).

$$p = p_0 \, e^{-\dfrac{M_a \, g \, h}{R \, T}} \qquad (2)$$

$$p_w = p_0 - \rho_w \, g \, h \qquad (3)$$

where M_a = molecular weight of air $\doteq$ 29, ρ_w = density of water = 1 gr/cm³, R = gas constant = 8.34 x 10⁷ erg/mol. deg, T = absolute temperature, g = acceleration of gravity = 980 cm/sec.², equation 2 is a so-called barometric formula and equation 3 a hydrostatic one. It could be considered for soil moisture in Figure 1 to have a direct contact with ground water through a small pipe.

Supposing the soil in Figure 1 put in a pressure-membrane apparatus, in which a pressure P is applied (Fig. 2), to keep the same moisture condition with that in Figure 1, a pressure in meniscus must be one atmosphere (p_0). It is now considered that the outside of the apparatus is saturated with vapor and kept in equilibrium with water under atmospheric pressure, and also at this condition water drops are expected to be on the outer surface of the membrane. As water can flow easily through the membrane, water pressure becomes p_0 by the hydrostatic relation just like equation 3.

Because the geometrical form of soil moisture in Figure 2 is the same as that in Figure 1,

$$P - p_0 = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \qquad (4)$$
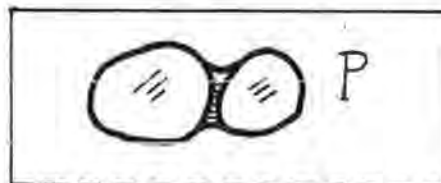
Figure 2. Pressure P in the chamber around soil particles.

From equations 1 and 4

$$P - p_0 = p - p_w$$

Substituting equations 2 and 3,

$$P - p_0 = p_0 e^{-\dfrac{M_a \, g \, h}{RT}} - (p_0 - \rho_w g h)$$

$$= \rho_w g h - p_0 \left(1 - e^{-\dfrac{M_a \, g \, h}{RT}} \right)$$

Dividing both sides of this equation by p_0, and putting $p_0 / \rho_w \, g$ = 1,034 cm =h. (water head equivalent of one atmosphere of pressure), gives

$$\frac{P - p_0}{p_0} = \frac{h}{h_0} - \left(1 - e^{-\dfrac{M_a \, g \, h}{R \, T}} \right) \qquad (5)$$

in which the left side shows an excess pressure in the apparatus expressed in units of atmospheric pressure, the first term and the right is an equivalent height based on h_0, and the second right hand term is a small correction and almost negligible in the ordinary conditions as shown in Table 1.

TABLE 1

RELATION BETWEEN h/h_0 AND $(P - p_0) / p_0$

h/h_0	0	1	10	100	1,000	10,000
$(P - p_0)/p_0$	0	0.9988	9.988	99.89	999.3	9,999

Water Extraction Into Saturated Air Out of the Apparatus

When soil moisture is so plentiful as to make all capillary water connect with each other and keep good contact with the other side (pressure = p_0) of the apparatus through cellophane membrane, it is easily understood that, by increasing the pressure in the apparatus, the pressure in the capillary water exceeds p_0, the pressure outside the apparatus; hence, soil water flows out through the membrane.

Even when soil moisture decreases, and the connection between capillary water disappears, the fact of water flowing out through the membrane under a higher pressure may be explained as follows: By vapor pressure is meant physically that pressure condition at which a surface of water is in equilibrium with its own vapor; the vapor pressure of water will tend to increase in case of the vapor coexisting with another gas (for example air).

Now, when air is pushed into the apparatus containing wet soil, the vapor pressure of water increases; since the water holding capacity of the air in the chamber increases with increasing air pressure soil water begins to evaporate. When the vapor pressure in the apparatus exceeds that on the outside, vapor goes out through the membrane and condenses outside if the air outside the apparatus is saturated with water vapor. As water goes out in that way, soil moisture decreases and the radii of curvature in the capillary water become smaller, also the vapor pressure decreases until it becomes equal to that outside. At that point water extraction stops. Thus the moisture inside and outside of the apparatus remains in equilibrium as a result of the exchange of water vapor. Starting from this concept, equation 5 can be obtained purely from thermodynamical considerations.

Water Extraction Into Unsaturated Air Out of the Apparatus

In this case equation 4 must be slightly modified. Supposing a small tube in the membrane shown in Figure 3, which has a water pressure p'. As this water is in equilibrium with capillary water, the pressure in the capillary water must be p' too.

Thus, instead of equation 4:

$$P - p' = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \qquad (6)$$

and instead of equation 5 there is obtained:

$$\frac{P - p'}{p_0} = \frac{h}{h_0} - \left(1 - e^{-\frac{M_a g h}{RT}} \right) (7)$$

On the other hand, there is a relation shown by

$$p_0 - p' = \sigma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \qquad (8)$$

between pressure p_0 outside of the membrane and p' in a small tube, where r_1, r_2 are radii of curvature of the water surface in this small tube.

Now, generally there is a relation[2]:

Figure 3. Pressures P, p' and p_0 in the chamber, Cellophane membrane and out of it respectively.

$$-\frac{\rho_W RT}{M_W} \ln \frac{p_v}{p_{v_0}} = \sigma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \qquad (9)$$

between vapor pressure p_v on a curved water surface and p_{v_0} on a plane one, where M_W = molecular weight of water, ρ_W = density of water.

Substituting equation 9 into equation 8, and setting $p_v / p_{v_0} = \phi$, the relative humidity outside of the apparatus, gives

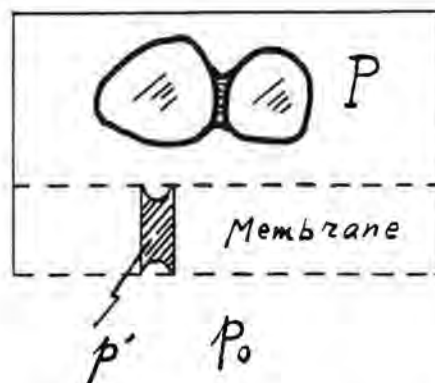$$p_0 - p' = -\frac{\rho_W RT}{M_W} \ln \phi$$

[2] Edlefsen, N. E. and Anderson, A. B. C., "Thermodynamics of Soil Moisture." Hilgardia, 15:2, 145 (Eq. 272) (1943).

$$\frac{p_0 - p'}{p_0} = - \frac{\rho_W RT}{M_W p_0} \ln \phi$$

$$= - \frac{\rho_W}{M_W} \cdot \frac{M_a}{\rho_a} \ln \phi$$

$$\frac{p_0 - p'}{p_0} = \frac{-22400}{18} \cdot \frac{T}{T_0} \ln \phi \qquad (10)$$

where ρ_a is the air density under atmospheric pressure and temperature T, and T_0 = 273.

From equations 10 and 7, neglecting the second right hand term in equation 7, gives

$$\frac{P - p_0}{p_0} = \frac{h}{h_0} + 1250 \frac{T}{T_0} \ln \phi \qquad (11)$$

in which the second term right is a correction for relative humidity and temperature. Because of the large numerical coefficient, this correction becomes exceedingly large; for example, when $\phi = 0.9$, the correction is 130. Thus, it can be understood that the outside of the membrane should be surrounded by saturated air to get the accurate amount of soil moisture to remain in equilibrium with the applied pressure in the apparatus.

In equation 11, when $P = p_0$, gives

$$h = - \left(1250 \frac{T}{T_0} \ln \phi \right) h_0 \qquad (12)$$

The effects of humidity and temperature expressed by this equation are shown graphically in Figure 4. This figure shows that humidity has a much greater influence than temperature.

In the apparatus commonly used, it can be expected that the space between the cellophane membrane and a brass screen under it, shown in Figure 5, to be always

Figure 5. Section of pressure-membrane apparatus.

Figure 4. Relation between equivalent height h m. and relative humidity.

saturated; if this is the case, then $\ln \phi = 0$ in equation 11 and there will be no effect on the soil moisture remaining in the chamber, of any changes in humidity and temperature outside of the apparatus.

To prove this assumption experimentally, humidity changes at a pressure of ten atmospheres and temperature change at a pressure of 15 atmospheres were considered. The amounts of soil moisture remaining in equilibrium are shown in Table 2 and 3 respectively.

To maintain a saturated condition outside of the apparatus (100 percent in

Table 2), the extracted water passed through a copper tube into a burette filled with water, thus the effect of humidity change can be eliminated. For the relative humidity of 70 percent the copper tube was connected with air possessing a relative humidity of 70 percent.

Table 3 gives the measured amounts of soil moisture remaining in the apparatus, which was kept at various air temperatures; the extracted water always passed into a burette filled with water.

Thus, from the results shown in Table 2 and 3 we can see no practical effects of humidity and temperature on soil moisture in equilibrium with the gas pressure inside the apparatus; but it would increase the stability of the experiment to connect a copper tube outlet with a burette with water for keeping a saturated condition outside of the pressure membrane.

TABLE 2

EFFECT OF AIR HUMIDITY OUTSIDE OF THE APPARATUS ON SOIL MOISTURE IN EQUILIBRIUM WITH PRESSURE, 10 ATMOSPHERES

Soil	Relative Humidity out of the Apparatus, %		Room Temperature
	100	70	C
Volcanic ashy loam	25.3	25.4	21.0 — 22.5
Sandy loam	5.54⁻	5.52	22.0 — 22.5

TABLE 3

EFFECT OF AIR TEMPERATURE ON SOIL MOISTURE EQUILIBRIUM WITH PRESSURE, 15 ATMOSPHERES

Soil	Structure	Diameter mm.	Room Temperature C			
			10.5-14.0	13-14	30-32	40-41
Clay	Single	< 0.25	22.0	22.8	20.9	20.6
	Granular	< 2.0	20.0	20.1	19.5	19.1
Volcanic ashy loam	Single	< 0.5	25.9	26.2	25.3	24.9
	Granular	< 0.5	31.8	31.6	30.2	29.3
Sandy loam	Single	< 0.5	5.0	4.9	4.6	4.6
	Granular	< 0.5	5.2	5.2	5.2	4.9

SUMMARY

In this paper a mechanism by which soil moisture is extracted in the case of the pressure-membrane apparatus developed by Richards was considered theoretically and the effects of air humidity and room temperature outside the apparatus on soil moisture in equilibrium with various pressures inside the apparatus were proved experimentally to be of little importance.

Mathematics of Isothermal Water Conduction in Unsaturated Soil

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Introductory Remarks by the Chairman

"I believe the day must come when the biologist will—without being a mathematician—not hesitate to use mathematical analysis when he requires it." This statement was made by Karl Pearson in the January 17, 1901, issue of "Nature." The day has come, indeed, not only for the biologist but also for his brother the soil scientist, as the author proves in his excellent contribution to this symposium. It may be appropriate to supplement Pearson's words by the following remarks which Dr. Johnson made in the fourteenth "Rambler," May 5, 1750: "The mathematicians are well acquainted with the difference between pure science, which has to do only with ideas, and the application of its laws to the use of life, in which they are constrained to submit to the imperfections of matter and the influence of accident."

● THE RATE of water movement in soil is of considerable importance in agriculture and is being actively investigated. The physical properties of soils influence water movement in two important ways. The sizes and structural arrangement of the soil particles determine the space configuration through which water moves, and the interaction between the soil and the soil water gives rise to water-moving forces. In soils in which the pores are completely filled with water, the fluid is a single phase. Forces originating from gravity, including the pressure gradient, determine the flow. The saturated flow process is described mathematically by Darcy's law and Laplace's equation.

It is more often the case in agricultural soils that the pores are not completely filled with water and the potential of the water depends not only upon its position in the gravitational field, but also upon adsorptive force fields associated with interfacial boundaries. The imbibition or retention of water by soil is due to a number of mechanisms which can be only briefly mentioned here. The total potential can be conveniently expressed as the sum of a gravitational potential, an osmotic potential, and a capillary potential. The osmotic term is usually omitted in considering water movement because the solutes generally move more readily than the water with respect to the soil. Of most concern is the capillary potential which here includes all the contributions from the various sorption mechanisms. These mechanisms are discussed in detail elsewhere and will not be elaborated upon. The capillary potential is often expressed in terms of the soil suction, or soil-moisture tension. The soil suction is defined as the pressure difference required across a permeable membrane to produce hydraulic equilibrium between soil water that is subject to surface-force action and free water that is not subject to surface-force action.

Permeable membranes are usually employed in the measurement of this suction. In the tensiometer, a manometer is connected to a porous cup placed in the soil. The water in the manometer is connected to the soil water through the porous cup. The soil suction is frequently expressed in terms of the height of a column of water which can be supported by the soil water and in equilibrium with it. This instrument cannot normally be used for suctions above about 800 cm of water, and for the higher suctions, Richards (19, 20) has developed the pressure membrane and pressure plate apparatus. In these apparatus, the soil is placed in a chamber on a porous membrane and air pressure applied to the chamber. Water flows between the soil and free water outside the chamber until equilibrium is attained. The pressure in the chamber is a measure

of the suction and the water content can be obtained, thus giving a functional relationship between water content and potential. A knowledge of the suction as a function of water content is extremely useful in understanding the retention and transmission of water by any given soil. Figure 1 shows the water retention plotted as a function of suction for three representative soils, Chino clay, Indio loam, and Pachappa sandy loam.

The freezing point depression of the soil water has been used to measure the potential, and methods for measuring the vapor pressure of the soil water which are now being developed should prove extremely valuable in potential measurements. These measurements include the osmotic term.

THE FLOW EQUATION

Water in the soil moves in response to potential differences and in the direction of decreasing potential. The basis of the theory of unsaturated flow is the assumption that the volume flux of water per unit area perpendicular to the direction of flow is directly proportional to the potential gradient. This gives an expression analogous to Darcy's law for saturated flow

Figure 1. Soil suction as a function of water content for three representative soils, Indio loam, Pachappa sandy loam, and Chino clay. Data is for the desorption cycle.

$$v = k \nabla \phi \tag{1}$$

where v is the volume flux and ϕ the potential. Mathematically, this expression differs from Darcy's law only in that the quantity k, the capillary conductivity or unsaturated permeability, is not constant but is a function of the soil-water content or the suction.

The movement of water must also obey the principle of conservation of matter, which is expressed in the equation of continuity

$$\frac{\partial \theta}{\partial t} = -\nabla \cdot v \tag{2}$$

where θ is the water content on a volume basis and t is the time. Combining Eqs. 1 and 2 gives the flow equation

$$\frac{\partial \theta}{\partial t} = -\nabla \cdot k \nabla \phi \tag{3}$$

It is usually convenient to separate the total potential into the gravitational and capillary potentials as in Eq. 4

$$\frac{\partial \theta}{\partial t} = -\nabla \cdot k \nabla \psi + \frac{\partial k}{\partial z} \tag{4}$$

where ψ is the suction.

As in the case of saturated flow, the description of the water movement in a soil system becomes a matter of establishing the boundaries of the system, specifying the conditions at these boundaries and at the initial time, and then solving the partial differential Eq. 4 subject to these boundary and initial conditions. To do this, it is necessary to know the functional relationships between the water content, the suction, and the capillary conductivity. This requires the use of single-valued functions, which can be obtained if the water content always decreases or increases, but which may have to be approximated otherwise because of hysteresis in the water content-suction curve.
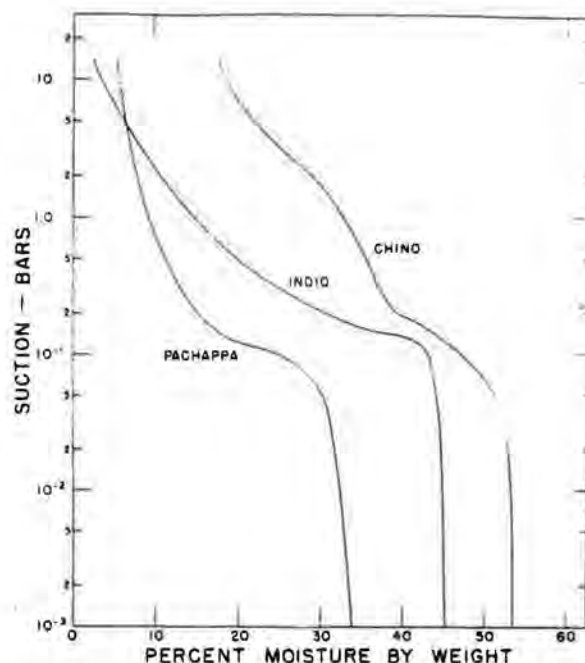
The problem is further complicated if inhomogeneities or temperature gradients are present, since the suction may then also depend upon position and temperature. This discussion will be restricted to isothermal homogeneous systems. Then either ψ or θ may be eliminated from Eq. 4 and the other used as the dependent variable, with x, y, z, and t as the independent variables. If the potential is eliminated from Eq. 4

$$\frac{\partial \theta}{\partial t} = \nabla \cdot D\nabla\theta + \frac{\partial k}{\partial z} \tag{5}$$

where

$$D(\theta) = -k \, (\partial\psi/\partial\theta) \tag{6}$$

For horizontal flow the last term on the right hand side of Eq. 5 is omitted and Eq. 5 is identical in form with the well-known diffusion equation, and $D(\theta)$ is called the diffusivity. This does not, however, imply that the mechanism of water movement is diffusion in the same sense as diffusion in gases, liquids, or solids due to random molecular motion. Several mechanisms are probably involved, depending upon the water content and the nature of the soil particles and their arrangement. Vapor movement is included in the equation to the extent that the water vapor is in equilibrium with the liquid water in the surrounding pore. Attempts are being made to elucidate these mechanisms through studies of the dependence of k and D upon water content, temperature, and soil properties, such as, specific surface, surface charge density, exchange cation, and clay type.

THE MEASUREMENT OF CONDUCTIVITY AND DIFFUSIVITY

The capillary conductivity and diffusivity vary markedly as a function of water content within a given soil and from soil to soil. Many of the features which characterize unsaturated flow are due to the extent of this variation. The fact that these quantities vary with water content makes them somewhat difficult to measure directly. Steady state measurements of k can be made fairly readily within the tensiometer range by a method used by Moore (11). In this method a water table is maintained at the bottom of a column of soil and evaporation is allowed to take place at the top. When evaporation is steady, the suction gradient is measured by means of tensiometers in the column and the flux is given by the evaporation rate. A wide range of suction values can be obtained within columns about 100 cm long. At suctions above the tensiometer range, indirect methods are required. Richards and Moore (21) placed the soil samples in a pressure chamber and by applying appropriate pressures raised the pressure in the soil water to atmospheric so that manometers could be used to measure the potential differences. A similar procedure was employed by Corey (2), who measured simultaneous movement of water and air. Measurements of D or k in transient systems ordinarily require numerical or graphical solution of the flow equation, as was done by Bruce and Klute (1) and Richards and Weeks (22). For measurements in the field, it is most convenient to replace the flow equation by a finite difference equation. Such a procedure was used by Staple and Lehane (23).
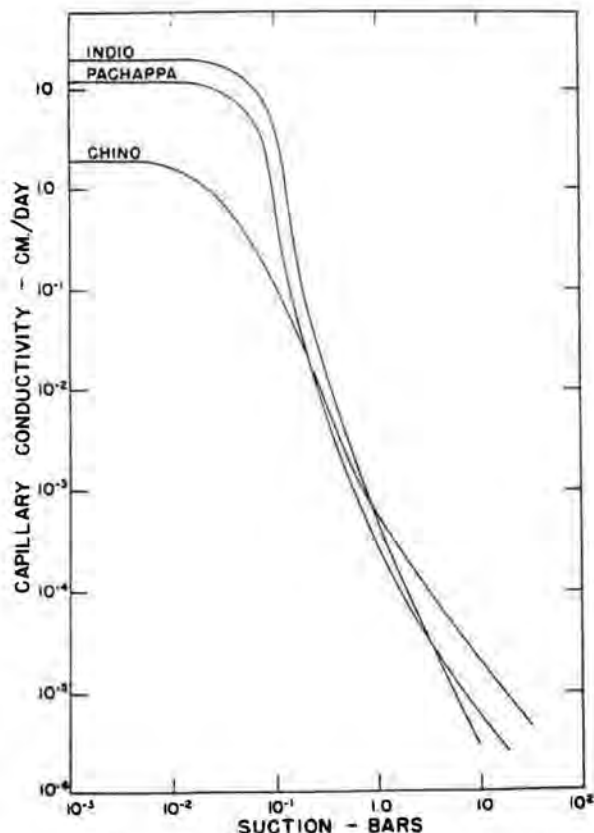

Figure 2. Capillary conductivity of three soils plotted as a function of soil suction on a log-log scale.

In a method developed by this author (4) and extended by Miller and Elrick (10), the flow equation is solved for the removal of water from a soil in the pressure plate apparatus. The water content is changed by small increments so that the diffusivity can be assumed to be constant during this change. The diffusivity and the conductivity can then be calculated from the rate and quantity of outflow. Figure 2 shows conductivity data obtained in this manner plotted as a function of suction. The many-fold variation of conductivity with suction is readily noted. While the coarser textured soils have higher conductivities at the low suctions, their conductivities drop off much more rapidly with increasing suction and are generally less than for the finer textured soils at the higher suctions. For a number of soils studied, the conductivity can be related to the suction quite well by an expression of the form

$$k = \frac{a}{S^n + b} \qquad (7)$$

Figure 3. Diffusivity of three soils plotted as a function of water content by weight on a semi-log plot.

where S is the suction, and a, b, and n are constants. The ratio a/b is equal to the saturated permeability. For most soils, n seems to lie between 1 and 4, although for sands of fairly large uniform particles it may become considerably larger. In Figure 2 a value of n = 2 for the Chino clay and n = 3 for the Pachappa sandy loam approximates the data quite well.

Figure 3 shows the diffusivities for these same three soils plotted as a function of water content on a weight basis. The diffusivity varies over a wide range of values also but not quite to the extent that the conductivity does. In addition to the soils represented in Figure 3, the diffusivities of several other soils can be related to the moisture content by an exponential function

$$D = D_0 \exp \beta(\theta - \theta_0) \qquad (8)$$

where D_0 is the diffusivity when $\theta = \theta_0$ and β is a constant.

If either k or D is known, the other can be calculated from the retention curve by means of Eq. 6.

SOLUTION OF THE FLOW EQUATION

Analytical solutions of the flow equation cannot be hoped for except in a very few instances. Where Eq. 7 is applicable, it may be possible to integrate the flow equation for some steady state problems. Even if Eq. 7 is only very approximate, it may be possible to set limits on the flow process and obtain useful results. For the most part, particularly for transient problems, numerical methods of solution of the flow equation will be necessary. Such methods also offer the only real possibility of treating inhomogeneous and nonisothermal systems. Developments in the solution of the flow equation for transient problems have followed closely the treatment of nonlinear diffusion in other fields (3). Only a few generalizations will be considered.
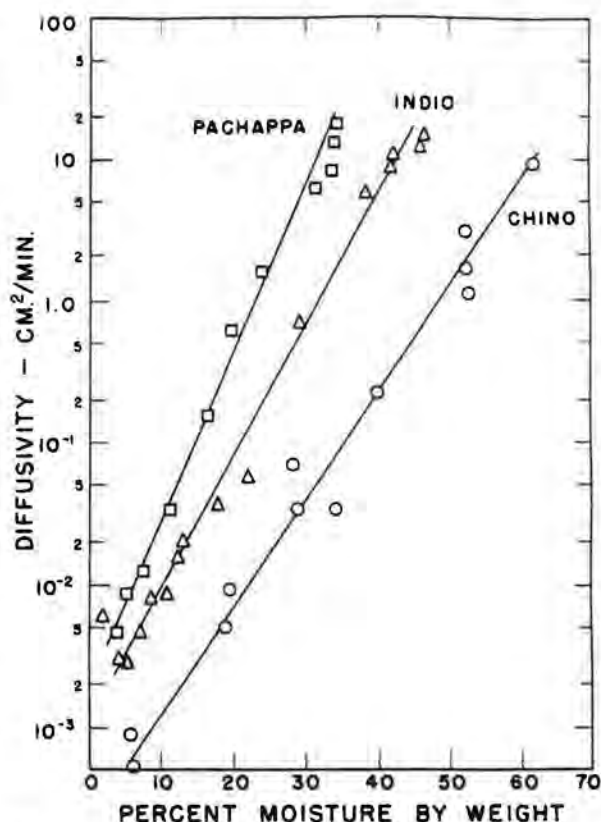
Steady State Problems

For steady state conditions $\partial\theta/\partial t = 0$, and Eq. 5 becomes

$$-\nabla \cdot k\nabla S + \frac{\partial k}{\partial z} = 0 \tag{9}$$

This equation can be solved by replacing Eq. 9 by a finite difference equation and using a relaxation procedure. This Luthin and Day (9) did in a study of flow above a sloping water table. In treating two and three dimensional problems, it is sometimes helpful to define a new variable

$$U = \int_{S_0}^{S} k\,dS = \int_{\theta_0}^{\theta} D\,d\theta \tag{10}$$

where this integration may be performed numerically if necessary. Introduction of this variable into Eq. 9 gives

$$\nabla^2 U + \left(\frac{\partial k}{\partial U}\right)\frac{\partial U}{\partial z} = 0 \tag{11}$$

and the boundary conditions are also transformed in terms of $U(x, y, z)$. When the gravitational term is negligible, Eq. 11 reduces to Laplace's equation for which solutions for the appropriate boundary conditions may be available. When the gravitational term is not negligible, Eq. 11 may be separated into three equations, one for each dimension, by the method of separation of variables.

For one dimensional flow, the problem is considerably simplified. Eq. 9 then becomes

$$\frac{d}{dz}\left[k\left(\frac{dS}{dz}-1\right)\right] = 0 \tag{12}$$

Integration of Eq. 12 once gives

$$k\left(\frac{dS}{dz}-1\right) = q \tag{13}$$

where the constant of integration, q, represents the flux per unit area. Solving for z then gives

$$z = \int\frac{dS}{1 + q/k} \tag{14}$$

If k is known as a function of S this integration can be performed, numerically if necessary, and analytically for some cases (5).

Nonsteady State Problems

Methods of solving the diffusion equation for variable diffusivity have been discussed by Crank (3) and will not be considered in any detail. In infinite or semi-infinite systems with certain boundary conditions, the Boltzmann transformation is useful. A new variable

$$y = x/2\sqrt{D_0\,t} \tag{15}$$

reduces the partial differential equation to an ordinary differential equation which is more readily solved numerically. For uniform initial conditions and a constant boundary condition, Philip (12) has developed a rapid method of solution which he has recently extended to include the gravitational term (13). For finite systems, replacement of the partial differential equation by a finite difference equation as in the Crank-Nicolson method (3, p. 207) is most promising. The increased availability of high speed computing devices offers the greatest hope that solution of many of the unsaturated flow problems will become feasible. To date such devices have received only limited use in the solution of soil waterflow problems.

SOLUTIONS OF SOME PARTICULAR FLOW PROBLEMS

Quantitative studies on unsaturated flow in soils have been directed mainly to investigations of the relative importance of various flow mechanisms and to testing the validity of Eq. 1. Of those few boundary problems for which solutions have been attempted, three will be mentioned here: (a) the entry of water into a soil at uniform initial water content, (b) the steady state evaporation of water from a soil in which there is a water table, and (c) the drying of a soil at uniform initial water content.

Entry of Water into Soil

The infiltration of water into soil has been treated in considerable detail by Philip (14, 15, 16, 17, 18). In the early stages of infiltration, the gravitational term in the equation is negligible. Introduction of the Boltzmann transformation into the flow equation for a semi-infinite system gives the ordinary differential equation

$$- \frac{y}{2} \left(\frac{d\theta}{dy} \right) = \frac{d}{dy} \left(\frac{D}{D_0} \frac{d\theta}{dy} \right) \tag{16}$$

The water content, θ, is now a function of y only. For a given θ, say, that just back of the wetting front, x is proportional to $\sqrt{t}$. This explains the fact that the distance to the wetting front during infiltration is observed to increase as $\sqrt{t}$, or very nearly so. It can further be shown that the rate of entry of water into the soil is inversely proportional to $\sqrt{t}$. This relationship holds for any dependence of D on θ for horizontal flow and the early stages of vertical flow if the initial water content is uniform. Using Philip's method, the author has obtained numerical solutions of Eq. 16 for exponential diffusivities (7). Figure 4 shows the water content distribution in horizontal samples of Chino clay for three different initial water contents compared with numerical solutions of the flow equation.
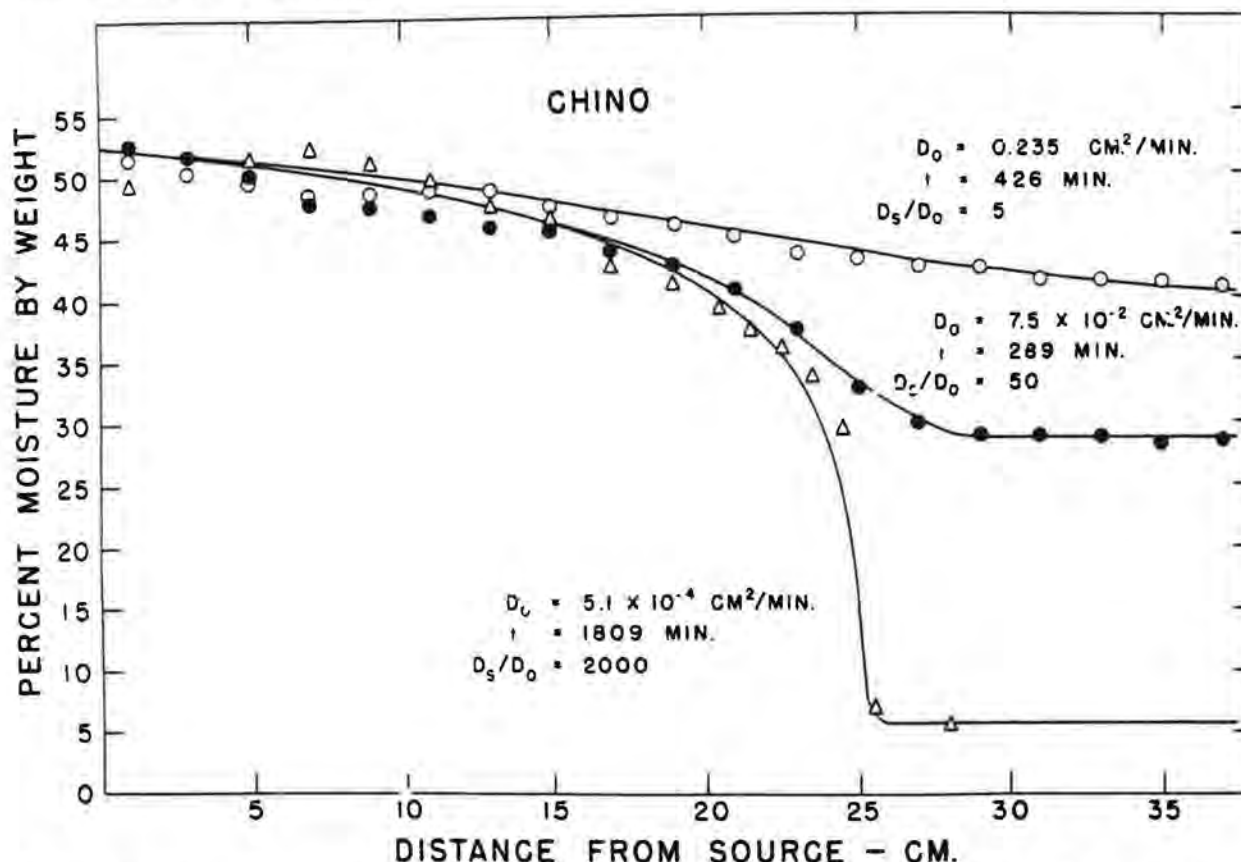

Figure 4. Water content distribution during horizontal flow of Chino clay for three different initial water contents. D_s is the diffusivity at saturation and D_0 the diffusivity at the initial water content. The smooth curves represent theoretical solutions of the flow equation for an exponential diffusivity-water content relation.

The results are somewhat modified when the gravitational term is included and this term increases in importance with time. Philip (14) showed that for this case x can be represented as a power series in $\sqrt{t}$ with the coefficients functions of (θ)

$$x = \sum_{m=1}^{\infty} f_m(\theta) t^{m/2} \quad (17)$$

and likewise the cumulative infiltration can be represented by a similar power series

$$Q = \sum_{m=1}^{\infty} a_m(\theta) t^{m/2} \quad (18)$$

Figure 5. Relative rate of evaporation from a soil as a function of the suction at the soil surface for the case $k = a/(S^3 + b)$ and with a water table 180 cm below the soil surface.

where the a_m are again functions of θ, k, and D. For most soils, this series converges rapidly and only the first two or three terms are needed. Philip also relates the solution of the equation to several useful but more nearly empirical infiltration equations (17).

Steady State Evaporation

The upward movement of water in a soil from a water table and its evaporation at the surface under steady state conditions can be described by solving Eq. 15. This has been done for several cases when Eq. 7 is obeyed and the constant n in that equation is an integer (5, 6). For values of n greater than one, the general features of the solutions are similar. Figure 5 shows the relative evaporation rate calculated for a soil for which n = 3 with a water table 180 cm below the soil surface. A low suction value at the soil surface occurs when the potential evaporation due to external conditions is relatively low and evaporation under these circumstances is controlled by the external conditions. However, as the potential evaporation, and therefore the suction at the soil surface, increases, the rate of evaporation from the soil rapidly increases until it approaches a limiting value. This limiting value is virtually attained by the time the suction at the soil surface reaches 1 or 2 bars. Thus, evaporation is limited by the potential external evaporation or the limiting rate of upward movement, whichever is the smaller.

The limiting rate of upward movement decreases with increasing depth to the water table and is given by

$$q_{lim} = \frac{A_n a}{d^n} \quad (19)$$

where a is the constant in Eq. 7, d is the depth to the water table and A_n is a constant determined from the solution of the flow equation. The movement of water in the vapor form near the soil surface can be taken into account in a simple approximate manner (5). This has the effect of increasing A_n by a factor of probably not more than 10 to 15 percent.

The results indicate that the exact dependence of the conductivity on the suction is not critical, particularly at the higher suctions, and small deviations from Eq. 7 do not affect the results appreciably. If the soil profile is not homogeneous, as is probable, it can often be treated as a composite of several homogeneous layers and with the solutions for adjacent layers matched at their common boundary.

The Drying of Soils

The diffusion equation has been applied to the drying of clays and other porous media by a number of workers. Except for the study by van Vorst (24) the variation
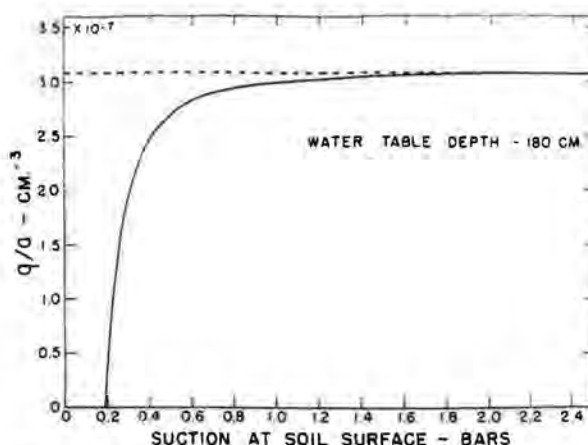
of the diffusivity with moisture content has not usually been introduced into the equations.

Certain analogies can be made with the case of steady state evaporation. In the early stages of the drying of a soil, the rate of evaporation is limited by the external conditions and if these are constant the evaporation rate is constant. In order to maintain this constant rate, the water content gradient through the soil increases with time and the water content at the boundary decreases. When the water content at this boundary reaches a value in equilibrium with the atmosphere, the constant drying rate can no longer be maintained and the drying rate then falls off. The length of time the rate is constant depends upon the magnitude of the rate and the properties of the soil. Under high evaporative conditions, this rate can be maintained for only a day or so by many soils. The maximum rate drying is achieved when the water content at the surface is brought immediately to the equilibrium value. In practice, this may be approached but can be achieved only by an infinitely high initial evaporation rate.

As in the case of water entry, application of the Boltzmann transformation to the equation for the drying of a semi-infinite soil sample in the absence of gravity, allows certain generalizations. It can be shown that the maximum accumulative evaporation should increase as $\sqrt{t}$ if the initial water distribution is uniform. Crank (3, p. 256) points out that desorption processes can be described by a weighted mean diffusivity of the form

$$\overline{D} = \frac{1.85}{(\theta_i)^{1.85}} \int_0^{\theta_i} (\theta_i - \theta)^{.85} D(\theta) \, d\theta \tag{21}$$

while, similarly, sorption processes can be described by a different weighted mean diffusivity
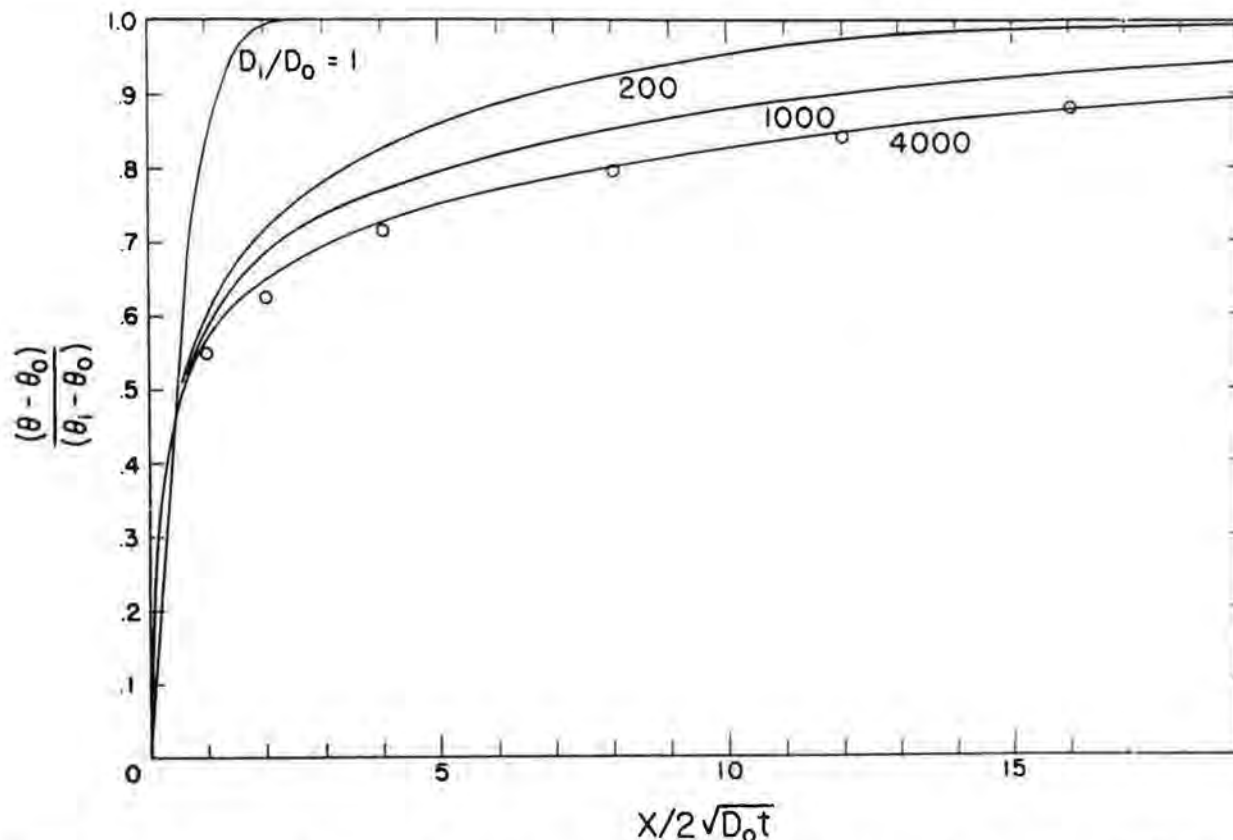

Figure 6. Theoretical relative water content distribution during drying of an infinite soil plotted as a function of the reduced variable $x/2\sqrt{D_o t}$, for exponential diffusivities. θ_i is the initial water content, θ_o is the water content at the surface and D_i and D_o are the corresponding diffusivities. Gravity is neglected.

$$\overline{D} = \frac{5}{3(\theta_i)^{5/3}} \int_0^{\theta_i} \theta^{2/3} D(\theta) \, d\theta \qquad (22)$$

for a variety of diffusivity-concentration relations, including exponential. The higher diffusivities are weighted more heavily for the sorption than the desorption, so, for corresponding initial and final water contents, a soil will absorb water more rapidly than it will evaporate it. The greater the variation of diffusivity with water content the more marked this difference in rates. Philip (14) suggests that his method of solution of the flow equation can also be used to treat drying of soils when gravity is taken into account. A solution for this case has not yet been carried out, however, solutions have been obtained for the horizontal case for an exponential diffusivity (8). The solution for the semi-infinite case applies also to the early stages of evaporation from a finite soil.

Figure 6 shows the distribution of water in a semi-infinite soil sample with initial water content θ_i and with the surface at $x = 0$ maintained at water content θ_0.

Figure 7. The theoretical fractional loss of water from a finite soil sample plotted as a function of the reduced dimensionless variable $\sqrt{D_0 \, t/L^2}$ where L is the length of the sample. Each curve is for a different value of the ratio D_i/D_0 when D is an exponential function of water content. Gravity is neglected.

Curves for several different ratios D_i/D_0 are given, where D_i is the diffusivity at water content θ_i, and D_0 the diffusivity at water content θ_0. Using a finite difference form of the flow equation, solutions have been obtained for the drying of a finite sample for an exponential diffusivity. Some of these solutions are shown in Figure 7 where the relative loss of water from the entire sample is plotted as a function of a convenient dimensionless ratio $(D_0 \, t/L^2)^{1/2}$ where L is the length of the sample. Curves for several ratios of D_i/D_0 are represented.

It is to be expected that for evaporation from a soil profile these curves will be somewhat modified by the inclusion of gravity, which tends to decrease the evaporation rate, and vapor movement, which tends to increase it. However, the general conclusions should be valid.

DISCUSSION

In addition to helping understand unsaturated flow problems of practical importance, the flow equation and its solutions can be helpful in studying the role of various soil and water properties in their influence on water movement. The equation provides means to evaluate the diffusivity and the conductivity. Departures of real systems from theoretical solutions of the equation indicate the importance of temperature gradients, vapor movement, inhomogeneities, concentration gradients, and other effects which are usually otherwise difficult to study. Studies of the diffusivity and the conductivity as functions of water content, temperature, specific surface, particle size and arrangement, etc., should facilitate an understanding of the mechanisms involved in water movement. Although in practice it may seldom be feasible to attempt complete solutions of the flow equation, solutions for certain ideal cases can provide upper and lower limits to the rate of movement and a greater insight into flow processes.

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Soil Water Movement in the Film and Vapor Phase Under the Influence of Evapotranspiration

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Introductory Remarks by the Chairman

One of the most widely used mathematical formulations in science is the transmission equation which states that the time rate of transmission through a unit cross-section equals the product of a specific property factor of the material and the rate of change in concentration of whatever is to be transmitted in the direction normal to the area of transmission. In first approximation, this equation holds true for many different systems and materials or forms of energy to be transmitted. It represents a major part of the engineering application of the so-called energy concept of soil moisture, or rather the suction concept, since important energy considerations have often been neglected or overlooked by the more extreme practitioners of this concept. An equation, or a theoretical concept expressed by it, that has as wide a field of application as the transmission formula can be expected to possess severe limitations in a field of application in which the substance to be transmitted is able to form structures and shapes that affect the transmission process. For the case of soil and water, Dr. Hallaire investigates these limitations experimentally and theoretically in a splendid piece of work. His results are extremely important and illuminating; one of the main lessons taught is that in aqueous systems, possessing appreciable amounts of internal surface, the peculiar structural properties of water, and especially the cohesive strength of its films, must not be overlooked if one wants to develop valid and useful concepts.

GENERAL CONCEPTS

● THE RATE of water diffusion in a direction z'z is usually given by

$$\frac{dQ}{dt} = \frac{\lambda d\phi}{dz} \tag{1}$$

in which $\frac{dQ}{dt}$ = the loss in a direction z'z (which can be given in mm/day or d g/day per cm^2);

ϕ = the sum of the potentials acting on the water: the capillary potential ψ, the hydrostatic pressure potential ϕ_1, the gravity potential ϕ_2; and

λ = a conductivity coefficient which increases with increasing moisture content; that is, with decreasing capillary potential.

When the soil moisture content H (water per 100 g of dry soil) is lower than field capacity, then the capillary potential gradient ψ is usually much larger than that of the other two potentials ϕ_1, and ϕ_2, and Eq. 1 can be reduced to

$$\frac{dQ}{dt} = \lambda(\psi)\frac{d\psi}{dz} \tag{2}$$

$\lambda(\psi)$ being a decreasing function.

In the experimental or theoretical study of capillary diffusion, certain authors have

tried to express the variation of λ as a function of ψ. Others, considering a homogeneous soil and transforming Eq. 2 into

$$\frac{dQ}{dt} = \lambda(\psi)\,\frac{d\psi}{dH}\,\frac{dH}{dz} \tag{3}$$

or

$$\frac{dQ}{dt} = \Lambda\,\frac{dH}{dz} \tag{4}$$

with

$$\Lambda = \lambda(\psi)\,\frac{d\psi}{dH}$$

have endeavored to define the values of this new coefficient Λ in front of the moisture gradient $\frac{dH}{dz}$.

There are experimental techniques in which water from a free water surface is made to rise into dry soil, and there are others in which continued water movement is assured by submitting a soil column to a definite pressure gradient. The results obtained by these methods are not always sufficient to explain and to interpret how water actually moves in a soil under natural conditions. Attempts to define the quantities of moisture that can be displaced by upward movement either to evaporate at the surface or to feed the vegetation and compensate for the transpiration losses show that the laws of moisture movement are much more complex than the previous equations indicate. The movement may be zero, despite an appreciable moisture gradient; on the contrary, a large movement $\frac{dQ}{dt}$ can be observed in the absence of a gradient or even against an existing gradient from relatively dry zones to zones of higher moisture content.

The purpose of this paper is to show the limits of the validity of the classical diffusion equations when the water movement in soil is caused by evapotranspiration. Two experimental studies are presented: (a) moisture profiles observed in the field under bare or cultivated soil during the drying period; and (b) drying of soil columns submitted in the laboratory to various conditions of evaporation.

MOISTURE PROFILES AND CAPILLARY DIFFUSION OF WATER IN SOIL

Moisture Profiles in Bare and Cultivated Soils

From a series of moisture profile determinations on different types of bare and cultivated soils during the drying period, it has been shown that the moisture content of the successive earth layers H_1, H_2, H_3, etc., remained in close correlation with respect to each other. This is the reason why moisture profiles, showing the change of moisture content with depth, present for each soil type a succession of characteristic forms (Fig. 1A), which can be easily demonstrated.

The moisture profiles shown in Figure 1 have been obtained on cultivated as well as on bare soils. If the cultivation causes a greater drying of the soil and thus leads to lower moisture contents, any discon-
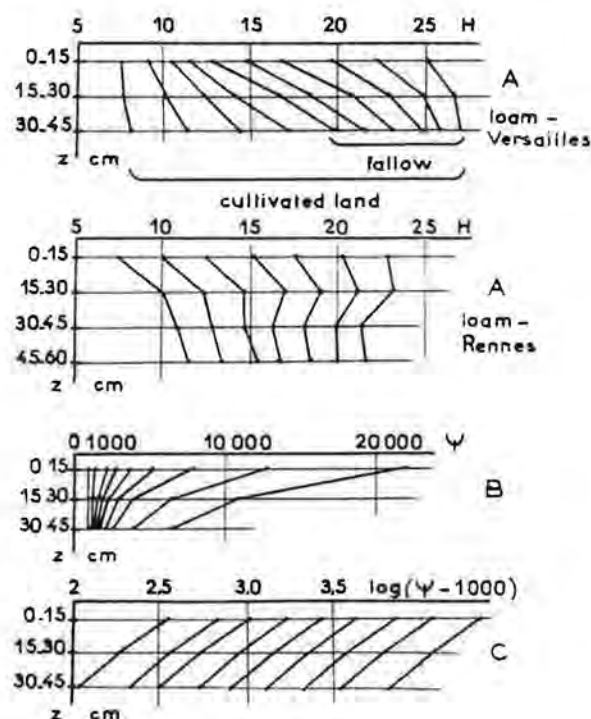

Figure 1.

tinuity between the series of profiles observed on bare or cultivated soils is not apparent.

These moisture profiles observed during the drying period correspond to an upward moisture movement to the surface of evaporation or to the root zone. If some show a very irregular form, or even an inversion of gradient, this is due to soil heterogeneity as a function of depth. The water diffusion is actually governed by the gradient $d\psi/dz$, for which the moisture gradient dH/dz can be substituted only if the physical nature of the soil remains the same throughout the entire depth Z. (See Eqs. 2 and 4.) To interpret the results obtained, the variation with depth of the capillary potential ψ must be considered, not the moisture content H. However, it is easy to pass from one expression to the other if ψ has been determined as a function of H for each layer of the soil under consideration.

The new profiles expressing the variation of ψ with depth z (Fig. 1B) possess exponential form. Thus, and in contrast to the moisture content, the capillary potential ψ varies with depth in a continuous and regular manner. ψ tends asymptotically toward 1,000. Assuming that this particular value corresponds for every soil to the field capacity, this result signifies that the moisture content H tends with increasing depth to reach the field capacity that is characteristic for the layer under consideration. Experience shows that as the desiccation of the soil proceeds, a profile $\psi(z)$ passes to another by a simple expansion of the corrected abscissas $(\psi - 1,000)$. These results suggest a third representation in the form of the
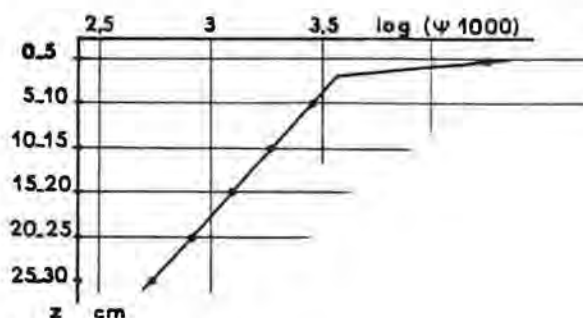
Figure 2.

variation of $\log(\psi - 1,000)$ with depth Z (Fig. 1C). Instead of the previous exponential curves, quasi-linear curves are obtained and the transition from one to the other is no longer by expansion, but by simple translation; as a matter of fact, the straight lines are practically parallel to each other. There is, however, an anomaly in the vicinity of the surface of evaporation: the profiles show a break reflecting marked drying of the surface layers. This phenomenon, which can be seen on the average profiles shown in Figure 1C, is more apparent if the profiles on thinner soil sections (Fig. 2) are determined. This is, of course, a commonly observed phenomenon; namely, the formation of a crust of dry earth, a veritable natural surface mulch.

The results can now be summarized by stating that during the drying-out period, and neglecting the uppermost layers which may dry out to an extreme extent, the shape of a profile expressed as a function of $\log(\psi - 1,000)$ remains almost constant for a given soil, whatever be its depth and its state of desiccation.

$$\frac{d\log(\psi - 1,000)}{dZ} = C \tag{5}$$

in which C = C te (for any Z or ψ). The results reported in this section have been verified on four different soils.

Hypothesis of the Permanent Regime

Assuming that the observed moisture profiles reflected a simple phenomenon in the upward movement of water, the initial hypothesis is that they corresponded with the conditions of the permanent regime. To say that the regime is permanent—or better, that the loss dQ/dt is the same at different depths Z, means that the loss is proportional to the gradient of $\log(\psi - 1,000)$ since this gradient according to Eq. 5 retains the same value at all levels. Accordingly,

$$\frac{dQ}{dt} = A \frac{d\log(\psi - 1,000}{dz} \tag{6}$$

in which A = C te.

Eq. 6, to which the proposed hypothesis leads, does not contradict the previously presented theoretical considerations. It shows simply that the coefficient λ in Eq. 2 decreases as ψ increases (at least within the range of variation of ψ obtained in the experimental study: $1,000 < \psi < 15,000$) in accordance with

$$\lambda = \frac{A'}{\psi - 1,000} \tag{3a}$$

where $A' = C$ te.

It will be seen that introduction of Eq. 3a in Eq. 2 gives Eq. 6. An equation similar to Eq. 6 was obtained by Derjaguin on the basis of theoretical considerations concerning the displacement of liquid films along the solid wall formed by soil particles (3).

With this hypothesis, application of the indicated transformation gives Eq. 3a or Eq. 4; therefore, the coefficient Λ appears to be almost independent of the moisture content if λ varies in accordance with the proposed law (Eq. 3a). Thus, a result is obtained which several authors have verified in a more or less precise manner.

The hypothesis of the permanent regime, which has been advanced here for the interpretation of the form of the moisture profile, raises, however, the following questions:

1. Why do the moisture profiles respond to the conditions of the permanent regime when as a result of the continuous variations of evapotranspiration the water regime in the soil should be extremely variable?

2. If the hypothesis of the permanent regime is exact, this implies also that the loss remains constant while the soil is drying: the slope of the profiles $d\log(\psi - 1,000)/dz$, actually remains constant, not only while the depth increases, but also when with more marked desiccation the entire profile in $\log(\psi - 1,000)$ moves toward higher ψ values; what then is the significance of this particular yield characteristic of each soil?

Permanent Regime Expresses the Irreversibility of the Desiccation Process

Starting with the proposed diffusion equation (Eq. 6) inquiry is made into the manner in which this equation applies in two distinct cases: that of soil desiccation and that of soil rehumidification.

It is specified first that the value of the capillary potential ψ is that of soil desiccation, ψ_s. In the investigations cited here, it has been obtained by means of the cryoscopic method. A profile giving the variation of ψ or of $\log(\psi - 1,000)$ as a function of the depth Z (the profile is obtained by substitution of ψ values for the directly measured moisture contents H) presents a true picture of the capillary potential if at every level under consideration the soil is actually in the drying phase; the picture is, however, false if the soil is in the remoistening phase, because the true potential corresponding to the respective moisture content is ψ_h, the capillary potential for remoistening, which is much smaller than ψ_s (phenomenon of hysteresis).

Under conditions in which every thin soil section is actually in the drying stage under the influence of a sufficiently large evapotranspiration, the capillary potential corresponding to the measured moisture content is truly ψ_s; the profile in $\log(\psi - 1,000)$ represented on the graph depicts the real situation, and Eq. 6 gives an exact value of the loss or yield.

If, on the other hand, certain thin soil layers tend to take up moisture, the water losses in evapotranspiration being smaller than the yield given by Eq. 6, the water potential in the layers under consideration is no longer the desiccation potential ψ_s considered in this study, but approaches the remoistening potential ψ_h. Then the profile in $\log(\psi - 1,000)$ as plotted gives an incorrect picture of the variation in potential and the diffusion formula no longer holds.

What then is the yield? The yield $\frac{dQ}{dt}$ at any depth Z cannot be greater than (a) that yield value given by Eq. 6 for the entire depth between 0 and Z, and (b) the evapotranspiration. Otherwise, one would be dealing actually with the remoistening phase. Thus, in the extreme cases in which the evapotranspiration is zero, the yield itself is zero
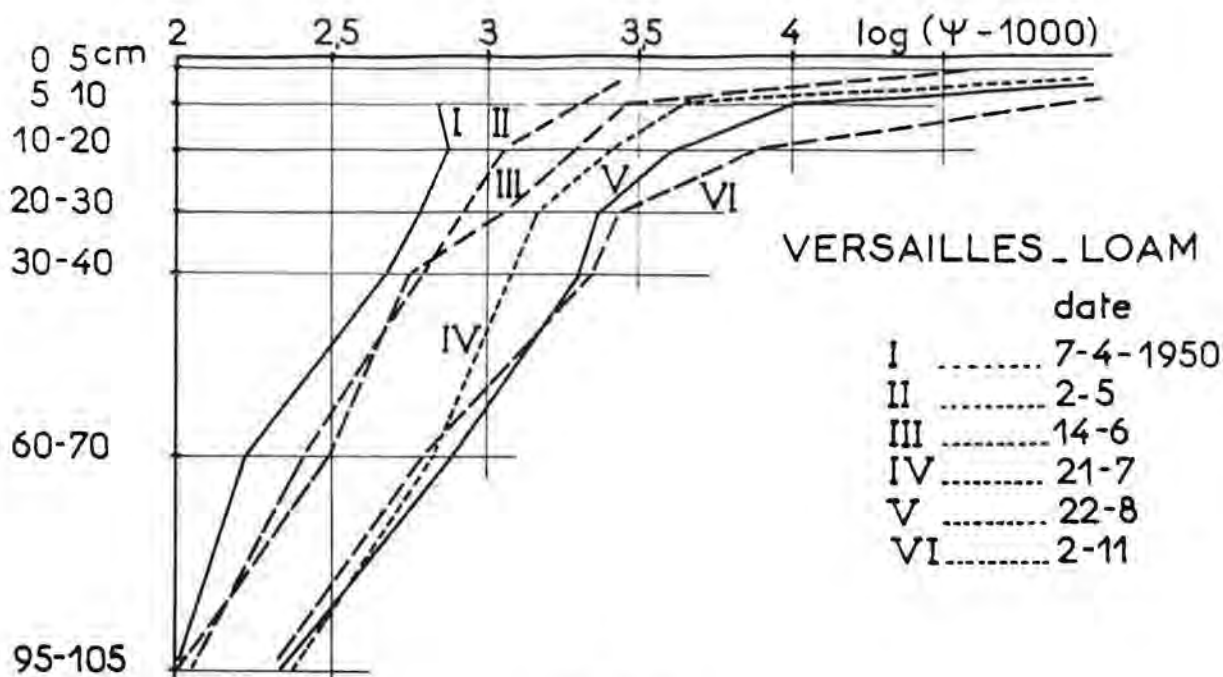
Figure 3.

even in the presence of an appreciable moisture gradient, because the least displacement by upward movement of water would lead to a moistening of the overlying soil layers and hysteresis would intervene to stop all movement. As a matter of fact, remoistening of the soil is possible if the moisture comes from a body of free water. The capillary potential is then ψ_h at all levels. This phenomenon can intervene at distances of less than 50 or 100 m above the ground water level.

With respect to the conditions of the permanent regime (linearity of the profiles in $\log(\psi - 1,000)$) they correspond to a state limited by the conditions of desiccation where the profile is concave toward the right and where the soil dries in accordance with Eq. 6. On the other hand, they correspond to a state limited by the conditions of remoistening where the profile tends to be concave toward the left. At this moment, the phenomenon of hysteresis intervenes to invalidate the diffusion equation and to stop the development of the moisture profile. The permanent regime, therefore, depicts the irreversibility of the drying process.

The following experiment confirms the reasoning so far presented. The evolution of profiles on a lot maintained without vegetation and protected against rain was observed for several months (Fig. 3). Displacement of the profiles in the direction of increasing ψ proved that diffusion can function to insure the desiccation of the soil. However, when at the end of the season the evapotranspiration falls to a value of practically zero (in consequence of the drying out of the surface and the cooling of the atmosphere) there was no tendency of the soil to rehumidify—the gradient of $\log(\psi - 1,000)$ is only an apparent one and does not indicate any upward movement of water.

Characteristic Gradient Corresponds to a Certain Critical Yield

The hypothesis of the permanent regime is advanced to explain the linearity of the profiles in $\log(\psi - 1,000)$, but the yield remains the same whatever the state of desiccation of the soil. It was shown that the slope of the profiles in $\log(\psi - 1,000)$ remained constant, although as the soil was drying the profiles were displaced toward increasing ψ- values. What then is the significance of this particular slope C? What, also, is the significance of this particular yield A.C.?

The experiment showed a critical yield that cannot be exceeded without causing an extreme desiccation of the soil which results in a marked reduction of the evaporation.

The top surface of a moist soil column is subjected to a certain evaporation E. If

E is small (less than 1 mm per day in the case of a loam from Versailles), the surface remains moist for a long time and water conduction to the surface, under these conditions, compensates for the losses into the atmosphere. With all other factors the same, the evaporation remains constant. If, however, a high evaporation (for example, larger than 2 or 3 mm per day) is caused by means of electric lamps and ventilators, there is a rapid formation of a dry surface crust, a true natural mulch. Then the evaporation decreases rapidly and approaches a value of about 1 mm per day. Thus, the slope of the profile in $\log(\psi - 1,000)$ observed in the open field and under the surface crust of dry earth corresponds to this particular critical yield of the order of 1 mm per day for the loam studied.

MECHANISM OF SOIL DRYING UNDER INFLUENCE OF EVAPORATION

Experimental Technique and Methods of Measurement

Experimental Technique. Tubes (30 to 50 cm long and 6 to 7 cm in diameter) are filled with homogeneous soil possessing throughout the same initial moisture content of approximately field capacity. The tubes can be filled with either specimens taken with the sampler in the field or broken-up soil which is then compacted to the desired density. The bottom of the tube is closed and the surface of the earth cylinder is subjected in the laboratory to well-defined conditions of evaporation that can be controlled by means of electric lamps or fans.

Measurement of Evaporation. For a certain period of time, Δt (days), the evaporation E (mm/day) is given by

$$E = \frac{\Delta P}{S \Delta t} \tag{7}$$

in which

ΔP = the loss of weight of the soil cylinder (dg); and
S = the cross-section of the cylinder (sq cm).

Total evaporation during the time interval $t_1 - t_2$ is given by

$$\int_{t_1}^{t_2} E\, dt = \frac{\Delta P}{S}$$

Measurement of Quantity Yielded by Successive Thin Layers. To determine the moisture quantities yielded by successive thin soil layers a series of soil filled tubes are prepared in the same manner as the test samples and subjected from the start of the experiment to the same conditions of evaporation. At each weighing for the determination of E, one or two tubes are sacrificed to determine, slice by slice, the new moisture content H (water per 100 g of dry soil). If H has decreased by ΔH during a period Δt (days), the quantity of water yielded at the depth z and for a slice 1 cm thick is (in mm per day):

$$u = \frac{\sigma \Delta H}{10 \Delta t} \tag{8}$$

in which σ is the apparent density of the soil.

If the moisture content H is determined on soil slices of a thickness Δz (in cm), the quantity of water yielded by these slices is (in mm per day):

$$U = u \Delta z \tag{9}$$

Measurement of Yields at Different Levels. The measured evaporation E is simply the yield $\left(\dfrac{dQ}{dt}\right)_0$ at the soil surface itself; that is, at the depth z - 0. If U_1, U_2, U_3, etc., designate the quantities of water lost by the successive soil slices of 0.6-cm thickness, for example, the yields are:

at 0.6 cm $\left(\dfrac{dQ}{dt}\right)_1 = E - U_1$

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$$\text{at } 1.2 \text{ cm} \quad \left(\frac{dQ}{dt}\right)_2 = E - U_1 - U_2$$

$$\text{at } 1.8 \text{ cm} \quad \left(\frac{dQ}{dt}\right)_3 = E - U_1 - U_2 - U_3$$

The error increases with greater depths.

Measurement of Moisture Gradient. Knowing the moisture contents H_1, H_2, H_3, etc., of the successive soil layers, the moisture gradients dH/dz at the levels of the soil slices (for example, 0.6 cm, 1.2 cm, 1.8 cm) can be deduced.

Relation Between Yield and Moisture Gradient (3)

Eq. 4 gives the yield as a function of the moisture gradient under the condition that the soil be homogeneous and in the drying stage. It has been shown that Λ varies but little with change in moisture content.

Figure 4.

If the yield could be measured in the soil columns at different depths, but during the same lapse of time, and if parallel determinations of the moisture gradient have been made it is possible to plot the variation of dQ/dt as a function of dH/dz. The yield will decrease in a regular manner from the value E at the surface, approaching zero with increasing depth. Eq. 4, accordingly, permits anticipation of curves of the type of Γ or Γ', shown in Figure 5.

If Λ is independent of the moisture content, the points must be located on a straight line (Γ) which passes through the origin and whose slope is exactly Λ (see Fig. 5A).

If Λ increases with increasing moisture content H, since H itself increases with increasing depth, the $\frac{dQ}{dt} / \frac{dH}{dz} = \Lambda$ becomes greater with larger values z. The points would be located on a curve Γ', which is concave toward the right (see Fig. 5B).

The actual curves (Fig. 6A) do not conform at all with the expected result: the upper part of the curve, which corresponds to the uppermost layers, has a remarkably linear shape obeying the equation
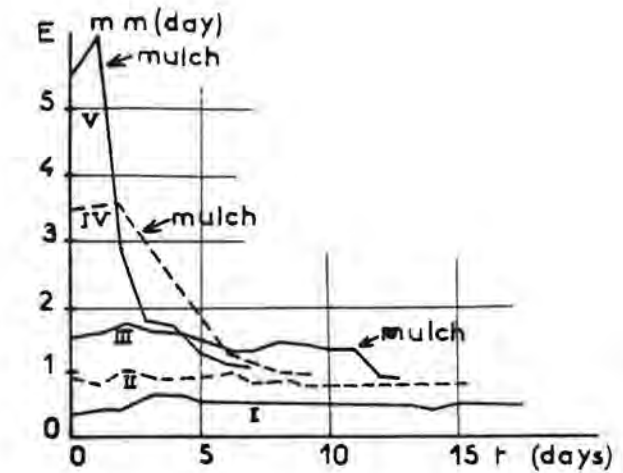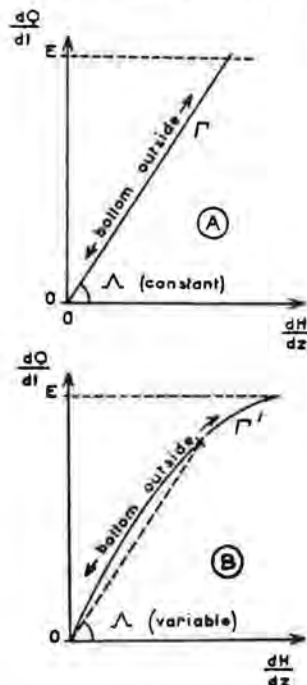
$$\frac{dQ}{dt} = B + A\,(t)\,\frac{dH}{dz} \qquad (11a)$$

the slope A being a constant at a given moment, but decreasing systematically with time. One can thus distinguish in the surface yield $\frac{dQ}{dt} = E$ the two components B and (E - B). The experiment shows that if one imposes a high degree of evaporation, the term B cannot exceed a value of the order of magnitude of 2 mm per day for the Versailles loam (Fig. 6B).

On the other hand, if the soil is simply poured into the tube and left in a non-coherent state, the term B is very small or equal to zero (Fig. 6C). Eq. 11a then approaches the form:

$$\frac{dQ}{dt} = A\,(t)\,\frac{dH}{dz} \qquad (11b)$$

Figure 5.

Relationships Between Yield and Moisture Gradient Explained by Depth
Distribution of Water Losses

If one plots the variation of log(u) as a function of the depth z, the curve obtained is normally linear from the surface to a certain depth z_1. At greater depths, log(u) decreases at a lesser rate than if the law of variation remained linear (Fig. 7A). This means that the curve for u or Γ coincides at first with the exponential function Γ'
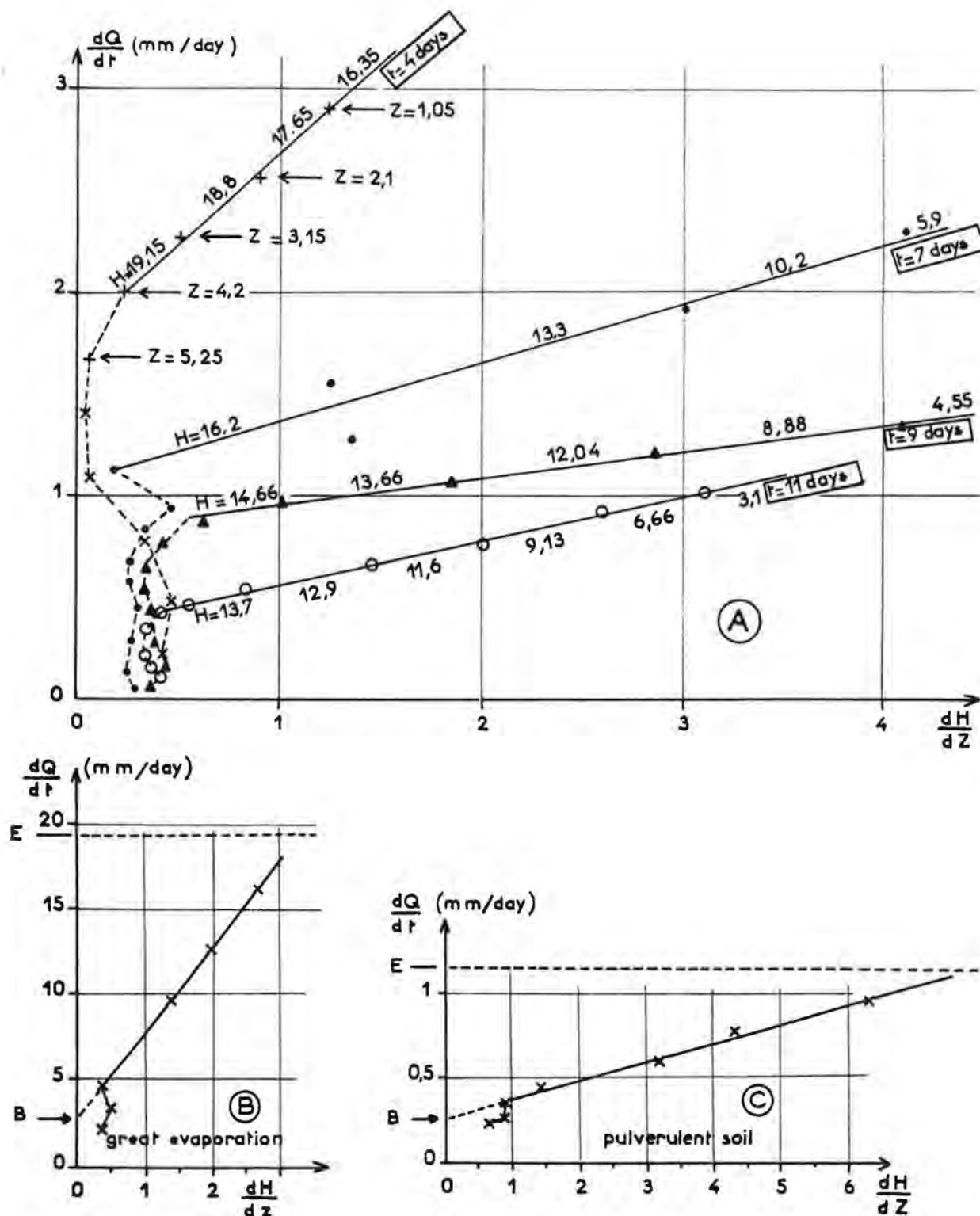
Figure 6.

(Fig. 7), or

$$u = u_0 \exp(-az) \tag{12}$$

then it deviates at depths greater than z_1 (Fig. 7B).

In the case of non-coherent soil, the variation of $\log(u)$ remains essentially linear (Fig. 7C); that is, u varies in accordance with an exponential law (Curve Γ, Fig. 7D).

From these results, it is easy to find the relationship between the yield and the moisture gradient (Eqs. 11a and 11b). If a coherent soil of normal density corresponding to Figs. 7A and 7B is considered, it is seen that the yield $\frac{dQ}{dt}$ at a level z ($= \int_z^\infty u \, dz$) corresponds to the area limited by Γ below the respective depth.

If β is the quantity of water (in mm per day) corresponding to the area comprised between the exponential curve Γ' and the actual curve Γ, at any depth z, located be-
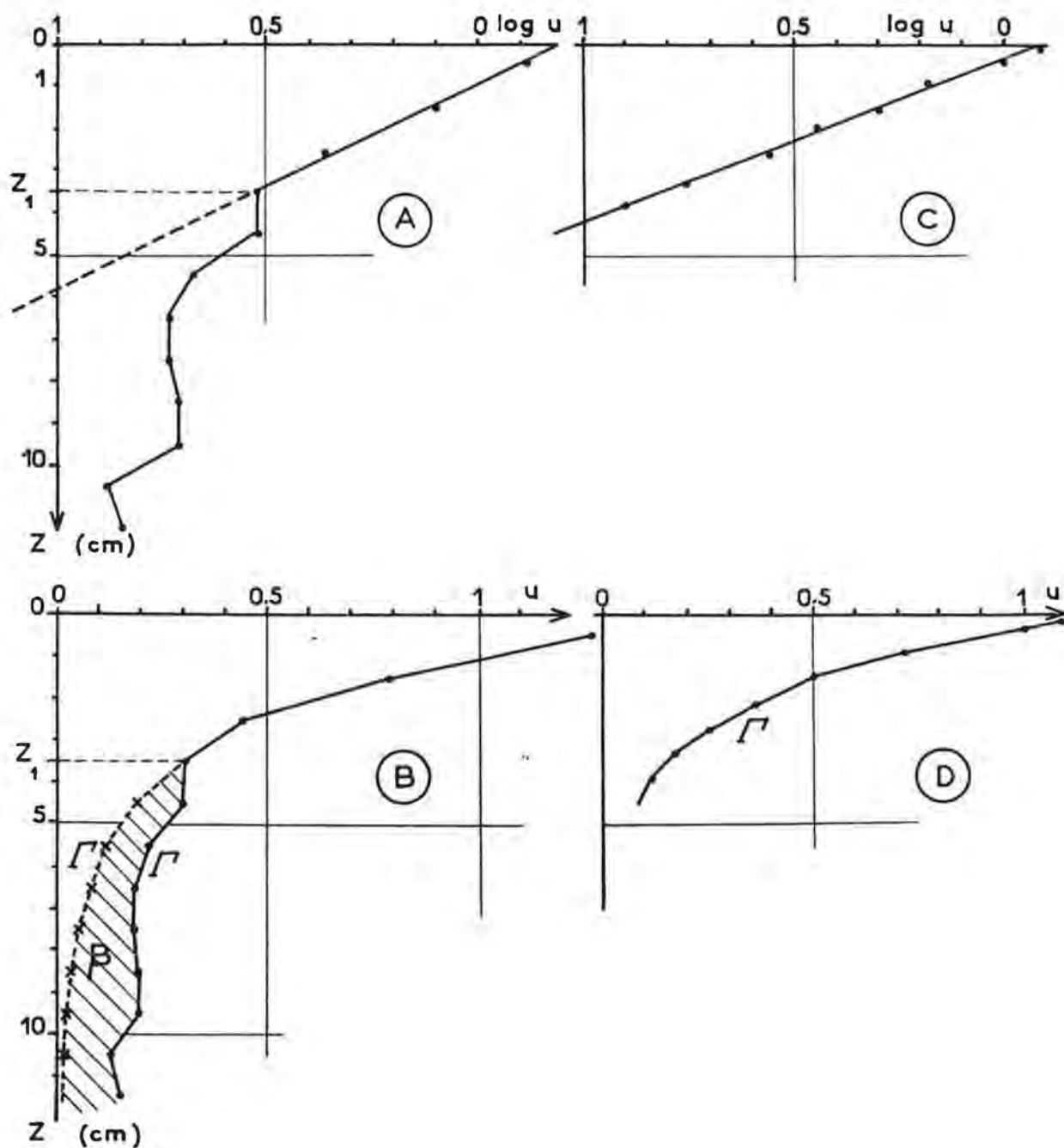
Figure 7.

tween zero and z, the yield is equal to the sum of β and the losses as defined by the exponential curve:

$$dQ = {}_z\!\int^{\infty} u_0 \exp(-az) + \beta, \text{ or}$$

$$\frac{dQ}{dt} = \frac{u_0}{a} \exp(-az) + \beta \tag{13}$$

Besides, if for any level of the slice $0 - z_1$ one seeks to evaluate the quantities of water q (in mm) yielded since time zero, when the moisture content was H_0, to the time t, when the moisture content is H, one obtains for a slice of 1-cm thickness one or the other of the expressions:

$$q = \frac{\sigma}{10} (H_0 - H) \tag{14}$$

and

$$q = \int_0^t u \, dt = -a \exp(-az) \int_0^t u_0 \, dt \tag{15}$$

Equating Eqs. 14 and 15 and differentiating with respect to z gives

$$\frac{-\sigma}{10} \frac{dH}{dz} = -a \exp(-az) \int_0^t u_0 \, dt \tag{16}$$

Finally, eliminating the term $\exp(-az)$ between Eq. 13 and Eq. 16 leads to:

$$\frac{dQ}{dt} = \frac{\sigma \, u_0}{10 \, a^2 \int_0^t u_0 \, dt} \frac{dH}{dz} + \beta \tag{17a}$$

Eq. 17a is the same as the experimental relationship (Eq. 11) inasmuch as the term in front of dH/dz, a constant for a given moment but decreasing with time, can be written as A(t) and β is like B, a constant as long as one is concerned with depths smaller than z_1.

In the case of non-coherent soil, for which u varies exponentially, calculation leads to

$$\frac{dQ}{dt} = \frac{\sigma \, u_0}{10 \, a^2 \int_0^t u_0 \, dt} \frac{dH}{dt} \tag{17b}$$

which is identical with the experimental relationship (Eq. 11b).

Hypothesis of Diffusion in the Vapor Phase (4, 5)

The experimental results reported in the preceding seem to invalidate the classical laws of liquid diffusion in soils. As a matter of fact, according to the latter the relationship between the yield and the moisture content should normally be represented by curves of the type of Γ or Γ' (Fig. 5), which clearly differ from the actual curves given (Fig. 6).

If it is admitted that the water losses are due in part to an evaporation in the soil and diffusion in the vapor phase into the atmosphere, it seems possible to explain the experimental findings. It is, therefore, proper to examine this hypothesis and to explain why, after all, it cannot be retained.

When at a depth z a saturation deficit exists in the atmosphere of the soil pores (the actual vapor pressure f being lower than the maximum pressure F(t), evaporation will take place at this level. The amount of water evaporated (in mm per day) and for the slice z, z + dz, will be

$$Y \, dz = M\left[F(t) - f\right] \tag{18}$$

with M = C te, and will represent a water vapor gain for the pore atmosphere. But the
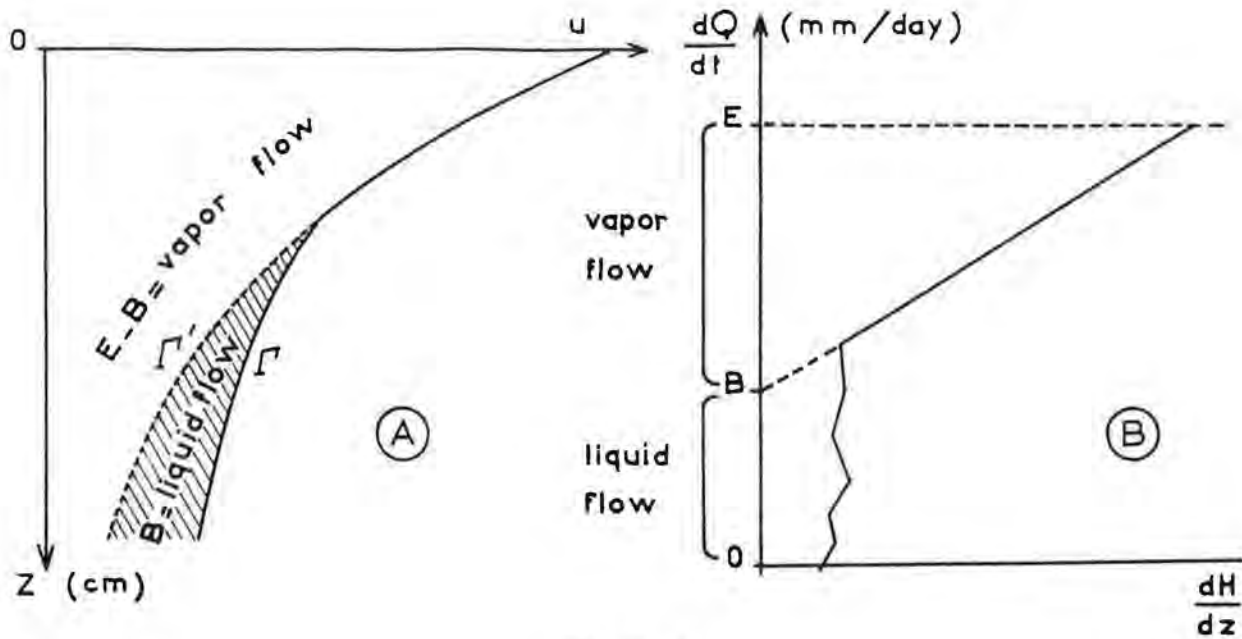
Figure 8.

same slice will lose at the level z a quantity of vapor equal to $K\left(\dfrac{df}{dz}\right)_z$ while it will gain $K\left(\dfrac{df}{dz}\right)_{z\,+\,dz}$ at the level z + dz. Assuming establishment of equilibrium between vapor gain and loss, one obtains

$$M\left[F(t) - f\right] + K\,\frac{d^2f}{dz^2} = 0 \tag{19}$$

But if one passes from the variable f to the variable Y, keeping Eq. 18 in mind, integration gives

$$Y = Y_0 \exp(-\,az) \tag{20}$$

with $a = \sqrt{\dfrac{M}{K}}$. The term Y, like u, represents water losses in mm per day and per slice of 1-cm thickness, and varies, therefore, in accordance with an exponential law.

Returning to the variation of u as a function of depth (see Fig. 8), one may ask if the exponential function Γ' does not express the losses Y attributable to vapor diffusion. In this case, the area β or B, comprised between the curves Γ and Γ', would represent the losses by liquid diffusion proper. The components B and (E - B) shown in Figure 6 would then correspond, respectively, to a liquid flux evaporating at the surface and to a vapor flux (Fig. 8).

In the case where the soil is non-coherent (relatively dry and unpacked), the losses u varied at all depths in accordance with an exponential law, while the term B was practically zero. According to the proposed hypothesis, this soil would dry out only by simple vapor diffusion, which seems to conform to common sense.

This hypothesis of a vapor diffusion is in error. In the first place, if the term (E - B) actually corresponded to a vapor loss, the water vapor diffusion in the soil would have to be turbulent as has previously been proven. As a matter of fact, the values for the coefficient of diffusion K calculated from certain experimental data were considerably larger than the coefficient of molecular diffusion in a porous medium such as soil.

Secondly, the following experiment shows that the loss of liquid cannot be covered by the term B alone:

A solution of calcium chloride is sprayed in a homogeneous manner over a soil with which column evaporation experiments are to be made. Some of the cylindrical speci-

mens represent packed soil with an initial moisture content of about 25 percent of field capacity; these are subjected to a mild evaporation (E about 1 to 2 mm per day) in a manner that the term B represents approximately 90 percent of E. The other soil cylinders consist of soil of lesser density and lower moisture content (H_0 about 17 to 20 percent) and are subjected to more severe evaporation (E > 5 mm per day). The term B will be here practically zero. ρ is defined as the concentration in Cl (mg per 100 g of dry soil) in the top layer of 3-mm thickness and $\Delta\rho$ as the increase in concentration since the start of the evaporation. Reasoning shows that $\Delta\rho$ should be proportional to the quantity of water gained by the surface in the liquid state, that is,

$$\int_0^t \left(\frac{dQ}{dt}\right)\,dt \quad \text{liquid}$$

and on the other hand to the term $\frac{\rho_0}{\sigma H}$, in which ρ_0 = initial Cl concentration;
σ = apparent density; and
H_0 = initial moisture content.

The variation of $\Delta\rho$ is plotted as a function of

$$\frac{\rho_0}{\sigma H_0}\,\int_0^t E\,dt \quad \text{(see Fig. 9), where} \quad \int_0^t E\,dt \quad \text{is the total evaporation}$$

in mm from the initial condition. The points group themselves along the same straight line irrespective of the soil condition (packed and coherent or loose) and irrespective also of the value B with respect to the evaporation E.

If it were true that the liquid loss could be covered by the term B, then the expres-
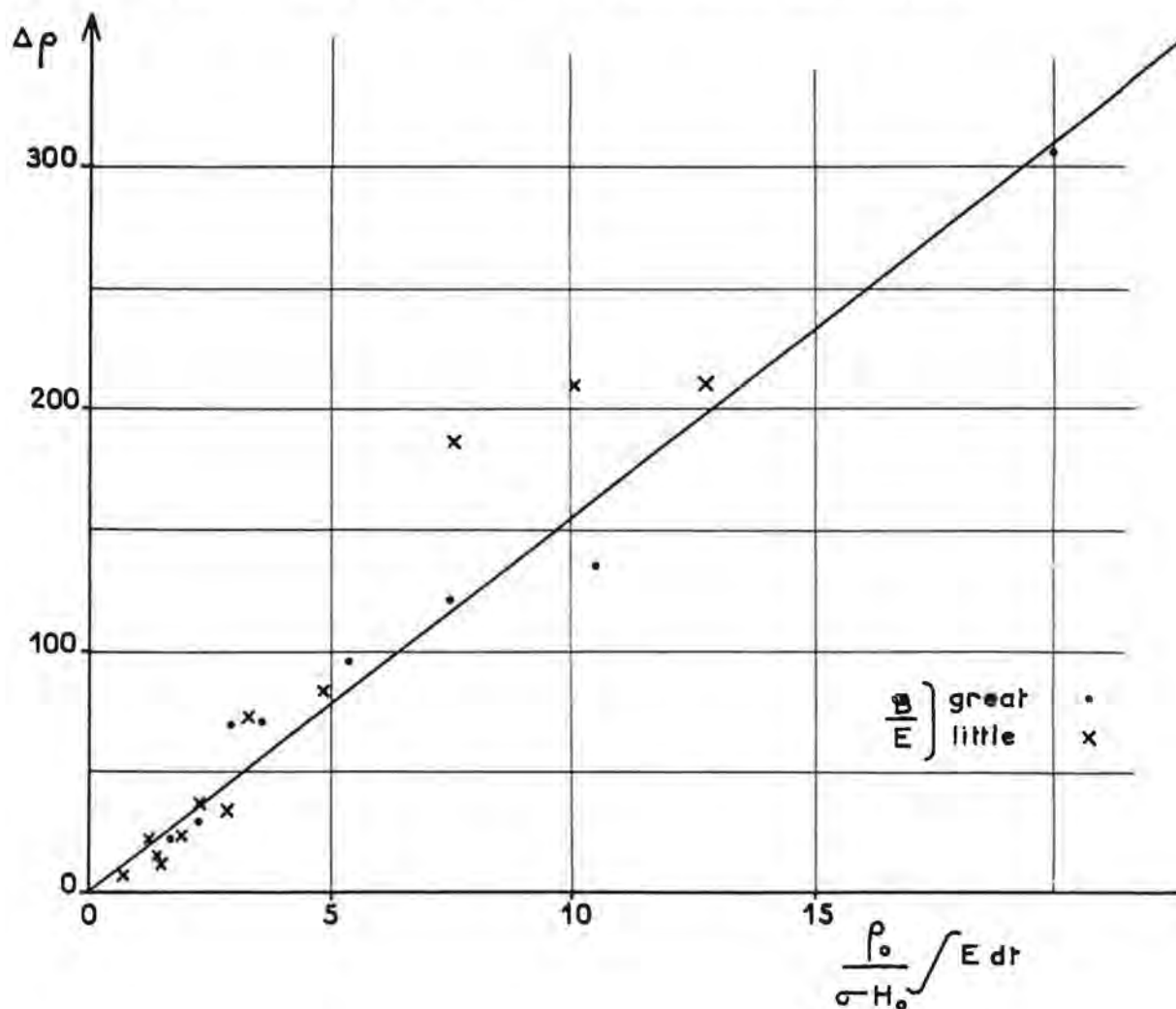
Figure 9.

sion $_0\int^t$ E dt would considerably overestimate the quantity of water that reaches the soil surface in the liquid state, since $\frac{B}{E}$ is small, and the corresponding points should lie lower than those relating to the higher $\frac{B}{E}$ values. The vapor diffusion hypothesis is rejected, therefore, as an explanation of the experimentally found relationships.

Cohesive Forces of Water

Eq. 4 is derived, as previously shown, from the diffusion equation (Eq. 2), or its equivalent

$$\frac{dQ}{dt} = \lambda(P)\frac{dP}{dH} \tag{2a}$$

where P represents the (negative) pressure of the water in the soil and is numerically equal to the capillary potential ψ. In deriving Eq. 4 from Eq. 2a the transformation

$$\frac{dQ}{dt} = \lambda(P)\frac{dP}{dH}\frac{dH}{dz} \tag{3b}$$

is effected. This operation is permitted, however, only if the water pressure P in the soil is rigorously defined by the moisture content H. In the first part of this study, there have been set forth two restrictions on this manner of thinking, which consequently pertain to the validity of the diffusion equation as a function of the moisture gradient. In order that P may be defined as a function of H and of H only, it is required that (a) the character of the soil be the same at every point, and (b) every soil element be in the drying-out phase (in order to avoid the hysteresis effect). To these two conditions a third one must be added: in order that the pressure P depend only on H, it cannot be modified by a tension due to the cohesion of the water which would be transmitted along the liquid films. Experience shows clearly that such a tension exists and that, therefore, at least under certain conditions, the actual pressure P of the water differs from P(H) in such a manner that in the absence of any liquid movement

$$P \neq P(H) \tag{21}$$
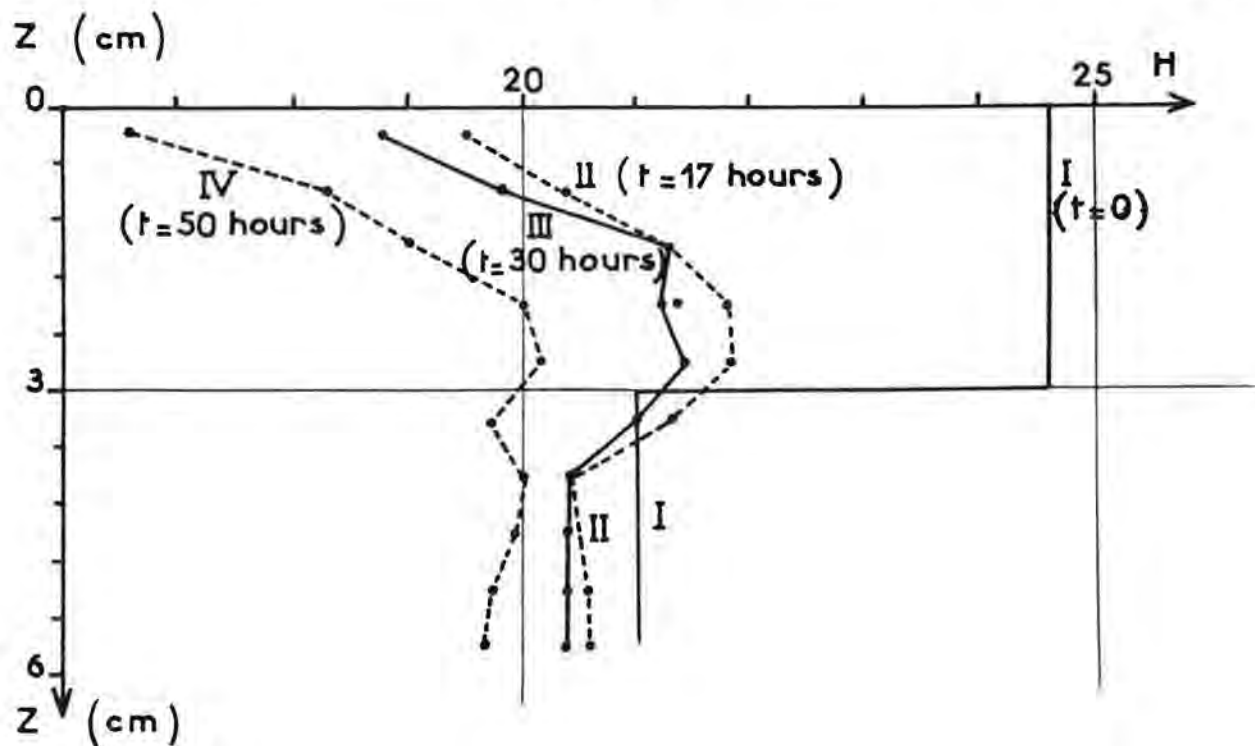
Figure 10.
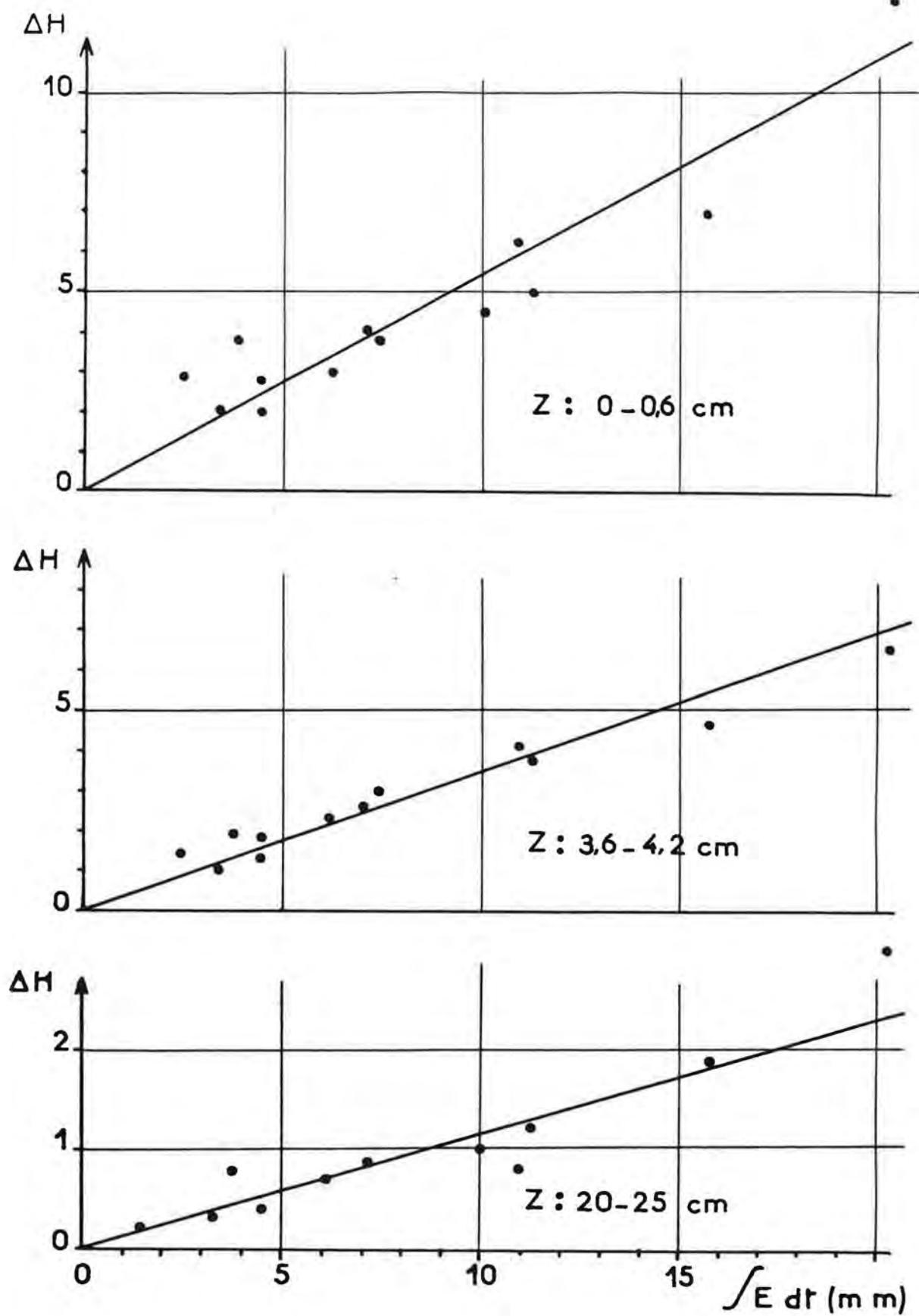
Figure 11.

Experiments. A soil cylinder prepared so that the moisture content H_0 of the top layer (of 3 cm, for example) is greater than the moisture content of the underlying layers, is subjected to evaporation. If the pressure P of the soil water were uniquely defined by H, the layers below the depth of 3 cm would not begin to dry out until the moment when the first layer had attained the moisture content H_1. Experiments, however, show that the layers in question are losing water from the start of the evaporation. The water which they lose moves toward the surface and passes through the more humid zones (see Fig. 10).

Examination of how the moisture content H varies at different depths of the soil cylinders by plotting ΔH as a function of the amount of water evaporated, $_0\int^t E\ dt$ (Fig. 11), gives straight-line curves, all starting from the origin, a fact which has already been pointed out by Abramova (6). Thus, desiccation starts throughout the sample as soon as the surface is subjected to evaporation. If the water movement were bound to the existence of a moisture content gradient, desiccation would gain progressively in depth; the beginning of the desiccation would correspond to a total evaporation $_0\int^t E\ dt$, which would be greater with greater depth of the layer; and the straight lines found would cut the abscissa axis (Fig. 11) at a distance from the origin which would increase with increasing depth.

These two observations show that the displacement of water toward the surface of evaporation corresponds to a concerted movement of the water films, to which an internal tension assures a certain cohesion. This tension modifies the water pressure P as defined by the moisture content H; hence, the yield $\frac{dQ}{dt}$ can not be expressed as a function of $\frac{dH}{dz}$.

However, when the water has been subjected for a certain time to a permanent regime, the moisture content tends for every depth toward such a value that the corresponding pressure P(H) coincides with the actual pressure and P = P(H). One can verify the law of variation with depth pertaining to the capillary potential ψ; that is, the pressure P(H) (see discussion on variation of ψ at the beginning of this paper, and Fig. 1). It is also under these conditions that a diffusion equation involving the moisture content can make any sense.

Distribution of Water Losses Throughout the Depth, and Probability of Rupture of the Liquid Films

Reexamination of the curve for the variation of losses u (mm per day and per slice of 1-cm thickness) as a function of depth z (Fig. 7B), shows that close to the surface, between levels zero and z_1 this curve u(z) coincided with the exponential curve Γ'. At greater depth, the real curve Γ deviates, at least when the soil has normal cohesion and density properties. It has been possible to show that every section of the curve Γ can be expressed by an exponential function such as Eq. 12, but that the modulus a, which is constant between zero and z_1, decreases at depths greater than z_1. Furthermore, it has been possible to prove that this coefficient a depends essentially on the yield. The curve for the variation of a as a function of $\frac{dQ}{dt}$ for the Versailles loam is shown in Figure 12 (D for coherent and D' for non-coherent soil).

It is proposed to show that the coefficient a, which is dependent on the nature and structure of the soil and on the yield $\frac{dQ}{dt}$, can be identified with the probability
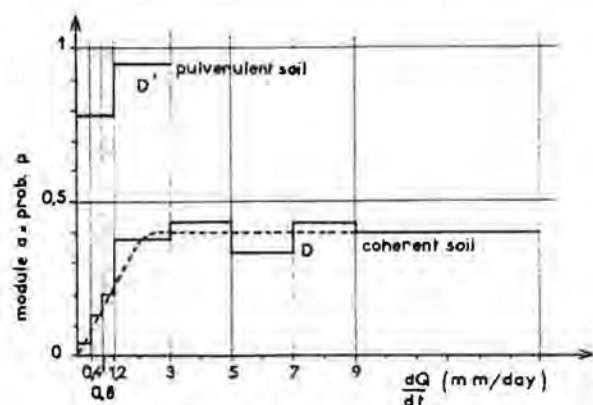
Figure 12.

of rupture p of the water films.

If two successive soil layers (1) and (2) of the same thickness dz, are considered, and p dz designates the probability of rupture of the water films in each of these layers and $\left(\dfrac{dQ}{dt}\right)_1$ represents the yield at the top of layer (1), the fraction of films ruptured in layer (1) is p dz; the fraction of those not ruptured is, hence, (1 - p dz). (The probability of rupture can be considered as proportional to the thickness dz of the layer if it is of very small thickness and if the probability in question is correspondingly small.) It is the non-ruptured films which assure the circulation of water in slice (2), where the yield would then be, in first approximation,

$$\left(\frac{dQ}{dt}\right)_2 \approx \left(\frac{dQ}{dt}\right)_1 (1 - p \, dz) \qquad (22)$$

Thus, the water losses in slice (1) will be

$$u_1 \, dz = \left(\frac{dQ}{dt}\right)_1 - \left(\frac{dQ}{dt}\right)_2 \approx \left(\frac{dQ}{dt}\right)_1 p \, dz \qquad (23)$$

The water losses in slice (2) will accordingly be

$$u_2 \, dz = \left(\frac{dQ}{dt}\right)_2 p \, dz \qquad (24)$$

which can be written

Figure 13.

$$u_2 \, dz - \left[\left(\frac{dQ}{dt}\right)_1 - u_1 \, dz \right] p \, dz \qquad (25)$$

that is,

$$u_2 = u_1 - p \, u_1 \, dz \qquad (26)$$

from which, finally,

$$\frac{du}{u} = -p \, pdz \qquad (27)$$

or

$$u = u_0 \exp(-pz) \qquad (28)$$

Eq. 28 corresponds well with the experimental relationship (Eq. 12) if one identifies the probability of rupture p with the modulus a of the exponential expression. Figure 12 shows how a (that is, the probability of rupture p) varies with the structure and with the yield. It is logical to find that p is larger in the case of a non-coherent soil than in that of a coherent soil, and also that p tends toward zero as $\dfrac{dQ}{dt}$ becomes smaller. On the other hand, one could expect that the probability of rupture p depended also on the moisture content H. No evidence of such an influence of the moisture content could be found.

Relationship Between Yield and Rate of Drying at a Given Level

Every element of the curve Γ, which gives the variation of u with depth z (Fig. 7),
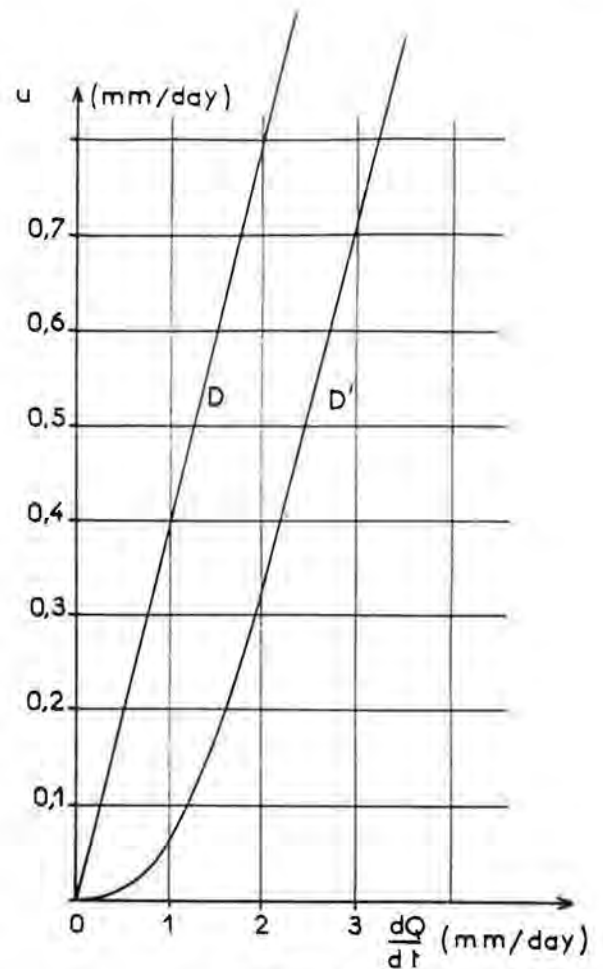
can, therefore, be expressed at any depth by an element of the exponential curve (Eq. 12) as long as the yield at the respective level is given by

$$\frac{dQ}{dt} = {}_z\!\int^{\infty} u \, dz \qquad (29)$$

If the coefficient a were constant, then the curve Γ would coincide completely with the respective exponential function and the integral giving the yield would be found immediately as

$$\frac{dQ}{dt} = u_0 \, {}_z\!\int^{\infty} \exp(-az) = \frac{u}{a} \qquad (30)$$

Thus, the speed of desiccation, characterized by u, would be proportional to the yield at the level under consideration; that is,

$$u = a \, \frac{dQ}{dt} \qquad (31)$$

(see Fig. 13; the straight line D corresponds to $a = C^{te} = 0.4$)

If a varies with the yield, the integration of Eq. 30 can only be approximate. It leads to a relationship between u and $\frac{dQ}{dt}$ which for the Versailles loam in a coherent state is shown by curve D' in Figure 13. In this case, the rate of desiccation is very low as long as the yield is less than about 1 mm per day; above this, it grows very rapidly. This result explains the conditions of mulch formation (Fig. 4). The latter requires an extremely long time to form when the evaporation E is just a little less than 1 mm per day and the surface losses u remain very small. The rate of mulch formation is practically proportional to (E - 1).

Besides, these results should permit explanation of the conditions of temporary wilting of plants: curve D' indicates the actual rate at which the soil dries out at the root level, where the yield by upward movement tends to compensate for the losses by transpiration.

SUMMARY AND CONCLUSIONS

Study of moisture profiles in the field and their evolution with time, as well as more refined laboratory experiments on the mode of drying of soil columns, show clearly the limits of the validity of the diffusion equation

$$\frac{dQ}{dt} = \Lambda \, \frac{dH}{dz}$$

where the yield is expressed as a function of the moisture content gradient. The latter equation implies a simple and unique relationship between the pressure of the water in the soil and the moisture content. Hence, it is inexact in three cases, as follows:

1. When one deals with a succession of earth strata of different textures.

2. When certain soil strata tend to increase their moisture content at the expense of other strata that are losing water. The relationship between the pressure and the humidity is then different for the two cases (phenomenon of hysteresis); the diffusion equation given becomes false; therefore an appreciable moisture content gradient $\frac{dH}{dz}$ may correspond to a zero yield.

3. At the start of soil drying. Actually, the displacement of water corresponds to a movement of the entire system of moisture films which bring the cohesive forces of water into play. The real pressure of the water is now modified by the tension that is transmitted along the films and is different from the pressure P(H) which is found to be defined as a function of the moisture content in the absence of any liquid movement. It is for this reason that the water in the deeper layers can be displaced toward the surface even if it must pass through zones of greater moisture content. Such a result evidently invalidates the diffusion equation presented, according to which water moves only in the direction of lower moisture contents.

The evaporation losses E (mm per day) correspond to the summation over all depths of the moisture losses u of the soil (mm per day per layer of 1-cm thickness).

It has been verified that at every level the curve of variation of u as a function of the depth z can be expressed by the exponential curve

$$u = u_0 \exp(-az)$$

but in this equation, the coefficient a varies within the limits 0 and 1, depending on the soil structure (coherent or non-coherent) and on the water yield at the level under consideration.

It has been possible to show that this coefficient is expressive of the probability of rupture p of the water films in a soil layer of given thickness.

The curve establishing the relationship between the modulus a (or the probability of rupture p) and the yield $\frac{dQ}{dt}$ is a fundamental characteristic of the soil, its structure, and its texture.

Finally, the relationship between the rate of drying and the yield $\frac{dQ}{dt}$ at the same level easily may be deduced from the probability-yield curve.

This drying-yield relationship, which also is characteristic of the soil and its structure, is ideally suited to interpret the conditions of surface mulch formation and the influence, in this respect, of cultivation methods. Finally, it explains why, under various conditions of evapotranspiration, the upward yield of water is quite constant (about 1 mm per day for the loam studied). The relationship (u, $\frac{dQ}{dt}$) shows that u, which is very small for yields below 1 mm per day, increases rapidly at greater yields. The yield, therefore, cannot exceed this value without causing rapid desiccation of the soil either at the surface or at the root zone. The consequences of this are a checking of the actual evapotranspiration and a definite self-regulation of water loss in soils.

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On the Correlation of Heat and Moisture Properties of Soils

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Introductory Remarks by Chairman

The great importance of thermal conductivity in soils not only for agriculture, but for many engineering problems, is becoming more and more realized. The bearing of the phase compositon (solid-liquid-gas) and of the dispersion and structural arrangement of these phases on thermal conductivity has been recognized and these factors have been taken into account to a greater or lesser extent in some of the available equations for approximate prediction of thermal conductivity in soils. A vexing phenomenon in all thermal conductivity measurements in moist soils is the water transfer that accompanies and modifies heat transfer. More knowledge on the character and the quantitative aspects of this coupling is seriously needed. Pure scientific analysis of similar phenomena in much simpler systems, such as the creeping of Helium II, has already proved to be rather a formidable job indicating that a semi-empirical, experimental approach must be applied in the case of soil systems in view of their well-known extreme complexity. The coupling of heat and moisture transfer must be related to the physical and physicochemical state of the water in the system under consideration. Flood in this symposium proposes to characterize this state by the use of absorption isotherms; others have utilized suction potentials for this purpose. Kolyasev for the same purpose of characterizing the water condition at certain moisture contents in specific soil systems employs the drying rate curves and the degree of water availability to plants. All these approaches are legitimate and valuable. The more of these approaches are developed, the greater are the chances that one may be found that is not only simple, but of wide applicability. This would enable the job to be done semi-empirically, but with sufficient accuracy for practical purposes, while the pure scientists continue to look for ultimate causes and mathematical correctness. In addition to presenting their combined theoretical and experimental approach, Kolyasev and his co-worker give an empirical formula and a nomographic chart on thermal conductivity of soils as a function of moisture content and dry density which differs somewhat from the well-known Kersten formulae.

● PROBLEMS of improving the thermal properties of soils are most actual and diverse.

The thermal conditions of soils may be influenced by different agrotechnical measures: hoeing, compaction, deep tillage, irrigation, etc. All these measures affect the soil heat conditions by changing its thermal characteristics: heat conductivity, thermal diffusivity and volume heat capacity. Consequently, in order to develop expedient agrotechnical measures for specific soil-climatic conditions, it is necessary, while cultivating various crops, to be acquainted with the correlation of the soil thermal characteristics and the soil properties.

As shown in previous investigations (2, 4), the thermal characteristics are widely dependent on the soil properties.

The thermal characteristics of the southern black earth (chernozem) have been de-

termined. As regards its mechanical properties, the investigated soil may be considered as light loam. The specific weight of the solid phase shows the values of 2.5 — 2.7 gm/cm³, while the bulk density if 1.2 — 1.5 gm/cm³ at the depth of 0 — 100 cm.

The purpose of the present paper is to discuss the results of the investigation concerning the dependence of the soil thermal characteristics upon its density. The experiment has been conducted with the soils of destroyed structure, because for the solution of the problem it was necessary to vary the density at constant moisture content and to vary the moisture content at constant density, which is not feasible under field conditions.

Recently the Soviet specialists have developed a few methods enabling to determine the thermal characteristics of soils. The coefficient of thermal diffusivity "K", using the method of G.M. Kondratjev (3) based upon the principle of the regular regime, for a sample of cylindrical shape has been defined.

Figure 1.

In the course of the experiments the density ρ varied from 0.1 to 1.5 gm/cm³ with increments of 0.1, while the moisture content w was characterized by the following terms: absolutely dry, air-dry, 10, 20 and 25 percent of moisture content based on dry weight.

The coefficient of thermal diffusivity has been measured for more than one hundred samples of plough layer soil. Identical measurements have been performed for the soil of the 80-100 cm layer. These "K" values differed from the plough layer "K" within the measurement accuracy. The conclusion suggests itself that for the southern black earth (chernozem) the coefficient of thermal diffusivity practically does not vary for the same density and moisture content. This may be explained by the uniformity of the soil dispersion in this layer. Therefore, in order to elucidate the principles of the "K" dependence upon moisture content and density the investigation was confined to the analysis of data for the plough layer.
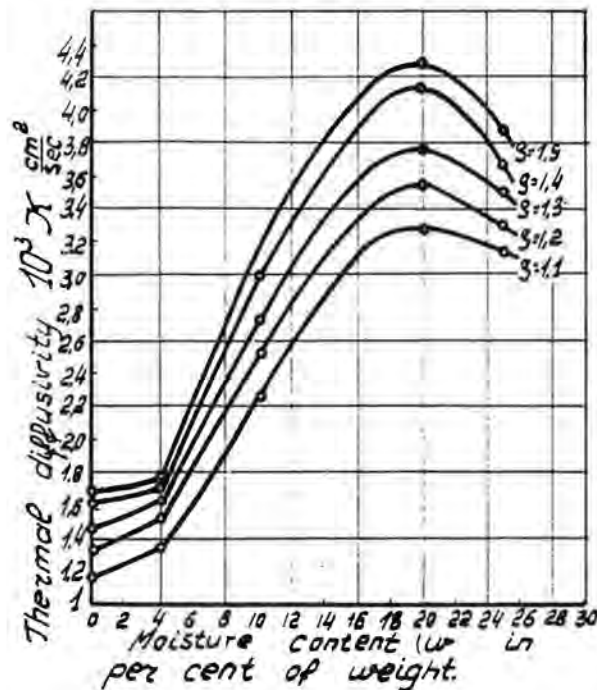
The obtained values of K = f(w) and K= ζ(ρ) are expressed graphically in Figures 1 and 2.

The volume heat capacity may be determined by means of the relation:

$$C\rho = \left(0.2 + \frac{w}{100}\right)\rho, \text{ where}$$

$C\rho$ is the volume heat capacity;
w is the moisture content in percent of weight;
ρ is the density, and
0.2 is the specific heat capacity of heavy loams.

The volume heat capacity increases linearly with increasing moisture content and density.

The coefficient of heat conductivity λ has been estimated by means of the formula λ = KCρ and the obtained data are shown graphically in Figures 3 and 4.

The coefficient of heat conductivity for any moisture content and density may be determined by using the empirical formula, inferred by the authors:

$$\lambda = 10^{-3}\left[\left(2.1\rho^{1.2-0.02w}e^{-0.007(w-20)^2}\rho^{0.8+0.02w}\right)\left(0.02 + \frac{w}{100}\right)\rho\right].$$

The formula being too complicated, a nomographic chart has been developed (Fig. 5), by means of which it is easy to determine all heat characteristics on the base of the predetermined values of moisture content and density; while knowing K, λ and ρ it is possible to determine the moisture content as well.

The coefficient of thermal diffusivity has been found also for soil samples with undisturbed structure. The "K" data obtained are somewhat smaller than in the case of the soils with destroyed structure, the value of the deviations not exceeding the experimental error.

Thus, the principles of the "K" relationship for the soils with destroyed structure may be used also for the soils under natural conditions.

On the Correlation of the Heat- and Water Properties of Soils

According to the data of previous investigations, K = f(w) increases to a maximum
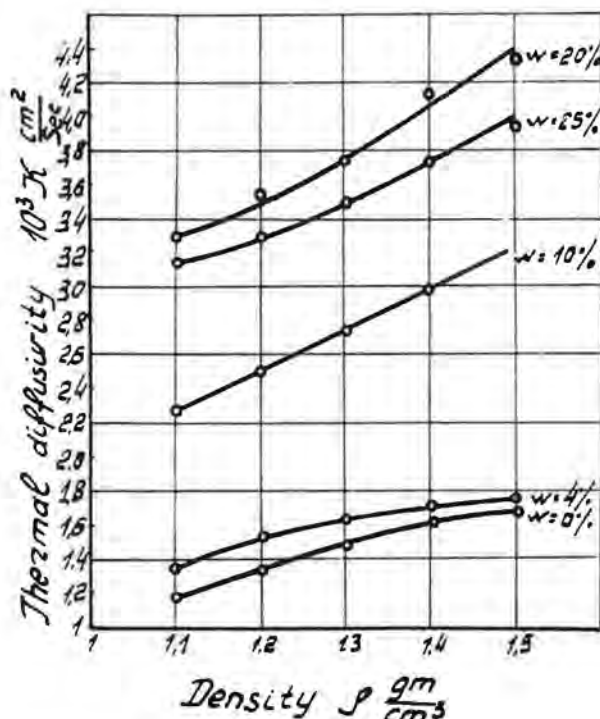
Figure 2.

within the different limits of moisture content depending on the properties of the soil. For the fine-grained sand the "K" maximum is within 8 to 10 percent of moisture content, for the coarse-grained sand—within 5-8 percent, for the clay—within 24-28 percent. The character of the K = f(w) curves is different too: for the sandy soil the curve is convex, while for the clayey soil it is concave.

As every soil has its own water constants, the above experimental data permitted drawing a conclusion about the connection between the heat and water properties of the given soil.

The coefficients of heat conductivity and of thermal diffusivity for the given soil increase with increasing moisture content unequally within the different limits of moisture content. This fact confirms the nonuniform character of heat transfer at the different stages of wetting.

A hypothesis about the dependence of the heat transfer mechanism upon the forms of water in the soil has been proposed by A. F. Chudnovsky.

In dry soil, as in a dispersion system (solid body—gas) the heat flow passes not as a continuous front, but as separate flows in the direction of the smallest spacings be-

Figure 3.

Figure 4.

tween the particles. The heat conductivity in the wet soil, as in a three-phase medium, is characterized by transferring heat through solid particles, water and air.

The value of heat conductivity depends on the shape, character and size of contacts of separate particles and on the quantity of water and air between them. Therefore, in order to ascertain the character of heat conductivity in wet soil, it is necessary to know the principles of the relationship between the soil particles and water for the different stages of wetting. Opinions concerning this problem differ, which again hampers the elucidation of the heat transfer process in soils.

In order to ascertain the connection between heat properties of the soil and its water properties, the so-called "theory of differential moisture" was used, which is the theory of the state and movement of water in soils developed by one of the authors on the base of laboratory and field tests. Following the theory of drying, F. E. Kolyasev developed a method for determining the mobility of water in soils in dependence of the soil moisture content. This method is founded on the rate of soil drying, because the rate of drying is connected with the rate of water movement; consequently it may characterize the degree of water mobility in soils at different moisture contents, as well as give an idea about the fundamental water properties of the soil, which determine the relation of the given soil to water ("Soil Science", ("Pochvovedenje"), No. 4, 1957).
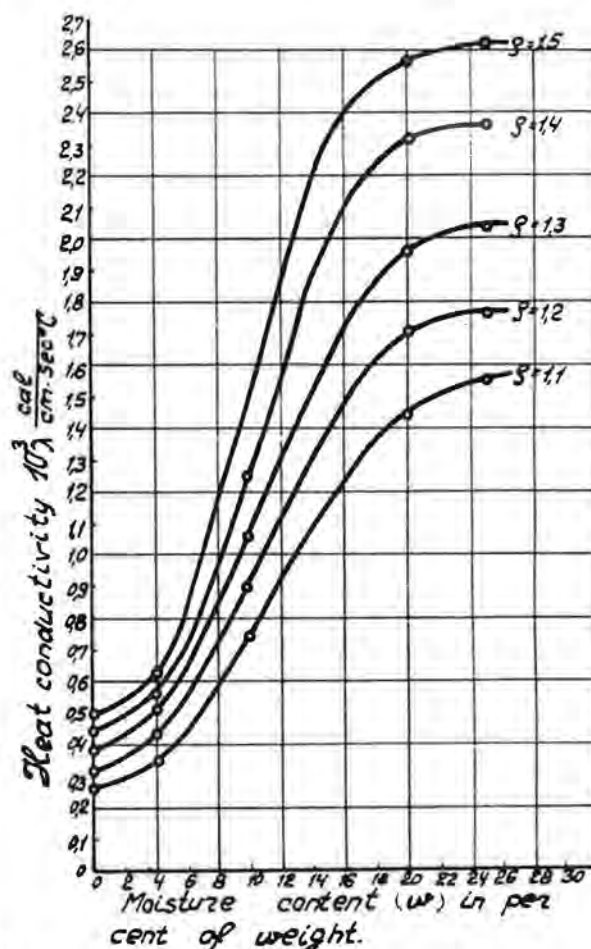
The experimental data prove that the curve of drying versus moisture content $\frac{dw}{dt} = f(w)$ is not smooth, but shows a few bends (Fig. 6). This indicates different rates of water movement towards the evaporating surface.

On the base of the drying rate curves F. E. Kolyasev has developed a scheme for the water movement in soil which enables to determine:

1. The fundamental water constants (using the break points on the drying rate curve).

2. The prevalent mechanisms of soil water movement for different moisture contents.

3. The degree of soil water availability for the plants.

The classification of the whole scope of soil water is based upon the physical causes of water movement at different moisture contents of the soil, as well as on its interaction with the soil particles.

By means of the drying method the water constants of black earth (chernozem) were determined, these constants being complemented and confirmed by the field and laboratory tests conducted according to the usual methods.

Four break points have been obtained for the investigated soil on the drying rate curve which correspond to definite conceptions in agricultural practice. The first break corresponds to "field capacity", the second—to the "moisture content of plant growth retardation"; the third—to the "moisture content of steady plant wilting"; the fourth—to the "maximum hygroscopicity". According to the drying rate data a general
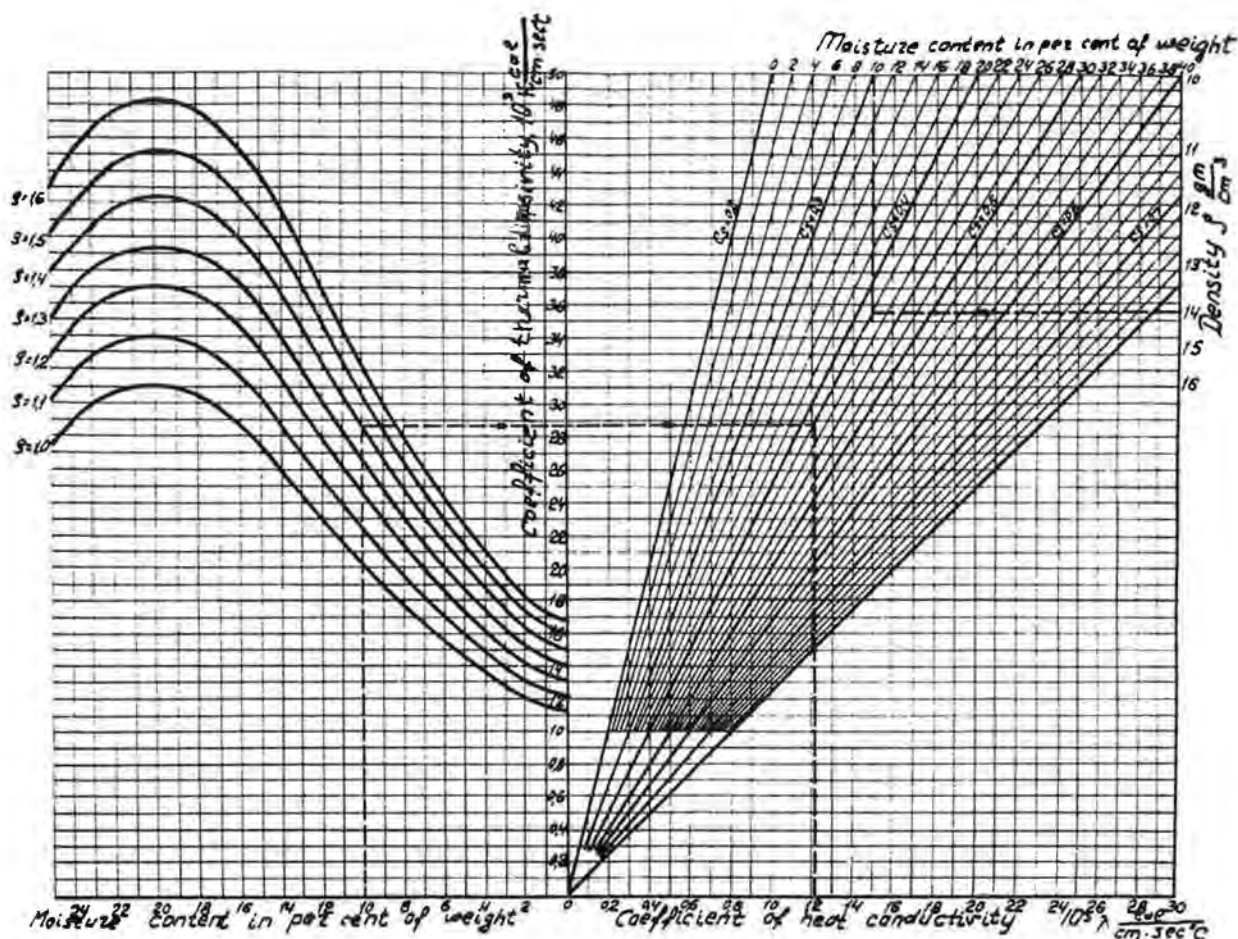
Figure 5.

scheme was developed by F. E. Kolyasev showing the predominance of different mechanisms in the soil water movement. An identical scheme for the southern black earth (chernozem) is given in Figure 7.

According to this scheme five mechanisms of water movement are ascertained: diffusion, film, film-meniscus, capillary and gravitational mechanisms. Such a conception of soil water movement provides the possibility to draw up a hypothesis about the heat transfer in humid soil as a function of the moisture content.

The relationship of $K = f(w)$ and $\lambda = \zeta(w)$ obtained in the course of the experiment may be explained if the values of "K" and "λ" are connected with the properties of soil water at the given stage of wetting and at a predetermined density.

The coefficients of thermal diffusivity and of heat conductivity increase with increasing density, the character of their increase being dependent on the moisture content.

If the soil is absolutely dry, the rate of increase in "K" and "λ" is greater at the lower density values, while at the higher values the increase slows down (Figs. 1 and 4).

The heat transfer in such kind of soil is accomplished mainly through the contacts between the soil particles, and with the increase of density evidently a certain limit of their drawing together and of the improvement of contact is reached.

The same condition for "K" and "λ" will be observed in the air-dry state, when their values are somewhat greater than in the absolutely dry state, because the sorbed water slightly improves the contacts.

At the 10 percent moisture content (film mechanism of water movement) "K" and "λ" increase rectilinearly with increasing density and their values increase sharply in magnitude as compared with the data for the air-dry condition. At this stage of wetting, water takes part in the heat transfer, creating at the points of the particles adjacency certain water contacts—"bridges"—through which heat transfer is accomplished.

Figure 6.

The 20 percent moisture content is such a stage of wetting at which the film-meniscus mechanism of water movement changes into the capillary mechanism. At the given moisture content the values of "K" and "λ" continue to increase with increasing density and at high values of density their increase will be greater. The increase of density brings the particles closer together which results in shortening and widening of the "bridges", i.e., in the decrease of thermoresistance. Besides, the mass of the solid phase is increased, the heat conductivity of the latter being about 5 times greater than that of water. The heat transfer will proceed not over the separate "channel-bridges", but by means of a certain continuous flow of heat created through water and solid phase, the part of the latter in the heat transfer being predominant.

At the 25 percent moisture content the capillary mechanism of water movement prevails. The character of change of "K" and "λ" with increase in density is the same as at 20 percent, but the magnitude of "K" for all density values is lower than at 20 percent. It is to be supposed that as the moisture content increases in the interval where the
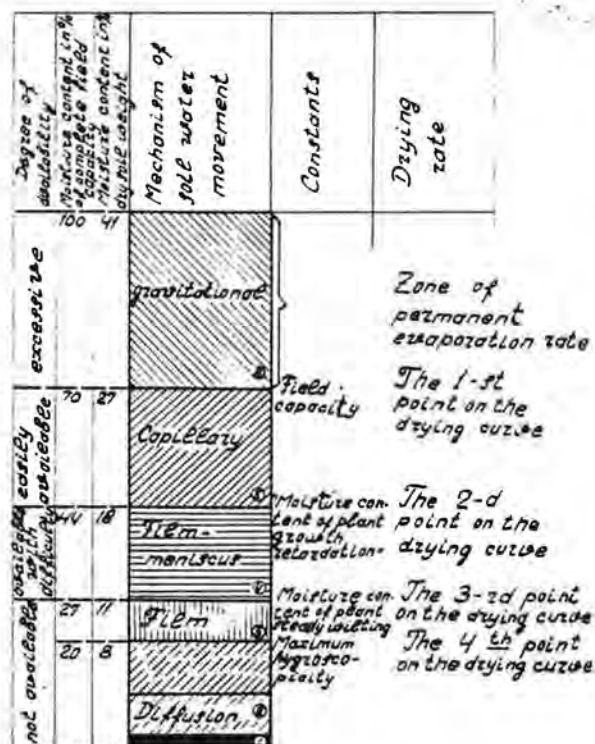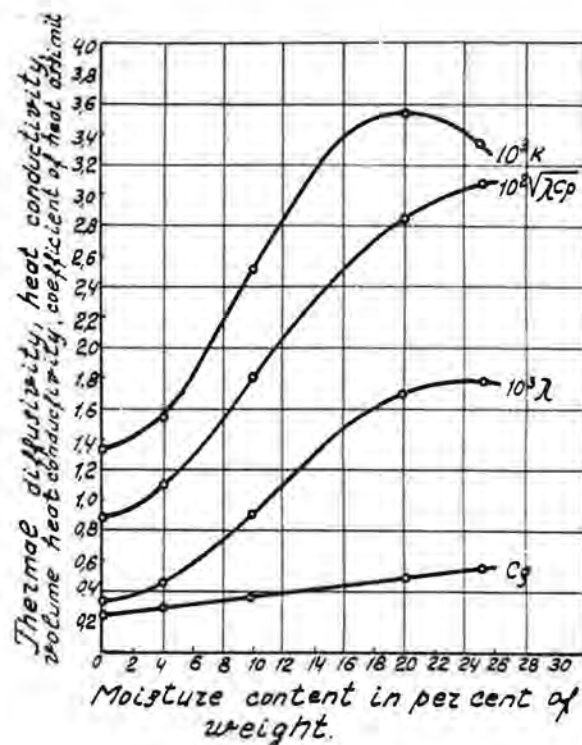
Figure 7.

Figure 8.

capillary mechanism prevails, water becomes not a connecting bridge between solid particles, but a medium through which the heat transfer is also accomplished. While the quantity of water increases, its part in the heat transfer also increases and the rise of the heat conductivity coefficient slows down approaching the heat conductivity of water (Fig. 3). But as the volume heat capacity continues to increase with increasing

moisture content, and as $K = \dfrac{\lambda}{C_\rho}$, the coefficient of thermal diffusivity decreases with the further increase of moisture content (Fig. 8).

Hence the coefficient of thermal diffusivity increases with increasing moisture content and reaches its maximum at such a moisture content where the film-meniscus mechanism changes into the capillary mechanism. The latter condition corresponds to the moisture content determined by the constant—"moisture content of plant growth retardation."

Each type of soil is characterized by its water constants and this evidently explains the experimental fact, that the coefficient of thermal diffusivity for different soils reaches its maximum not at the same, but at different moisture contents.

Evidently the break point in the $K = f(w)$ curve will take place for all kinds of soils at the "moisture content of plant growth retardation."

There are reasons to suppose that the break points on the $K = f(w)$ curve will also exist at the moisture contents which correspond to the "maximum hydroscopicity" and to "steady plant wilting" constants.

This is a problem for further investigations which may be solved with the development of a method for continuous recording of the moisture content.

At present such a method is being developed at the Laboratory of Soil Physics at the Agrophysical Institute in Leningrad.

CONCLUSION

The basic principle underlying measures to improve the thermal properties of soils is the dependence of the soil thermal characteristics upon the moisture content and density. The thermal diffusivity which determines the warming up of the soil along its profile increases with increasing water content up to the "moisture content of plant growth retardation." Consequently, in the soil with a greater moisture content the rate of temperature equalization will be greater and the warming up throughout the profile will be more intensive. At the moisture content which is greater than the "moisture content of plant growth retardation" the warming up is slowed down, because "K" decreases with increasing moisture content.

Proceeding from the conjecture about the dependence of the heat transfer mechanism in wet soil upon the water transfer mechanism at different stages of wetting, it is possible to draw a conclusion about the existence of a certain connection between the heat and water properties of a given soil.

The accumulation of experimental data on the dependence of thermal characteristics upon the moisture content for different soils accompanied by the determination of their water properties ensures the possibility of proving more extensively the theory of differential moisture content on the basis of which the heat transfer in moist soils has been explained.

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Moisture Flow Induced by Thermal Gradients Within Unsaturated Soils[1]

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Introductory Remarks by the Chairman

There can be little doubt that the most complex and least understood area in the field of soil-water relationships is that of the effect of temperature gradients applied to moist soils. One reason for the real, and also the imaginary but no less vexing, difficulties is that soil-water relationships and their dependence on temperature are uniquely individual for each soil system depending not only on the volumes and degrees of dispersion of the solid, liquid and gaseous phases, but also on the character and extent of the physico-chemical interactions at the phase boundaries and their temperature susceptibilities. Obviously, here is not a single effect, but an entire science that has areas of greater or lesser complexity depending on soil composition and condition; it is the science of soil thermodynamics in its widest sense. Before this science can be properly organized, a great deal of dependable experimental work must be done on well defined systems. Professor Hutcheon is presenting the results of an excellent and carefully executed experimental investigation on three soils of different texture under conditions of phase composition that favor moisture transmission in the vapor phase. Even under these conditions, the observed coefficients of vapor diffusion were from six to eight times greater than those calculated from known relationships for isothermal conditions. Grateful acknowledgment is given to Professor Hutcheon for his fine experimental contribution in one important area of the total problem.

●OBSERVATIONS and investigations of the influence of temperature gradients, and variations in temperature, on the retention and movement of water in the soil have been recorded periodically since the beginning of the century. One of the earliest reports was made by King (19) who noted evidence of diurnal fluctuations in the rate of discharge of water from tile drains, and in the level of ground waters in shallow wells. Similar observations have been made for very moist soil conditions by Roseau (39).

In the course of field experiments, Lebedeff (21) and Edlefsen and Bodman (7) noted substantial upward movements of water in unsaturated soils during the winter months, under frost free conditions. They attributed the movement to the influence of thermal conditions on the surface tension and vapor pressure of water.

Moore (25, 26) observed a considerable change in the rate of vertical capillary flow in soil columns under constant moisture-tension gradients when the columns were subjected to a change in ambient temperature conditions. Qualitative observations of the influence of temperature changes on moisture movement have also been made by Hilgeman (16), Haise and Kelley (11) and Pavlovski (27).

One of the earliest laboratory studies of thermal influences on moisture flow was conducted by Bouyoucos (3). He found a marked transfer of water from warm to cold regions of soil specimens. He attempted to segregate liquid and vapor flow characteristics by means of screen gaps and concluded that thermal effects were largely related to flow in the liquid phase.

Smith (41) considered that the effects of temperature on the surface tension of water were not sufficient to cause any appreciable transfer of moisture. However, in later

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experiments (42) he considered that moisture movement under the influence of a thermal gradient was the result of a combined cyclical process of vapor condensation and local capillary flow.

MacLean and Gwatkin (22) and Jones and Kohnke (18) concluded that the thermal migration of moisture occurred largely as a result of vapor pressure gradients induced by the unequal distribution of temperature.

Winterkorn (48) proposes that there is a flow of moisture, in the film phase, along the internal surface of the porous system due to a change in water affinity with change in temperature. He states, "The physical explanation of the phenomena is that the exchangeable cations possess a greater activity (or are more dissociated) at the cold than at the warm side; they cannot move to the warm side because they are held by negative charges of the mineral surfaces. The only way to decrease the concentration potential is by movement of water from the warm to the cold side."

The distribution of moisture under the influence of a thermal gradient has also been studied by Gurr, Marshall and Hutton (10), Rollins, Spangler and Kirkham (38), and by Taylor and Cavazza (44). It is of interest to note that by different techniques these authors have arrived independently at similar conclusions. Gurr, Marshall and Hutton evaluated the magnitude of liquid and vapor flow by measuring changes in the distribution of a small amount of sodium chloride dissolved in the moisture added to the soil. Any movement of the chloride ion was assumed to be due to moisture flow in the liquid phase.

Rollins, Spangler and Kirkham constructed an apparatus in which water vapors, which condensed at the cold plate, were returned to the warm plate by means of an external capillary tube. They compared the distribution of moisture in systems where the external circuit was both open and closed.

Taylor and Cavazza compared the thermal distribution of moisture in continuous and segmented soil columns with similar initial moisture contents. The segmented columns were prepared in five sections isolated by narrow air gaps.

The general conclusions of the above mentioned investigations may be summarized as follows: When a column of soil is subjected to a temperature gradient, the flow of moisture from warm to cool regions occurs largely in the vapor phase. The condensation of excess vapors in the cooler regions results in a flow of moisture, in the liquid phase, from cold to warm regions once a favorable pressure gradient within the liquid has been established. When the soil is sufficiently moist to permit active liquid flow, a state of equilibrium cannot be reached and a continuous circulation of water takes place within the enclosed column.

Croney and Coleman (5) have presented a theoretical analysis of the influence of temperature on both the relative and absolute vapor pressures of soil water, and on the internal pressures of the liquid, under various conditions of soil moisture. Similar calculations have been proposed by Edlefsen and Anderson (8), who also recognize the need for a somewhat different treatment of very dry soil conditions as compared to relatively moist soils.

This discussion is intended to give a critical appraisal of existing theoretical and experimental data relating to the behavior of unsaturated soil-moisture systems under the influence of a linear temperature gradient. Qualitative and quantitative data will be presented on the nature and magnitude of thermally induced moisture flow within the soil. All studies were conducted under laboratory conditions.

Previous investigators have employed relatively short soil columns subjected to temperature gradients ranging from 1.5 to 3 C/cm. In the present study soil columns 30 cm long were enclosed in split lucite tubes with an internal diameter of 10 cm, and a wall thickness of 0.6 cm. Various hot and cold face temperatures were used within the range from -4 to 25 C with temperature gradients ranging from 0.5 to 0.8 C/cm.

The long soil columns and low gradients of temperature were intended to provide a more sensitive evaluation of the relationship between liquid and vapor flow at various initial soil moisture contents, and between various segments of any particular column.

Figure 1. A vertical transverse section of the thermal apparatus showing one soil column in position.

METHODS AND MATERIALS

The necessary bulk of soil, previously conditioned to the required initial moisture content, was poured in a continuous stream into the taped lucite tube which was agitated on a vibrator at 140 vibrations per minute during the filling operation. The soil column was then compacted from each end to a standard length of 30 cm and an apparent density of approximately 1.3 gm per cu cm. The hollow brass circulation plates were placed in position, and the whole unit was sealed with Scotch electrical tape. One hundred grams of Ottawa sand were spread uniformly across the soil surface, before seating the brass plates, to provide a uniform and standard thermal contact.

The details of construction of the thermal unit, with a prepared soil column in position, are illustrated in the vertical transverse section shown in Figure 1. The prepared soil column was positioned in a compartment inside a metal box G. The copper tubes of the brass hot and cold plates H and C were connected in parallel to the circulating hot and cold liquid systems DE and AB respectively. The whole column was then packed tightly around the sides, and over the top, with rock wool insulation. The metal box G, open both top and bottom, was constructed of 16 gauge galvanized iron. The copper tubes K and L were brazed onto the respective upper and lower perimeters of the box, and were also connected in parallel to the hot and cold circulation systems. The metal box was therefore subjected to the same temperature gradient as the soil column. In this way the ambient temperature of each segment of the soil column approximated the desired temperature within the segment when a stable gradient of temperature was attained.

The hot and cold liquids, conditioned to the desired temperatures, were circulated through the respective systems at the rate of 40 to 60 gallons per hour by means of vertical immersion pumps. The rate of flow of the liquids to each of the thermal units, and to the tubes of the metal box, was regulated to provide an equal distribution at all times.

The thermocouple installations were inserted horizontally to the center of the column at predetermined positions as shown in Figure 1. Potentials were read to give a precision of ± 0.05 C.

There were minor variations in temperature at similar depths within columns subjected to the same hot and cold plate conditions at the same time. However, within any particular column studied, the observed gradient of temperature across any six centimeter segment never deviated more than 12 percent from the average gradient for the column as a whole. Some of this deviation could have been due to inaccuracies in positioning the thermocouples which were inserted after the column was prepared. Soil columns, prepared and stored at room temperatures, reached a stable distribution of temperature throughout the column within 24 to 36 hours after they were subjected to a gradient temperature. Under the conditions of temperature applied in the study a stable distribution of moisture was attained within 30 to 40 days.
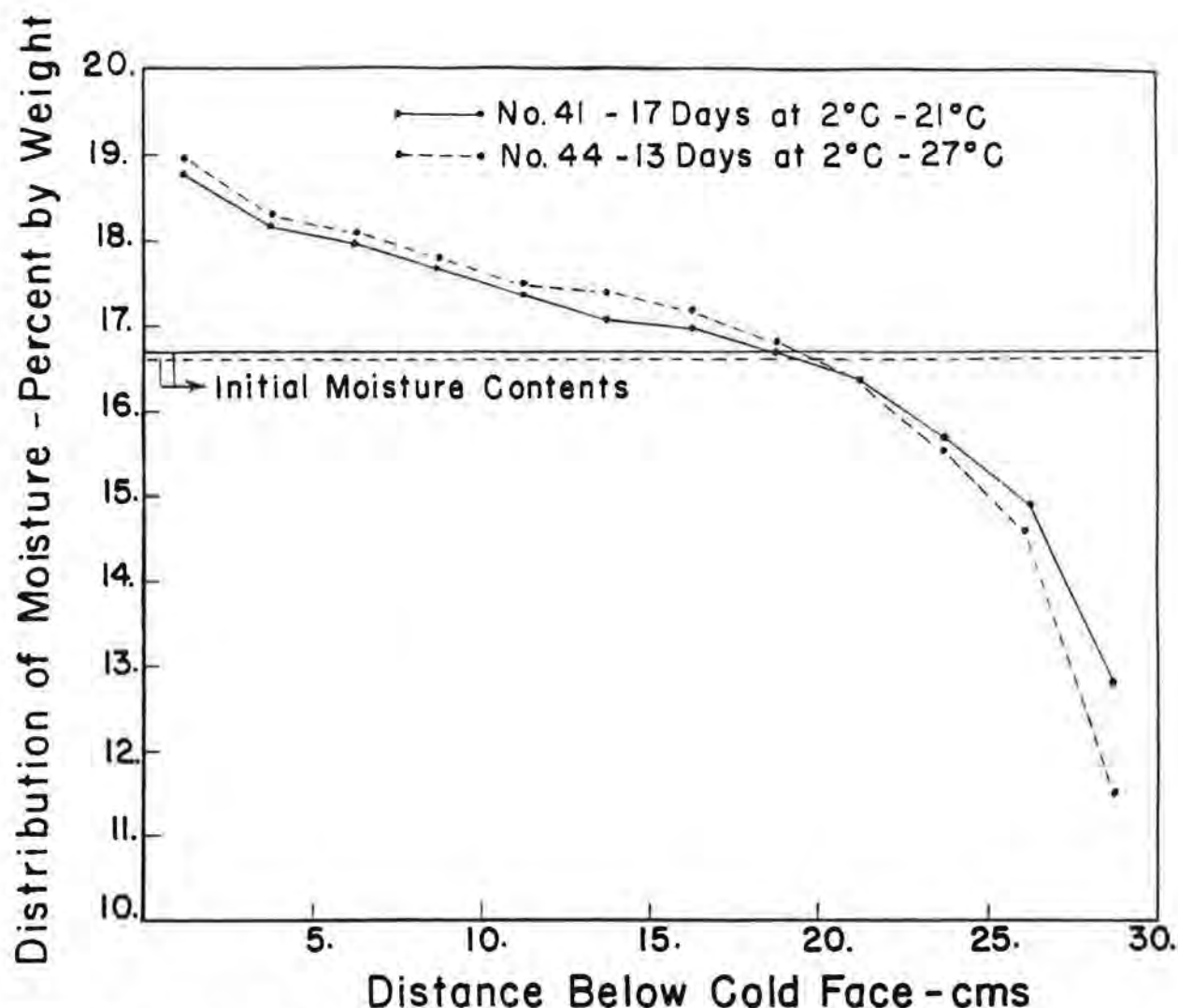
Figure 2. Moisture distribution in columns of clay loam soil subjected to a temperature gradient of 2 to 21 C and 2 to 27 C for 17 days and 13 days, respectively.

Figure 2 illustrates the reproducibility of data under the conditions imposed in the thermal apparatus. After the data for column 41 were analysed, column 44 was prepared to the same initial moisture content and was exposed to a different temperature gradient for a time calculated to give the same degree of moisture movement as occurred in column 41.

The mechanical composition and some moisture characteristics are shown in Table 1 for the three soils studied. All samples were taken from cultivated horizons and had approximately the same organic matter content (3.5 percent). The hygroscopic coefficient is defined here as the moisture content (expressed as percent of oven dry weight) of the soil in equilibrium with an atmosphere of 45 percent relative humidity at 20 C. The permanent wilting percentage, which normally denotes the lowest practical limit of available moisture for plant growth, was determined in the pressure membrane apparatus (36) and is equivalent to the 18 atmosphere percentage. The 3/10 atmosphere percentage was determined on the pressure plate apparatus (36).

TABLE 1

MECHANICAL COMPOSITION AND SOME MOISTURE CHARACTERISTICS OF THE SOILS

Texture	Clay Loam	Very Fine Sandy Loam	Loamy Fine Sand
Percent Sand (2 - 0.05 mm)	40.2	53.5	86.4
Percent Silt (0.05 - 0.002 mm)	28.7	33.4	5.3
Percent Clay (finer 0.002 mm)	31.1	13.1	8.3
Hygroscopic Coefficient	3.4	1.8	1.3
Permanent Wilting Percentage	12.6	7.1	4.5
3/10 Atmosphere Percentage	28.7	15.5	10.8

PRESENTATION AND DISCUSSION OF RESULTS

The moisture distribution under the influence of a thermal gradient, imposed with hot and cold plate temperatures of 10 and 25 C, respectively, was investigated for six columns of clay loam with an initial uniform distribution of moisture ranging from 9.1 to 26.3 percent, for five columns of very fine sandy loam ranging from 4.8 to 15.8 percent initial moisture, and for four columns of loamy fine sand ranging from 5.0 to 13.1 percent in initial moisture content. The distribution of moisture within the various columns of each soil, after a condition of zero net flow was attained, is illustrated in Figures 3A, B, and C for the clay loam, very fine sandy loam and loamy fine sand, respectively.

In all cases illustrated there was a net transfer of moisture from warm to cold regions of the column, which was induced by the imposed thermal conditions. At initial moisture contents below the permanent wilting percentage, the net movement of moisture was very small. As the initial moisture content was increased, there was a gradual increase in the net transfer of moisture towards the cold plate, until a condition of maximum moisture gradient was attained in the case of the columns having initially uniform moisture contents of 16.0, 7.6 and 5.0 percent in the clay loam, very fine sandy loam and loamy fine sand, respectively. These moisture contents are approximately 50 to 60 percent of the moisture content characterized by the 3/10 atmosphere percentage for these soils. As the initial moisture content was increased to higher values, there was a gradual decline in the net transfer of moisture and very little net transfer occurs at moisture contents characterized by soil moisture tensions in the vicinity of 3/10 of an atmosphere. The general relationships between initial moisture content and the net transfer of water, under the influence of a thermal gradient, are similar to those obtained for a loam soil by Gurr, Marshall and Hutton (10). Similar observations were also made by MacLean and Gwatkin (22), who also noted that the net movement of moisture was markedly influenced by the bulk density of the soil column under any particular conditions of initial moisture content.

An analysis of the relationships between soil temperature and the relative and absolute vapor pressures of soil water, together with a consideration of the physical state of the water, will provide an explanation for the characteristic moisture distributions produced by a thermal gradient imposed on a closed soil column. Table 2 shows the moisture content of the clay loam soil characteristic of various soil moisture tension conditions on the drying curve at 20 C. The vapor pressure data and relative humidities were calculated from a modification of the thermodynamic relationships proposed by Bodman and Edlefsen (2) and Edlefsen and Anderson (8) which express soil-moisture potential as a function of relative humidity.

The osmotic pressure of the soil solution is generally considered to be negligible in the case of well drained, non-saline soils at moisture contents within the range between the permanent wilting percentage and the 3/10 atmosphere percentage (37). The internal pressure of the soil water will therefore be due entirely to capillary forces. Under these conditions the following relationship was assumed to be valid for the soils and soil moisture conditions studied:

$$h = -\frac{RT}{Mg} \ln \frac{p}{p_S} \quad \text{where;}$$

h = soil moisture tension as gm cm/gm
R = gas constant
T = absolute temperature
M = molecular weight of water
g = gravitational constant
p = vapor pressure of soil water
p_S = vapor pressure of free, pure water
p/p_S = relative humidity

The relative humidities and vapor pressures characteristic of soil moisture tensions at and above 18 atmospheres

TABLE 2

MOISTURE RELEASE DATA FOR CLAY LOAM SOIL AT 20 C

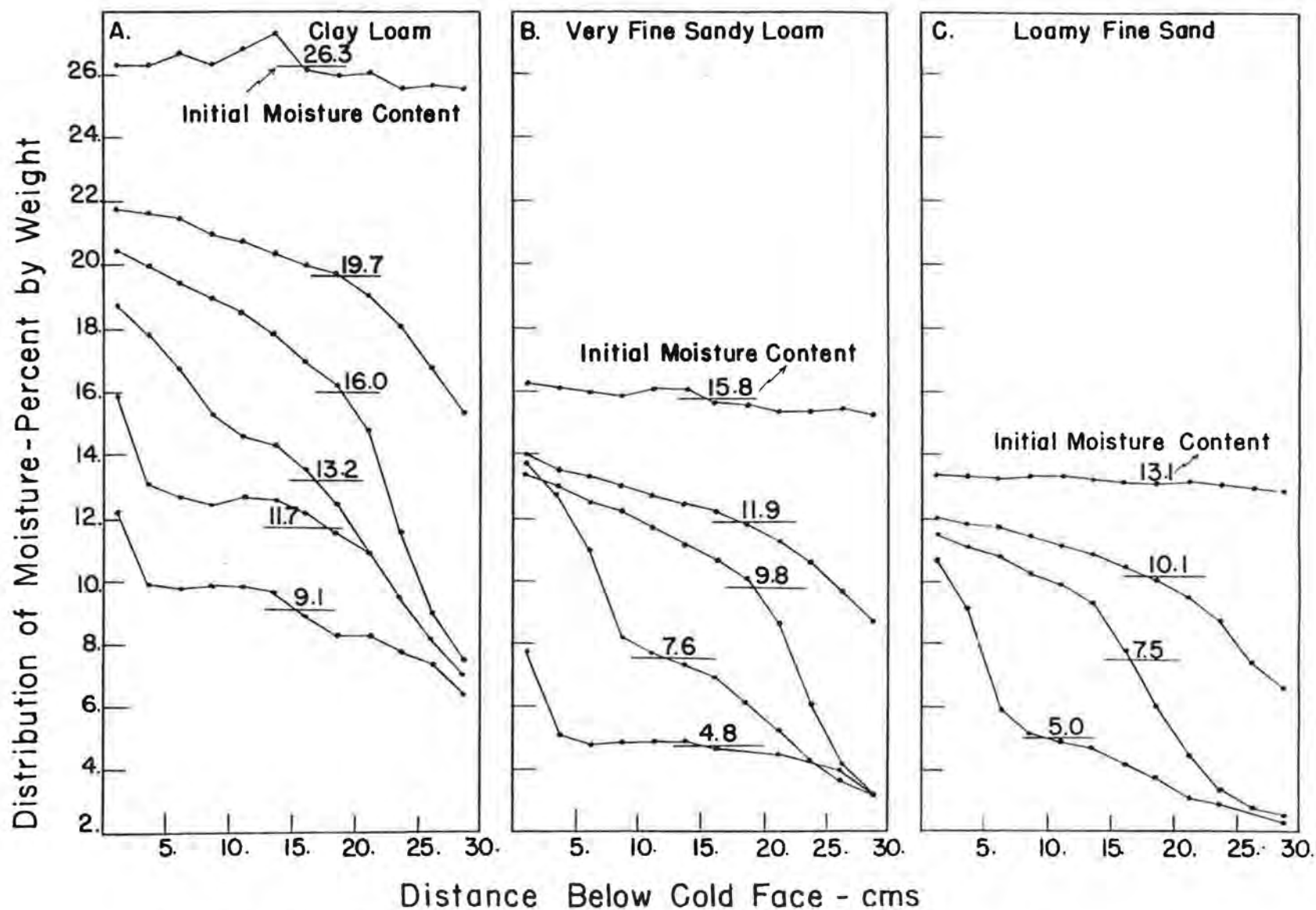| Moisture Tension (atm)	Percent Moisture	Vapor Pressure Soil Water at 20 C (mm Hg)	Calculated Relative Humidity at 20 C (percent)
0.1	35.4	17.534	99.992
0.3	28.7	17.533	99.978
0.5	25.8	17.528	99.962
1.0	23.4	17.522	99.925
3.0	19.6	17.495	99.780
8.0	16.6	17.430	99.400
15.0	14.0	17.339	98.880
18.0	12.8	17.300	98.660
280.0	6.1	14.221	81.100
-	3.4	7.890	45.000

Figure 3. Comparison of moisture distribution at different initial moisture contents within soil columns subjected to a temperature gradient from 10 to 25 C.

were calculated from this relationship. The moisture content characteristic of relative humidities of 81.1 and 45.0 percent respectively were actual determinations obtained by drying the soil samples to equilibrium with a preconditioned atmosphere.

An examination of the data presented in Table 2, and a comparison of the results illustrated in Figure 3 for the various soils, indicate that the behavior of the soil moisture system under the influence of a thermal gradient is closely related to the physical condition of both the soil and the soil moisture. All of these factors must be clearly defined since they will delineate the general relationships which exist between the solid, liquid and vapor phases under any particular thermal state.

It is evident from the data in Table 2 that at soil moisture contents characteristic of relative humidities below 98 percent, the vapor pressure of soil water is a very close function of moisture content. A gain or loss of water will result in a very significant change in vapor pressure. Water will not flow as a liquid (24), and movement will be confined to the vapor phase if unbalanced energy conditions occur within the soil mass. The energy of retention is very great and the free energy of the water molecules is dominated by adsorptive forces. At water contents characteristic of relative humidities below 70 or 80 percent it is likely that the moisture is present as oriented molecular water (1, 8, 13, 23, 40, 45, 47) of various types. The adsorption or desorption of water, as water vapor, will be accompanied by a considerable exchange of heat (5, 9).

At moisture contents above those characterized by 98 percent relative humidity the free energy of the liquid arises from the action of surface forces at the interface boundaries between the solid, liquid and vapor phases (8, 37). This energy condition is commonly described in terms of moisture tension, which is: "A stress equivalent to the surface force action in producing a certain energy status of water" (37, p. 92). Flow of water through the soil takes place under the influence of pressure gradients within the liquid phase, the magnitudes of which are a close function of the relative moisture contents of the soil system. The relationship between moisture content and soil moisture tension is illustrated in Table 2. It will vary considerably depending on the physical nature of the soil system (35).

In the absence of a temperature gradient, movement of water in the vapor phase will be negligible under soil moisture conditions above the permanent wilting percentage. The vapor pressure of soil water will be very close to the saturation vapor pressure over a wide range of soil moisture conditions. Adsorption or condensation of water into the soil will not result in any significant change in vapor pressure. Also, reduction in moisture content as a result of either evaporation or liquid flow, will not produce any real changes in vapor pressures until the soil moisture condition is reduced below that characterized by 98 percent relative humidity. The movement of water within the soil, in the liquid phase, is dependent on both the potential gradient, and on the capillary permeability which is also a variable function of the moisture characteristics (33, 34, 37). This is understandable from the geometry of the system of solids since the liquid is held over the surface of the particles, and in concave form in the pores or wedges between the particles. As the moisture content is decreased, within the range of capillary moisture content, the water will be more strongly influenced by the surface energy of the solids, and in addition, the proportion of total free space within the soil which is occupied with water in the liquid phase will also be decreased. As the soil moisture content approaches the permanent wilting percentage, very large pressure gradients, and therefore large moisture gradients, will be required to produce any appreciable flow in the liquid phase.

It is evident from the preceeding discussions that the influence of an unequal distribution of temperature will likely vary, depending on the physical condition of the soil, and of the soil moisture. At initial moisture contents well below the permanent wilting percentage, a temperature gradient will likely produce a marked gradient of vapor pressure from warm to cold regions of the soil, but will have no influence on liquid flow since the major portion of the soil water is in the absorbed and oriented molecular state. The required shift of water, as water vapor, to produce a state of uniform vapor pressures throughout the soil mass, will be relatively small since the rate of change of vapor pressure is a very significant function of changes in the moisture characteristic. This is confirmed in Figure 3 by the equilibrium moisture distributions for the

clay loam and very fine sandy loam columns at initial moisture contents of 9.1 and 4.8 percent respectively, when exposed to a temperature gradient from 10 to 25 C.

Within the range of soil moisture conditions characteristic of moisture tension below the 18 atmosphere percentage, the effects of temperature changes must be considered for both the liquid and vapor phases. Richards and Weaver (35) studied the moisture content of a series of soils of varying texture, at temperatures ranging from 10 to 40 C, in equilibrium with extraction pressures of 0.5 and 15 atmospheres in the pressure membrane apparatus. Their data indicate that the changes in soil moisture tension, induced by a change in temperature conditions, are extremely small. This behavior is also confirmed by a consideration of the calculated changes in moisture tension induced by a change in temperature using equations proposed by both Edlefsen and Anderson (8) and Croney and Coleman (5). Such calculations are based on the assumption that the major changes in the magnitude of the surface forces affecting the energy of the liquid will be due to changes in the surface tension of water. This can be justified at least in very moist, non-saline soils at moisture contents in the vicinity of the 3/10 atmosphere percentage. The following is a modification of the equation proposed by Edlefsen and Anderson:

$$\log H_2 = \frac{T_1}{T_2} \cdot \frac{S_1}{S_2} \cdot \log H_1 \qquad \text{where}$$

T, H and S refer to the absolute temperature, the surface tension of water and the relative humidity expressed as a fraction, respectively.

If a column of clay loam soil, at an initial moisture content of 28.7 percent, and uniform temperature of 20 C, is subjected to a temperature gradient from 10 to 25 C, the relative humidity at the cold face will be reduced to 99.977 percent or will be decreased by 0.001 percent. On the basis of the relationship between moisture content, moisture tension and relative humidity as shown in Table 2 for this soil, an increase of 0.18 percent in moisture content should be sufficient to restore the relative humidity, and therefore the moisture tension, back to the original conditions. Similarly, the slightly decreased moisture tension in the soil at the warm face will be restored to its original value by a comparable small loss of moisture. Similar calculations for other temperature conditions indicate that the pressure gradients induced within the liquid phase as a result of a temperature gradient will not cause any appreciable shift of water, as liquid, from warm to cold regions of the soil under moisture conditions characteristic of those between the 3/10 atmosphere percentage and the permanent wilting percentage. This is confined by the characteristic moisture distribution data shown in Figure 3 for the clay loam, very fine sandy loam and loamy fine sand soils at 26.3, 15.8 and 13.1 percent initial moisture content, respectively.

TABLE 3

APPROXIMATE DISTRIBUTION OF INITIAL VAPOR PRESSURE CONDITIONS WITHIN A COLUMN OF CLAY LOAM SOIL SUBJECTED TO A TEMPERATURE GRADIENT FROM 10 TO 25 C, WITH INITIAL MOISTURE CONTENT ABOVE THE PERMANENT WILTING PERCENTAGE

Distance from Cold Face cm	Temperature C	Initial Vapor Pressure mm Hg	Average Gradient Vapor Pressure mm Hg/cm	Relative Humidity for Zero Vapor Flow
0	10	9.21		100.0
2	11	9.84	0.32	97.2
6	13	11.23	0.35	82.0
12	16	13.63	0.40	67.5
18	19	16.48	0.47	55.8
24	22	19.83	0.56	46.4
26	23	21.07	0.62	43.7
28	24	22.38	0.66	41.2
30	25	23.76	0.69	38.7

Although a temperature gradient will only produce a very slight instability within the liquid phase under soil moisture conditions above the permanent wilting percentage, it will produce a much greater instability within the vapor phase. Since the vapor pressure of soil water at any soil moisture content above the permanent wilting percentage is very near the saturation vapor pressure, the relationship between temperature and vapor pressure can be considered similar to that for free pure water. Table 3 shows the calculated initial distribution of vapor pressures within a column of clay loam soil having an initial uniform moisture content above the permanent wilting percentage, and exposed to a linear temperature gradient from 10 to 25 C. It is interesting to note that the gradient of vapor pressure is not a linear function of temperature; an unsteady state of vapor diffusion should therefore occur. These factors were overlooked by both MacLean and Gwatkin (22) and Rollins, Spangler and Kirkham (38) in some of their conclusions regarding the transfer of moisture induced by a temperature gradient. The vapor pressure gradient will be markedly changed by either a change in temperature gradient or a change in mean temperature conditions while the same gradient of temperature is maintained across the soil column.

The conditions illustrated in Table 3 will apply initially to any column of clay loam soil having an initial moisture content above the permanent wilting percentage and exposed to a linear temperature gradient from 10 to 25 C. Since vapor pressures will not be changed by condensation of moisture, water vapor should continue to diffuse into, and condense in, the coldest segment of the soil column until the vapor pressure of every warmer segment has been reduced to 9.21 mm of Hg by a net evaporation of water. The characteristic relative humidity at various points within the soil column, if a condition of equilibrium vapor pressure were to be attained, are shown in the last column of Table 3. An approximation of the moisture content of the soil characterized by each of these conditions of relative humidity may be obtained from a study of Table 2. The moisture content in the soil at a distance of 6 cm from the cold face would have to be reduced to approximately 6.1 percent before the vapor pressure was reduced to 9.21 mm Hg. Similarly, at 26 cm below the cold face, the moisture content would have to be reduced by net evaporation to approximately 3.3 percent if a condition of equilibrium vapor pressures were to be attained. If the initial moisture content of the soil column was 16.6 percent, it is obvious that the coldest segment of the column could not possibly retain all of the water which must be evaporated from every other warmer segment before a condition of equilibrium vapor pressure could be attained.

The above considerations will indicate that the major mechanism of water transport, under the influence of a temperature gradient, must be due to water vapor diffusion. In addition, since the changes in moisture tension induced by a change in temperature are very slight, the condensation of diffused water vapors within the coldest regions of the soil will create a moisture gradient, and therefore a pressure gradient within the liquid, from cold to warmer regions in opposition to vapor flow. This latter state can only occur under soil moisture conditions at which some of the water is retained in the soil as liquid. The comparative magnitude of the liquid flow will depend on the rate of diffusion and condensation of vapors within the coldest regions of the column, on the capillary permeability and on the magnitude of the induced pressure gradient within the liquid resulting from the condensation of vapors.

In order to substantiate the deduction that moisture movement from warm to cold regions of the soil will occur principally as water vapor, and to substantiate the existence of opposing liquid and vapor circulation systems, soil columns were prepared to initial moisture contents comparable with those presented in Figure 3, and were subjected to a temperature gradient with freezing conditions within the coldest segments. Frost action should create a pressure gradient within the liquid phase from warm to colder regions and should therefore inhibit any tendency for liquid to flow from cold to warmer regions of the soil columns. In these latter experiments, cold and hot plate temperatures of -4 and 18 C were used. In all columns the soil temperature at a distance of 2.5 cm below the cold face was approximately -1.7 C. The over-all gradients of vapor pressure should have been approximately equal to those induced within similar columns subjected to cold and hot plate temperatures of 10 and 25 C, respectively. The distribution of moisture within paired columns of the clay loam soil having
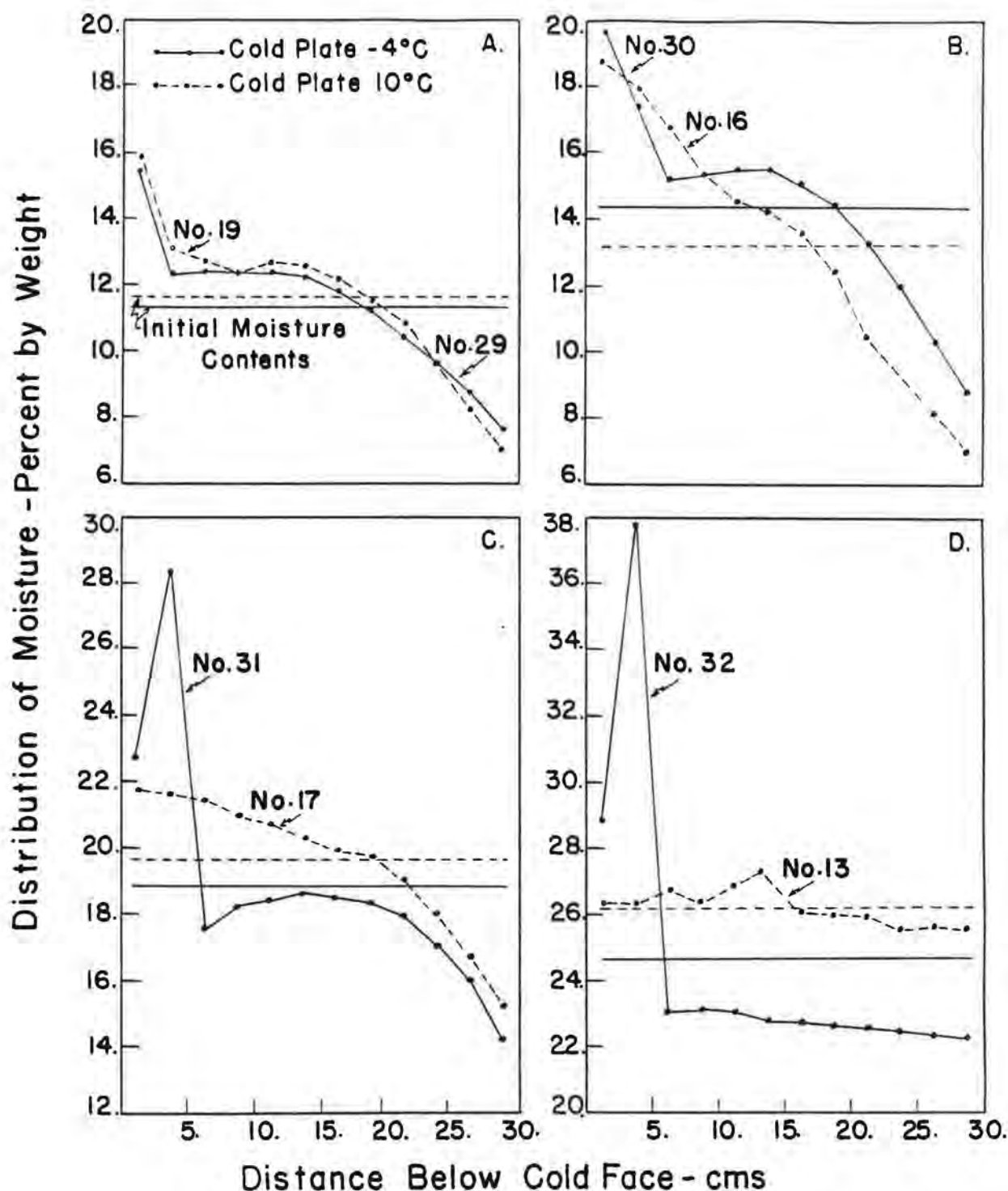
Figure 4. Distribution of moisture within columns of clay loam soil subjected to a temperature gradient from -4 to 18 C for 30 days.

approximately the same initial moisture contents, but subjected to cold and hot plate temperatures of 10 to 25 C and -4 to 18 C, respectively, for 35 days are shown in Figure 4.

In Figure 4A the characteristic distribution of moisture has not been influenced by the frost action at the cold plate although the soil was frozen to a depth of 2 cm below the plate. At this initial moisture content it was not expected that any considerable flow of moisture would occur within the liquid phase. However, the close agreement of the induced moisture distributions within similar periods of time indicates that the over-all vapor pressure conditions must have been similar within the two columns sub-

jected to differing temperature conditions. The initial uniform moisture distribution in both columns was approximately one percent below the permanent wilting percentage.

In Figure 4B the pattern of moisture distribution differs slightly between the two columns in the region from 5 to 20 cm below the cold plate. The frost action has retained all of the condensed vapors within the zone above 4 cm in column No. 30, otherwise the moisture distribution between 5 and 12 cm would have been linear as in the case of the same region of column No. 16. Since there was no appreciable flow of condensed vapors from the coldest segment back into this latter region, the net accumulation of water in column No. 30 between 5 and 20 cm could only have occurred as a result of a small continuous net condensation during an unsteady state of vapor diffusion from warm to cold regions of the column. On this basis the moisture gradient between 6 and 16 cm must have been very small throughout the time of exposure to the temperature gradient. It must be concluded therefore, that the net loss of water from the region between 20 and 30 cm could only have occurred as a result of evaporation and vapor diffusion, under the influence of a vapor pressure gradient induced by the unequal distribution of temperature.

Column No. 17, Figure 4C, was exposed to a temperature gradient from 10 to 25 C for 47 days, and column No. 31 was exposed to a temperature gradient from -4 to 18 C for 32 days. The moisture distribution indicated for column No. 17 is a stable one since a duplicate column exposed to the same temperature conditions for only 30 days had a similar distribution of moisture. In column No. 31 the freezing temperatures near the cold plate have retained all of the condensed vapors as ice, and in addition the frost has induced a small net flow of liquid towards the cold face within the cold half of the column as indicated by the induced moisture gradient, and therefore moisture tension gradient, between 5 and 13 cm. Since the moisture content at the 13 cm depth has not been reduced below initial moisture conditions there cannot have been any transfer of water in the liquid phase from the warm half of the column. This is confirmed by a comparison of conditions at sampling time between column No. 31 and column No. 32, Figure 4D. In this latter column, vapor diffusion conditions must have been similar to those within column 31, but active liquid flow towards the freezing zone has also occurred throughout the column under the influence of the frost induced pressure gradient. Liquid flow was more pronounced in the case of column No. 32 because of the higher capillary permeability, which is a direct function of moisture content. It must be concluded therefore, that if there had been any appreciable flow of water in the liquid phase from the warmest to the coldest regions of column No. 31, the moisture content at the 13 cm depth should have been reduced considerably below initial conditions. The loss of water between 13 and 30 cm must have occurred as a result of vapor diffusion as in the case of column No. 30. It must be assumed that conditions within the column were still unstable at sampling time, and that continued exposure of the column to the temperature gradient would eventually produce a moisture distribution pattern similar to that of column No. 30, with the exception of the freezing zone.

Since columns 17 and 30 were very similar with regard to initial moisture distribution the induced conditions of vapor pressure gradient must have also been approximately the same. A stable distribution of moisture could only have been attained in column 17 if there was a return flow of liquid from cold to warm regions which was equal in magnitude to the vapor diffusion from warm to cold regions in every segment of the column. A similar situation must be responsible for the very small net transfer of water which has occurred within column No. 32. Since the capillary permeability was greater at this mean moisture content, a much smaller pressure gradient (and therefore moisture gradient) will be required to produce a return liquid flow which is equal in magnitude to the vapor diffusion from warm to cold regions of the column.

In the case of column No. 32, Figure 4D, the column was sampled after 32 days of exposure to a temperature gradient from -4 to 18 C. Continued exposure to these conditions should produce a moisture distribution pattern which would pass through the stage indicated by the distribution obtained for column No. 31, and if the freezing zone could contain all of the condensed water vapors, the moisture distribution outside of the freezing zone should eventually resemble that attained within similar regions of column No. 30.

No. 32 at sampling time, as compared to initial conditions, it must be assumed that there has been no appreciable change in the distribution of vapor pressures as a result of moisture movement towards the freezing zone.

If conditions were still dynamic at the stage of moisture distribution indicated in column 32 at sampling time, any further transfer of moisture in the liquid phase from the regions below the 12 cm depth, towards the cold face, would have to take place against a pressure gradient within the liquid phase from cold to warmer regions. The gradient of moisture content from 12 cm towards the 30 cm depth suggests that the liquid should now flow from cold to warmer regions. This condition has likely been induced by the net evaporation within the very warmest segments. Earlier discussions indicated that evaporation of water from the soil would not produce any appreciable change in the vapor pressure of soil water until the moisture content was depleted below the permanent wilting percentage. However, examination of the moisture characteristics and moisture-tension data of Table 2 indicates that differential rates of evaporation could produce a pronounced pressure gradient within the liquid phase without appreciably altering conditions within the vapor phase. It is suggested that, under conditions of unequal temperature distribution within the soil, liquid flow in opposition to vapor flow can be induced by net evaporation within the warmest regions, as well as by net condensation within the coldest regions. The presence of such a circulation system would appear to be characteristic of conditions within the warm half of column No. 31 , Figure 4C, at the time of sampling. The net loss of water within the zone between 13 and 25 cm must have occurred as a result of liquid flow from this region into the net evaporation sink between 25 and 30 cm. The beginnings of such conditions are also indicated in column 32 since the decreased moisture content, and therefore decreased capillary permeability, have begun to restrict the frost induced liquid flow to the colder segments of the column. The over-all net flow of liquid towards the cold
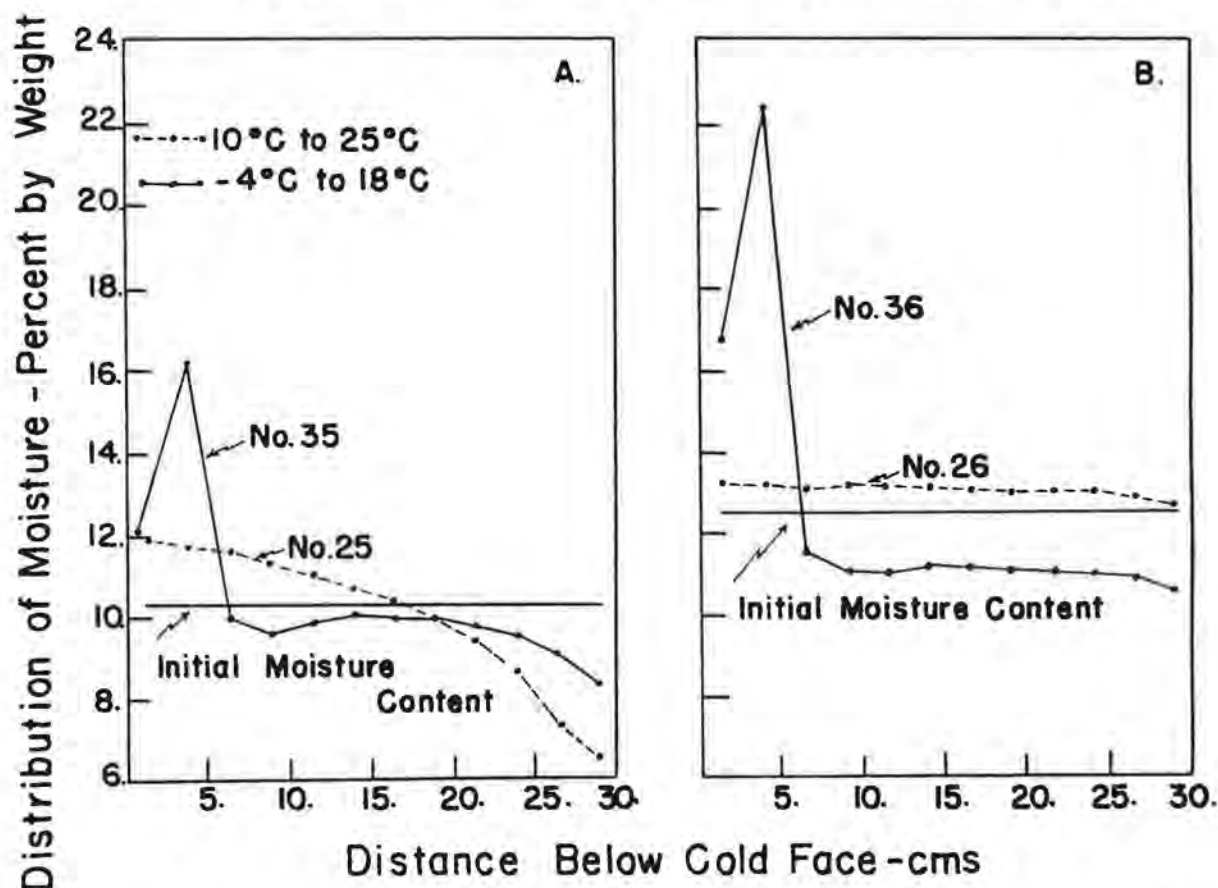

Figure 5. Distribution of moisture within two columns of loamy fine sand subjected to a temperature gradient from -4 to 18 C for 16 days.

face had previously masked the effects of net evaporation at the warm face.

In order to further investigate the influence of net evaporation on the movement of water in the liquid phase, two columns of loamy fine sand were prepared to initial moisture contents of 12.6 and 10.4 percent, respectively, and were subjected to a temperature gradient from -4 to 18 C for 16 days. The net distribution of water, as determined by sampling at this time, is illustrated for these two initial moisture conditions by the data for columns 35 and 36, Figures 5A and B. The moisture distribution data for two other columns prepared to the same initial moisture contents, but which were exposed to a temperature gradient from 10 to 25 C until a condition of zero net transfer of moisture was attained, are also presented for purposes of comparison.

The initial moisture content in column No. 36 was approximately two percent above the 3/10 atmosphere percentage (Table 1). Since the capillary permeability would be relatively high at this moisture content, it is quite likely that, in the early stages of exposure to the temperature gradient, the moisture was flowing in both the liquid and vapor phases from the warmest to the coldest regions; the direction of liquid flow having been reversed in comparison to that of column No. 26 as a result of the frost induced pressure gradient, towards the cold face, within the liquid phase. As the mean moisture content was reduced, and therefore the capillary permeability, the frost-induced liquid flow would be restricted to the colder regions of the column. This is indicated by the comparative depression of moisture content in the region between 7 and 14 cm in column No. 36. When the over-all net flow of liquid towards the cold face had ceased to affect the warm half of the column, the influence of net evaporation on liquid flow became apparent. This is indicated by the slight depression of moisture content in the warmest segment between 27 and 30 cm, which has also initialed a small pressure gradient within the liquid towards the warm face in the region between 20 and 27 cm. At the time of sampling, the moisture content was uniform between 13 and 20 cm in column No. 36. This indicates that, by this time, liquid was no longer flowing from the warm half of the column towards the cold face. At this stage, it must be assumed that there was still an over-all unsteady state diffusion of water vapor from the warmest to the coldest segments, with a small net condensation occurring in every intermediate segment. The net evaporation within the region between 27 and 30 cm has also initialed a flow of liquid into the evaporation sink, as indicated by the small moisture gradient, and therefore moisture tension gradient, from 20 to 27 cm. Within the cold half of the column liquid was flowing along a moisture tension gradient from 13 cm towards the freezing zone.

At the time of sampling in column 36, the mean moisture content between 5 and 30 cm was approaching the initial moisture conditions of column No. 35. The sequence of events that occurred within column No. 35 during the period of exposure to the temperature gradient from -4 to 18 C could be considered to be similar to those which would have occurred if column No. 36 had been exposed to these temperature conditions for a much longer time period. The moisture distribution at the time of sampling as shown in Figure 5A for column No. 35, illustrates very well the beginnings of the pronounced parabolic distribution of moisture which was characteristic of that found in the clay loam column No. 31, Figure 4C.

The decrease in moisture content in the region between 14 and 18 cm in column No. 35 was due to flow in the liquid phase towards both the cold and warm faces. Within the warm half of the column, water had been flowing in the liquid phase along the pressure gradient into the evaporation sink of the warmest segments between 25 and 30 cm. From this latter region the water then diffused as vapor towards the coldest regions of the column, and into the freezing zone. Within the cold half of the column the loss of water has been due entirely to flow within the liquid phase under the influence of the frost induced pressure gradient. Since the temperature gradient conditions were very nearly linear throughout the time of exposure of column No. 35, the foregoing explanation is the only possible mechanism by which the moisture content within the central regions of the column could have been depleted below initial conditions. Previous investigators (10, 38, 44) have postulated that the return circulation of liquid, in opposition to vapor flow, was due entirely to net condensation within the coldest regions of the column, and at the cold plate. However, it is only logical to conclude that, if net con-
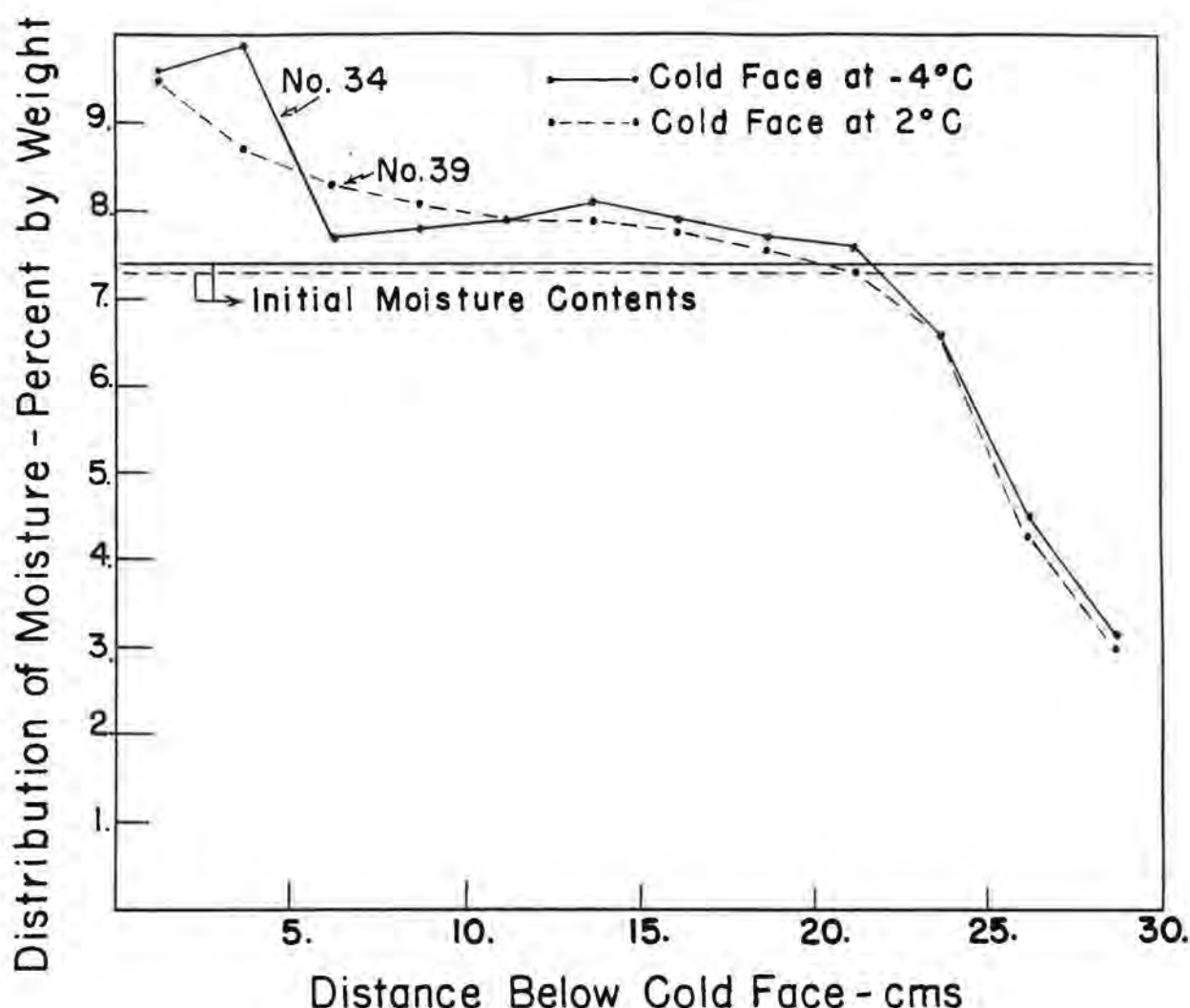
Figure 6. Comparison of moisture distribution within two columns of loamy fine sand subjected to temperature gradients of -4 to 18 C and 2 to 21 C for 16 days.

densation can induce a pressure gradient from cold to warmer regions, net evaporation within the warmest region should also induce a return flow of liquid from adjacent regions into the evaporation sink. The distribution of moisture obtained in soil columns where the cold circulation system was inhibited by frost action would appear to confirm this theory. This latter system will be designated as the warm circulation system; it will not be as active as the cold circulation system since it is associated with a general decrease of water content, and therefore of capillary permeability.

The data of Gurr, Marshall, and Hutton (10) also indicate that a warm circulation system, induced by the net evaporation within the warmest segments of the column, was functioning during the early stages of redistribution of moisture within soil columns exposed to a temperature gradient. The existence of two maxima and two minima of chloride concentration as illustrated in Figure 2 of their published data can only be explained by this mechanism. If these columns had been examined at the end of two or three days, instead of five days, the depletion of chloride within the region between 5 and 7 cm would have been more pronounced, at least in those columns which had an initial moisture content above 7.9 percent. This explanation would also account for the apparent flow of water in the liquid phase at very low moisture contents.

In order to minimize any discrepancies which might be attributed to the wide differences in temperature conditions in the previous comparisons between comparable soil columns exposed to temperature conditions of 10 to 25 C and -4 to 18 C, some further studies were conducted. Soil columns of similar initial moisture contents were exposed

to temperature conditions of -4 to 18 C and 2 to 21 C for 16 days. Figure 6 shows the comparative distribution of moisture at the end of 16 days exposure to the respective temperature gradients within two columns of loamy fine sand. Column No. 34, which was subjected to freezing temperatures within the coldest segments, had an initial uniform moisture content of 7.4 percent. The initial moisture content of column No. 39, which was exposed to cold plate temperatures just above freezing, was 7.3 percent. These moisture distributions may also be compared to the loamy fine sand column of Figure 3C which had an initial moisture content of 7.5 percent, and which was exposed to cold and hot plate temperatures of 10 and 25 C, respectively, for 44 days. This latter column had reached a stable distribution of moisture before sampling time. The data for column 39 therefore represents an intermediate stage in the sequence of redistribution of moisture under non-freezing conditions, since continued exposure to the temperature gradient produced a moisture distribution very similar to that shown for the comparable column in Figure 3C.

The very close relationship of the induced moisture distributions within the warm halves of columns 34 and 39 indicates that the operating mechanisms of water transport must have been identical. The small net accumulation of moisture in the regions between 10 and 20 cm in both columns could only have occurred as a result of condensation of diffusing water vapors, during an unsteady state diffusion. The distribution of moisture, and therefore of pressure gradients within the liquid phase, eliminates the possibility that there has been any transfer of water in the liquid phase from the warmest to the coolest regions. The existence of independent cold and warm circulation systems is also confirmed by a comparison of moisture distribution between the two columns in the regions from the cold plate to 10 cm and from 15 to 30 cm, respectively. It must be assumed that, at the time of sampling, water must have been flowing in the liquid phase within column No. 39 from the cold plate to a depth of 10 cm. This flow was inhibited in column 34 due to the freezing conditions which retained all of the condensed vapors as ice. Within the warm half of both columns, water must also have been flowing in the liquid phase from within the region between 15 and 23 cm into the net evaporation sink between 23 and 30 cm.

If column No. 39 had been exposed to the temperature gradient for a longer period of time, the net evaporation sink would have extended above the 23 cm zone, and eventually the cold and warm circulation systems would have merged to give a continuous flow of liquid from the cold face back to the evaporation sink. It must be assumed that these conditions are established within the stable system at the time of sampling of the loamy fine sand column of Figure 3C which had an initial uniform moisture distribution of 7.5 percent. Within all the segments above the 18 cm depth in this column, it is assumed that liquid and vapor flow were equal in magnitude and opposite in direction.

The comparisons discussed in the preceding sections would appear to confirm the fact that moisture transfer from warm to cooler regions within the soil, when a condition of unequal temperature exists, would appear to take place largely within the vapor phase. Either net condensation, or net evaporation, may induce a flow of liquid in the opposite direction to the vapor flow. The relationship between moisture content and capillary permeability will determine the magnitude of the induced moisture gradient, and therefore moisture tension gradient, which must be created before any appreciable flow in the liquid phase will occur.

The existence of a warm circulation system was indicated earlier by Preston (32). Cold circulation systems have been described in other types of porous materials by other workers (17, 20).

THE CHARACTER AND MAGNITUDE OF VAPOR DIFFUSION

Very little experimental data are available for the prediction of the magnitude of vapor diffusion within the soil. Penman and Schofield (28) applied Penman's equation (29, 30) to the calculation of the magnitude of vapor diffusion through the soil when an unequal condition of temperature exists. They indicated that it was of very little consequence. More recent evidence however indicates that such calculations may be considerably in error (10, 38, 44). It is of interest therefore to examine the apparent

coefficients of vapor diffusion, and the nature of the diffusion process, within some of the soil columns in which the flow of moisture from warm to cold regions was known to have occurred within the vapor phase.

In a number of instances, such as columns 34 and 39, Figure 6, the columns were sampled after a relatively short exposure to the temperature gradients, and well before a condition of zero net flow had been attained. It was quite evident, as was pointed out in the case of column No. 39, that the moisture accumulation within intermediate segments must have occurred as a result of condensation accompanying an unsteady state diffusion of water vapor. The data from a number of such columns were selected for a study of the apparent coefficients of vapor diffusion. The segment of each column which was still at the initial moisture content, at the time of sampling, was chosen as the one across which vapor diffusion rates were calculated. The data were all selected from columns in which it was well established that the liquid flow from the cold face had not affected the moisture status of any segment of the warm half of the column. The total of accumulated moisture within regions colder than the segment selected for analysis, should then represent the total of diffused vapors which had passed through the segment.

The coefficients of vapor diffusion were calculated by the equation for steady state, undirectional flow of vapor (29), where a linear gradient of concentration exists between vapor concentrations C_1 and C_2 at a distance dX apart. Therefore:

$$\frac{dQ}{dt} = D A \frac{dc}{dX}$$

Q/A = total vapor diffused in time t, through a unit of cross-sectional area, expressed as gm per sq cm;

D = coefficient of vapor diffusion as sq cm per sec;

c = volume concentration of vapor as gm per cu cm; and

X = distance across segment, normal to the concentration gradient.

The vapor concentration gradients were calculated on the assumption that the soil moisture vapor pressures were approximately equal to the vapor pressure of free pure water at the respective temperatures. All columns studied had an initial moisture content well above the permanent wilting percentage. Even though the vapor pressures are slightly in error as a result of this assumption the calculated gradients of vapor concentration should not be affected to the same degree. It should also be noted that all evidence indicates that the vapor diffusion was an unsteady state condition. However,

TABLE 4

COEFFICIENTS OF VAPOR DIFFUSION, UNDER VARIOUS CONDITIONS, FOR THE SEGMENT OF EACH COLUMN WHICH REMAINED AT THE INITIAL MOISTURE CONTENT DURING EXPOSURE TO A TEMPERATURE GRADIENT

Texture	LFS	LFS	LFS	VSL	VSL	VSL
Air-filled pore space, percent	39.8	40.4	39.6	37.3	37.7	38.2
Mean temperature of segment, C	13.5	17.3	11.5	13.4	17.4	10.7
Average temperature gradient in column, 9C/cm	0.65	0.79	0.67	0.63	0.81	0.53
Moisture content, percent	7.3	6.3	7.4	7.8	7.5	13.4
Total diffusion, gm/cm^2	0.26	0.32	0.26	0.26	0.27	0.22
Coefficient of diffusion, cm^2/sec	0.41	0.34	0.42	0.39	0.33	0.40
Cold and hot plate temperature, C	2 + 21	2 + 27	-4 + 18	2 + 21	2 + 27	1 + 16

the coefficients calculated from the steady state equation should still represent conditions across that plane segment of the column at which the vapor concentration gradient was equal to the one used for the calculations shown in Table 4.

The calculated coefficients of vapor diffusion, together with other data characterizing the temperature and air-filled pore space conditions, are shown for six columns of very fine sandy loam and loamy fine sand in Table 4. The six columns had approximately the same percent air-filled pore space, and were exposed to temperature gradients of from 2 to 21 C, 2 to 27 C, and -4 to 18 C. There is remarkably close agreement between all columns in which the mean temperature conditions were similar, the coefficients varying from 0.39 to 0.42 sq cm per sec. The two columns exposed to the higher temperature gradient from 2 to 27 C showed a marked decrease in the magnitude of the coefficient of diffusion.

It should also be noted here that coefficients were calculated for the clay loam columns No. 41 and 44, Figure 2. The calculated coefficient of vapor diffusion for conditions within column No. 41 was 0.36 sq cm per sec. Using this calculated coefficient, it was estimated that if column No. 44, which was prepared to the same initial moisture content, was exposed to a temperature gradient from 2 to 27 C for 13 days it should give approximately the same distribution of moisture. This calculation was based on conditions at the 20 cm plane within the column. It can be seen from the distributions of moisture that the total of diffused vapors was very similar to that of column 41. The calculated coefficient of vapor diffusion for column No. 44 was 0.34 sq cm per sec.

The coefficients calculated for the clay loam columns differed quite widely from those calculated for the loamy fine sand and very fine sandy loam columns under similar temperature conditions. They were approximately 20 percent lower. It has been suggested by other workers that vapor diffusion characteristics within granular structured soils may cause deviations from the observed vapor diffusion coefficients for single grain soils.

The calculated coefficients of vapor diffusion, based on conditions at the 20 cm segment, for columns 34 and 39, Figure 6, were 0.42 and 0.41 sq cm per sec, respectively. On the assumption that liquid flow had not appreciably affected conditions at the 11 cm plane, and that the total of accumulated moisture between 11 cm and 20 cm was due to unsteady state condensation, coefficients of vapor diffusion were also calculated for temperature conditions at the 11 cm plane. The total diffused vapors were calculated from the moisture accumulations between the cold plate and the 11 cm depth. These coefficients agreed very closely with those calculated at the 20 cm plane and were 0.43 and 0.41 sq cm per sec, respectively.

The accumulated moisture between the 11 cm and 20 cm planes of columns 34 and 39 was considered to be due to the fact that the vapor concentration gradient was not a linear function of temperature. Accordingly, coefficients of vapor diffusion were calculated from the unsteady state diffusion equation:

$$\frac{dQ}{dt} = D \ A \ d^2c/dX^2 \ dX$$

where Q in this case was calculated from the total of accumulated vapors between 11 and 20 cm. It was then assumed that all of these accumulated vapors had condensed within a small segment across which d^2c/dX^2 was equal to the rate of change of the vapor concentration gradient as expressed by the difference between the gradients calculated for the 21 cm and 11 cm planes, respectively. The calculated coefficients using this latter equation, and based on conditions within columns 34 and 39, were 0.44 and 0.42 sq cm per sec, respectively. This would appear to confirm the fact that the major movement of water from warm to cold regions of soil columns exposed to a gradient of temperature does occur within the vapor phase, and that where the temperature gradient conditions are nearly linear, the diffusion of vapors is an unsteady state condition which produces a small net condensation within every intermediate segment of the column between the evaporation sink and the net condensation sink near the cold plate.

The observed coefficients of vapor diffusion for all the columns studied were from six to eight times greater than those calculated from the relationship proposed by

Penman (29, 30); D/Do = 0.66S, where Do is the coefficient of vapor diffusion in air at the appropriate temperature, S is the fraction of air-filled pore space, and 0.66 is a constant which corrects for the increased length of the diffusion path resulting from the tortuous nature of the pore space.

It should be noted that Penman's relationship for calculating diffusion of gases and vapors through the soil was derived from experimental conditions where gases and vapors were used which had no appreciable thermal reactions with the solids, or liquids, of the soil system. In addition, the experimental conditions imposed a linear gradient of gas, or vapor, pressure throughout the system. In the case of water vapor diffusion through the soil it is only under very special circumstances that there will be a linear gradient of vapor pressure; and under all moisture conditions an appreciable exchange of heat will accompany the evaporation, condensation or adsorption of vapors. The total exchange of heat involved in these processes will be due to (a) the latent heat released or absorbed during condensation or evaporation of vapors, which will always be present, and its magnitude will be directly related to the quantities of water involved; and (b) the heat of wetting arising from the interactions between the water and either the surfaces of the solid or the surfaces of the liquid in the capillary pores.

Henry (14, 15) has analysed the conditions of both heat and vapor transfer through porous media in which there is a coupled diffusion resulting from the interactions between the porous media and the diffusing vapors. His conclusions may be summarized as follows: the observed diffusion coefficients, where coupled diffusion occurs, are always such that one is greater and the other less than they would be if they occurred independently. The faster diffusion rate, which may be either for heat or for moisture, may be many times the "isothermal diffusion constant" for moisture or the "constant vapor concentration, diffusion coefficient" for heat, whichever is the smaller. This may explain the deviations between the observed coefficients of water vapor diffusion in these experiments and those calculated for the same conditions from Penman's relationship. This may also explain the reasons for the marked depression of the observed vapor diffusion coefficients, as shown in Table 4, for the columns subjected to hot and cold plate temperatures of 2 and 27 C, respectively. Under these latter temperature conditions the unsteady state condensation would be markedly increased as compared to that which occurred within the columns subjected to temperature gradients from either 2 to 21 C, or -4 to 18 C. There is need for a good deal of further study and analysis of the characteristics of the diffusion of water vapors through soil, and other porous media, in relation to both temperature and moisture conditions.

SUMMARY

Qualitative and quantitative data have been presented to illustrate the character and magnitude of thermally induced moisture flow within unsaturated soils, with particular reference to soil moisture conditions characteristic of moisture tensions in excess of 0.1 atmospheres.

The comparative data obtained from the exposure of relatively large soil columns to temperature gradients which were calculated to give similar conditions of vapor pressure distribution, but which produced both freezing and non-freezing conditions adjacent to the cold plate, would indicate the following conclusions with regard to the character and magnitude of thermally induced moisture flow within the soil:

1. A temperature gradient imposed on a soil column, initially of uniform moisture content and temperature, will create a relatively large gradient of vapor pressure from warm to cold regions, but only a very slight gradient of moisture tension within the liquid phase in the same direction.

2. If soil moisture conditions are below the permanent wilting percentage, small changes in moisture content will produce a large change in the vapor pressure of soil water. An equilibrium of vapor pressure conditions can be attained by a relatively small net diffusion of water vapor from warm to cold regions of the soil.

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2. If soil moisture conditions are below the permanent wilting percentage, small changes in moisture content will produce a large change in the vapor pressure of soil water. An equilibrium of vapor pressure conditions can be attained by a relatively small net diffusion of water vapor from warm to cold regions of the soil.

3. When soil moisture contents are above those characteristic of the permanent wilting percentage, the induced conditions of vapor pressure gradient will be such as

to create an unsteady state diffusion of water vapor from warm to cold regions, and since the soil-water vapor pressures are very close to the saturation vapor pressures at similar temperatures, the condensation of vapors will produce no change in vapor pressure conditions; and the evaporation of water will only affect the vapor pressure conditions if the soil moisture content is reduced below the permanent wilting percentage within the evaporation zone. In the initial stages of vapor flow, there will be a net evaporation within the warmest segments, and a maximum of condensation within the coldest segments due to the presence of the cold plate. Every intermediate region will show a small net condensation of water vapor due to the unsteady state diffusion; the magnitude of the latter condensation will be greatest within the warmest parts of the soil adjacent to the net evaporation sink. The magnitude of the unsteady state condensation will also be closely related to both temperature gradient and mean temperature.

4. Since the temperature-induced gradients of pressure within the liquid phase will be extremely small, the net condensation and net evaporation will induce a pressure gradient within the liquid phase and will create a flow of liquid in opposition to the vapor diffusion within both the warmest and coldest regions. These systems have been designated as the warm and cold circulation systems, respectively, and under certain conditions they may operate independently within the respective regions of the soil. In the absence of a cold plate, or any other feature which might initiate a zone of net condensation, a considerable readjustment of moisture distribution could occur, within relatively moist soils, under the influence of a net evaporation or warm circulation system. A zone of net evaporation will always be present within any soil at initial moisture conditions above the permanent wilting percentage, and within which an unequal distribution of temperature is characteristic.

5. Under soil moisture conditions in the vicinity of, and slightly above the permanent wilting percentage, a large gradient of pressure within the liquid phase will be required to initiate liquid flow from cool to warmer regions, since the capillary permeability will be very low. A condition of maximum moisture gradient will therefore be attained.

At soil moisture conditions approaching those characteristic of the 3/10 atmosphere percentage, the capillary permeability will be relatively much greater, and the magnitude of the vapor diffusion will be somewhat reduced due to the decreased content of air-filled pore space as compared to moisture conditions near the permanent wilting percentage. The cold and warm circulation systems will merge, and a continuous flow of liquid will occur from the coldest to the warmest regions, in opposition to vapor flow, under the influence of a relatively small pressure gradient within the liquid, and therefore with a relatively small gradient of moisture between the warmest and coldest regions. A state of equilibrium vapor pressure cannot be attained and a continuous circulation of soil moisture will take place with liquid and vapor flow being equal in magnitude, but opposite in direction, within every segment.

6. The conditions described above will be responsible for the parabolic relationship observed between net moisture movement under the influence of a thermal gradient and the mean moisture content of the soil.

7. For moisture conditions above the permanent wilting percentage, the observed coefficients of vapor diffusion were from six to eight times greater than those calculated from known relationships for isothermal conditions. The magnitude of the observed coefficient appears to be affected by temperature, gradient of temperature, and the structural nature of the soil.

8. Frost-induced pressure gradients within the liquid phase will not cause any appreciable flow of water when soil moisture conditions are drier than those characteristic of moisture tensions in the vicinity of one atmosphere.

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On the Mechanism by Which Water Moves Through a Porous Material Subjected to a Temperature Gradient

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Introductory Remarks by the Chairman

In his excellent symposium paper on the Physics of Water Movement in Porous Solids, Dr. Philip has traced with sure hand the architecture of the theoretical structure that provides room and general accommodations to all those that are interested in water movement through systems in which physico-chemical interaction between the different phases is small enough to be justifiably neglected. However, all structures of scientific theory must be based on facts and these facts must be obtained by careful observation and experimentation. It is new facts that force modification or abandonment of even well established theories, but the facts on which an old theory was based remain and must fit into the new theoretical structure. To provide such facts in as complex a field as ours requires painstaking, patient and devoted experimental work. By such work, Dr. Kuzmak and Mr. Sereda have produced important facts that increase our understanding of a well defined area within our total field of interest.

● THE MOVEMENT of moisture from the hot to the cold side of a porous material has been observed by many workers, however, the mechanism by which this movement takes place has not yet been definitely established (1, 4, 6, 8, 9). The moisture may move in the vapor phase, the driving potential being the vapor pressure difference which corresponds to the temperature difference across the material. The observed rate of flow through the material, however, is about ten times the rate calculated using the above vapor pressure difference (1, 4). To account for the difference, it has been suggested that the water also moves in the liquid (film) phase.

There has been no direct experimental evidence to show that the discrepancy between the experimental and calculated rates is due to flow in the liquid phase. Attempts to obtain such evidence of flow in the liquid phase from the hot to the cold side are described in this paper.

THE VAPOR GAP EXPERIMENT

Apparatus and Procedure

The theoretical relationships involved and the practical aspects of the construction of the apparatus have been described by others (3, 5). The main principle involved is that, under isothermal conditions, the moisture content of a porous material in contact with a saturated porous plate is determined by the difference in pressure across the plate. The moisture content decreases as the difference in pressure increases. The maximum pressure difference that can be used is less than the pressure required to empty the pores of the plate.

The apparatus used in the present investigation was a modification of that developed by Swenson and Sereda (7) to maintain a fixed moisture content in a sample at the same time that the movement of moisture due to a temperature gradient is taking place. The apparatus is shown in half section in Figure 1. A cylindrical sample, A, was confined by two identical ceramic porous plates, B, which were sealed into cylindrical lucite
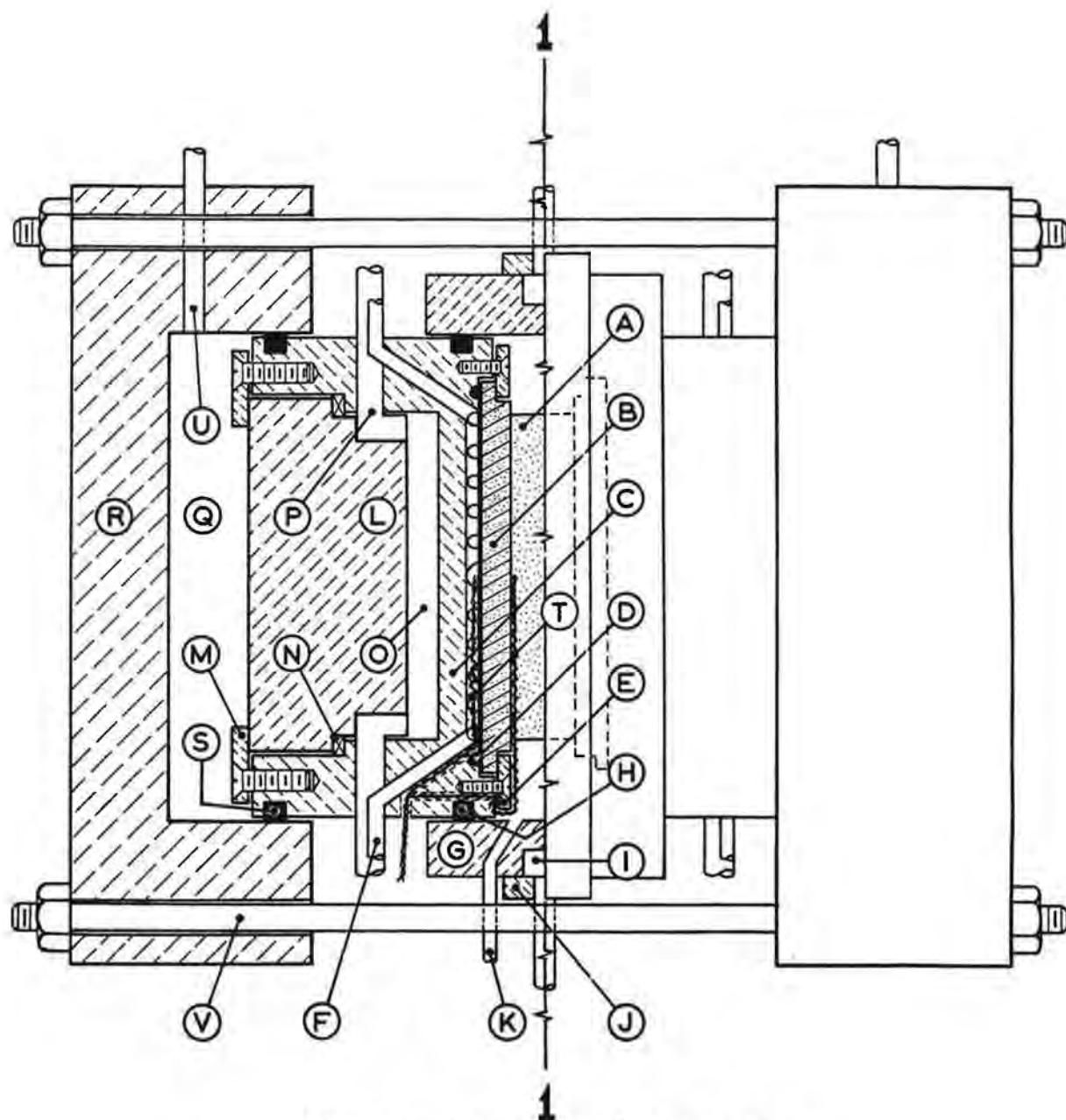
Figure 1. Moisture transfer apparatus.

sections, C, by rubber "O" rings, D, and fibre rings, E. The other side of the porous plates was kept in contact with water at atmospheric pressure. The grooved reservoir holding this water was connected to horizontal measuring pipettes by glass tubing, F. The space surrounding the sample was confined by a lucite ring, G, and rubber seals, H. This arrangement permitted the two porous plates to come into alignment with the two faces of the sample and to remain so throughout the experiment. To prevent condensation on the ring, G, heated water from a constant temperature bath was circulated through the circumferential groove, I. This groove was confined by a tightly fitted lucite ring, J.

Air at any given pressure, controlled by a pressure regulator, was introduced into the space around the sample through a tube, K. The pressure was read from a mercury manometer. Pressures larger than those which could be read on the manometer were read on the gauge of the pressure regulator. Since the pressure on the other side of the

porous plate was atmospheric, the manometer pressure gave the pressure difference or suction to which the sample was subjected. By varying this pressure, the moisture content of the sample was varied.

The cylindrical spaces, O, were confined by the lucite plugs, L, which were retained by brass rings, M, and sealed by rubber rings, N. To produce a temperature difference across the sample, the spaces, O, were connected by tubing, P, to sources of water controlled at two different constant temperatures. During the movement of moisture due to this difference, the porous plate at the higher temperature acted as a source of water while the other acted as a sink.

The outer lucite cylinders, R, permitted parts C and their assembly to function as pistons. The seals, S, allowed the parts to slide freely.

Firm contact of the porous plates against the faces of the sample was achieved by an air pressure in the spaces, Q, larger than that in the space surrounding the sample. The difference in pressure between these two spaces was kept constant at 135 cm of water to maintain a constant contact pressure between the sample and the porous plates. The air was admitted into the space, Q, through metal tubing, U.

To measure temperatures inside the apparatus, copper-constantan thermocouples, T, were brought out through small holes in the body of part C. The holes were sealed up with wax. The entire assembly was held together by six tie bolts, V.

In the present experiment, the apparatus was used without a sample between the porous plates. The faces of the two porous plates were brought in contact with one another. Because the faces were planar, there were numerous points of contact. This produced a definite pore system at the interface. It was the effect of the gap composed of these pores as well as the effect of the gap between the separated plates that was studied.

The gap was varied as follows: The pore system at the interface was varied by altering the texture of the surface of the faces by grinding them with carborundum powder, No. 80 to produce a coarse surface and No. 600 to produce a fine surface. Figures 2 and 3 show
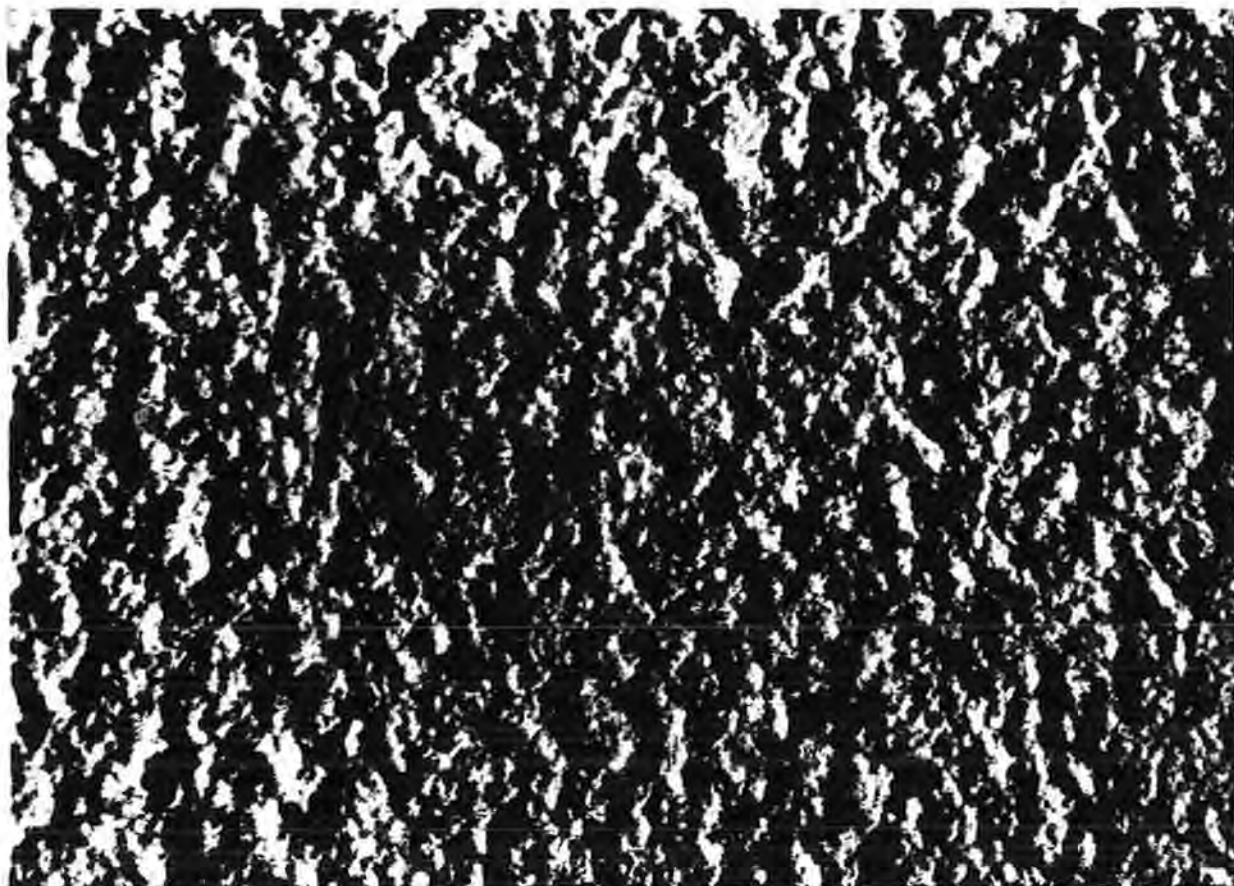

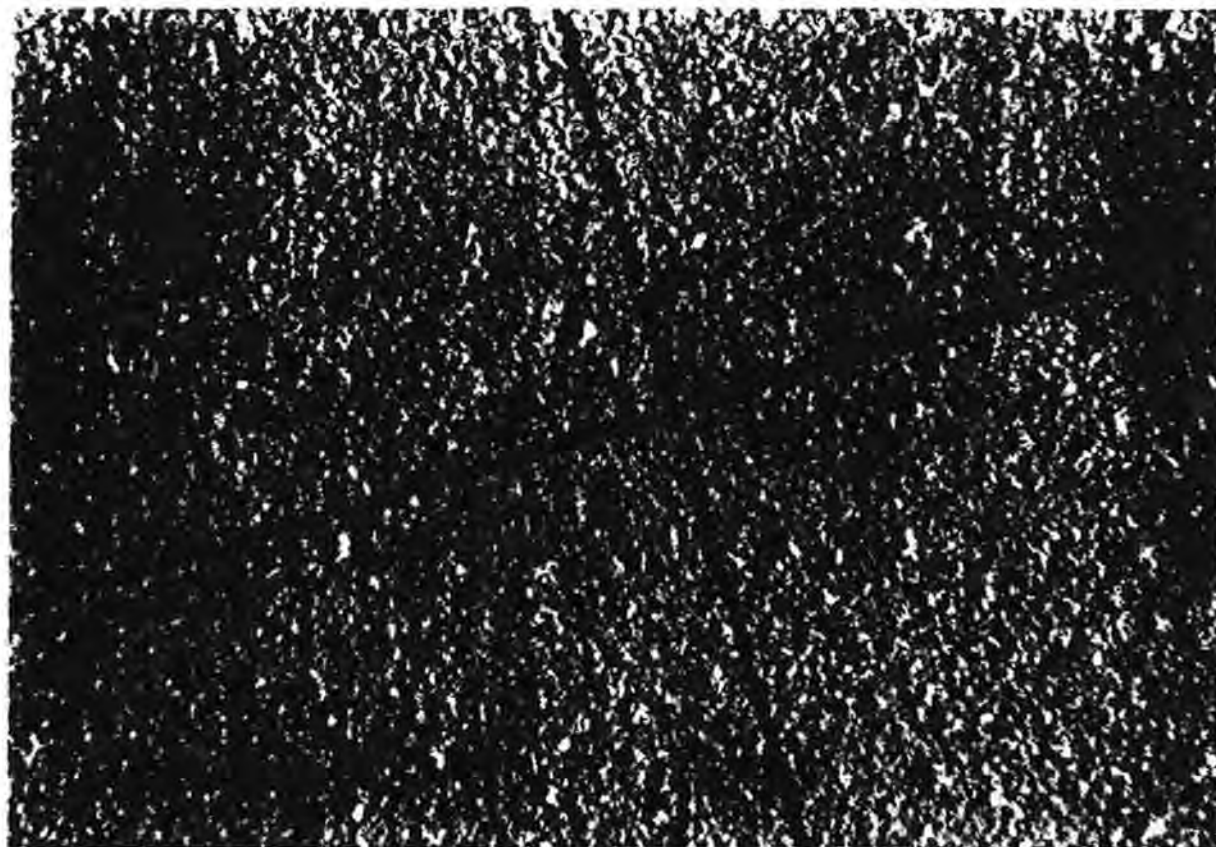Figure 2. (x21) Surface of porous plate ground with carborundum powder No. 80.

Figure 3. (x21) Surface of porous plate ground with carborundum powder No. 600.

the texture of these surfaces. A rotating automatic polishing machine was used to ensure that the faces were planar. Next the fine surfaces were separated by four shims, equally spaced around the perimeter, between the two porous plates. Shims 0.0025 and 0.119 cm thick were used; each shim was 0.4 cm square.

A temperature gradient across the two porous plates was imposed, as described, by circulating water at 0.6 deg C through one side of the apparatus and water at 49.0 deg C through the other. When the 0.119 cm shims were used, an attempt was made to get a rough idea of the temperature of the surfaces across the gap by placing No. 30 B and S gauge copper-constantan thermocouples on these surfaces. It was realized that the temperatures obtained in this manner would probably be in error since the size of the actual junction of the thermocouple wires is relatively large when compared with the distance between the plates. No attempt was made to obtain this temperature when the thinner shims were used or for the experiments with no shims. To ascertain whether the temperature across the plates varied during an experiment, thermocouples were placed in contact with the outside surfaces of the plates.

The amount of water in the gap was varied by varying the air pressure in the chamber supplied through tube, K. Contact between the plates was maintained by an opposing pressure as described.

The rate of flow of the water was obtained by observing the rate of movement of the menisci in the two horizontal pipettes. Two pipettes were used, one to measure the flow into the system, the other to measure the flow out. A steady-state condition was indicated when these rates were equal.

The rate of flow through the porous plates due to a hydraulic head was measured.

The porous plates were 7.6 cm in diameter and about 0.76 cm in thickness. The pressure required to empty the pores was experimentally determined as 5000 cm of water.

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Results

For the four gaps used, Figures 4, 5, 6, and 7 show the relationship between the rate of flow due to the temperature gradient and the pressure used to unsaturate the gap. Each curve is the average of three runs which were in good agreement. A curve showing the relationship between the rate of flow through the porous plates and hydraulic head is also shown in these figures.

In each figure, as the pressure increases, the rate of flow increases, passes through a maximum, and then decreases. The maximum flow is smallest for the gap between the fine surfaces in direct contact, larger for the gap between the coarse surfaces, and largest for the gap between the fine surfaces separated by the 0.0025 cm shims.

The maximum for the gap formed by the 0.119 cm shims is smaller than that for the 0.0025 cm gap. The pressure at which the maximum flow occurs is highest under the conditions illustrated in Figure 4 and decreases for conditions illustrated in Figure 4 through Figure 7. Figures 4, 5, and 6 exhibit a hysteresis.

Discussion of Results

Since the width of the gap formed by the shims was known, the pressure required to empty the gap could be calculated.
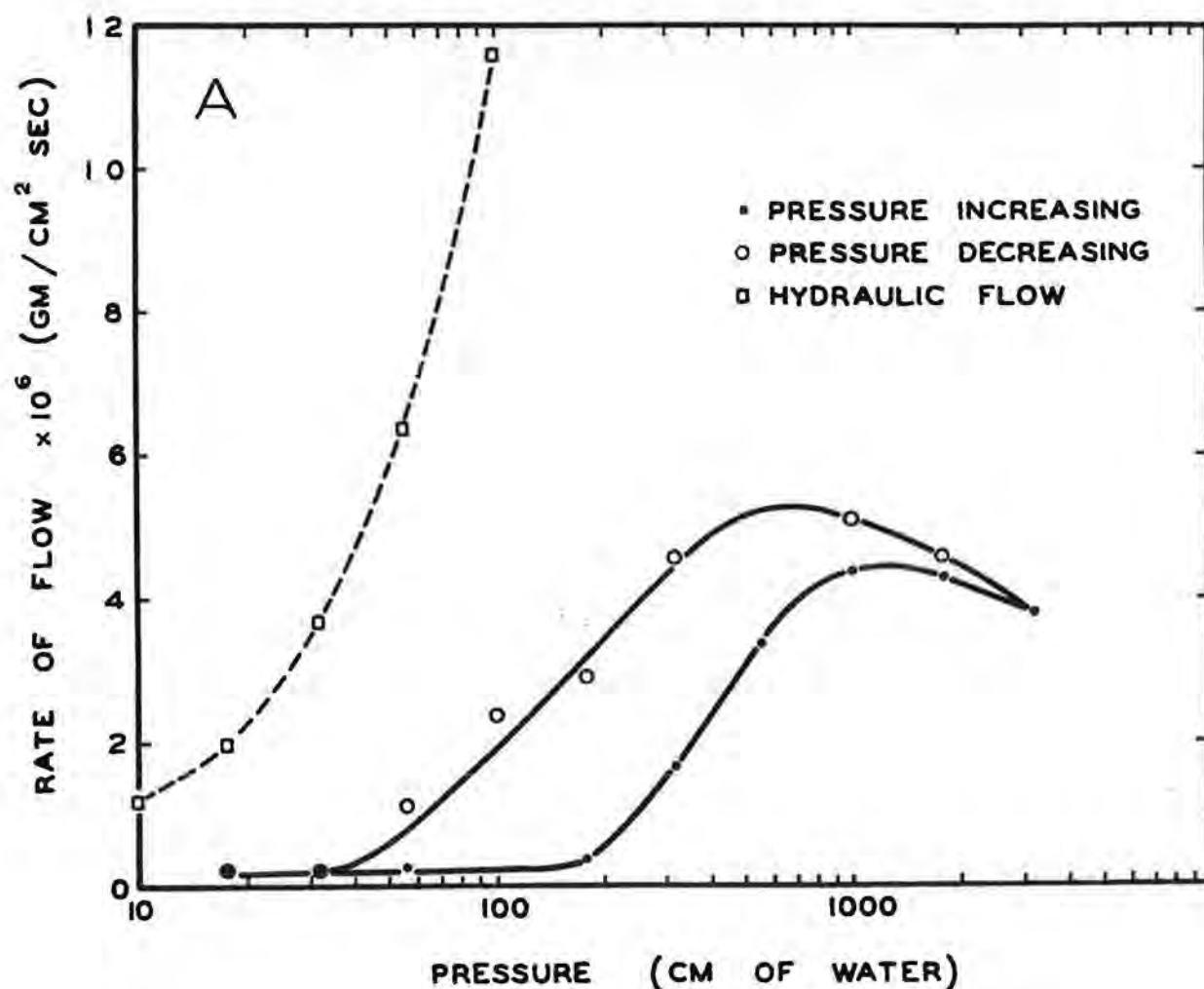
Figure 4. Flow due to the temperature gradient when the fine-textured surfaces are in contact vs the pressure used to unsaturate the pore system at the interface.
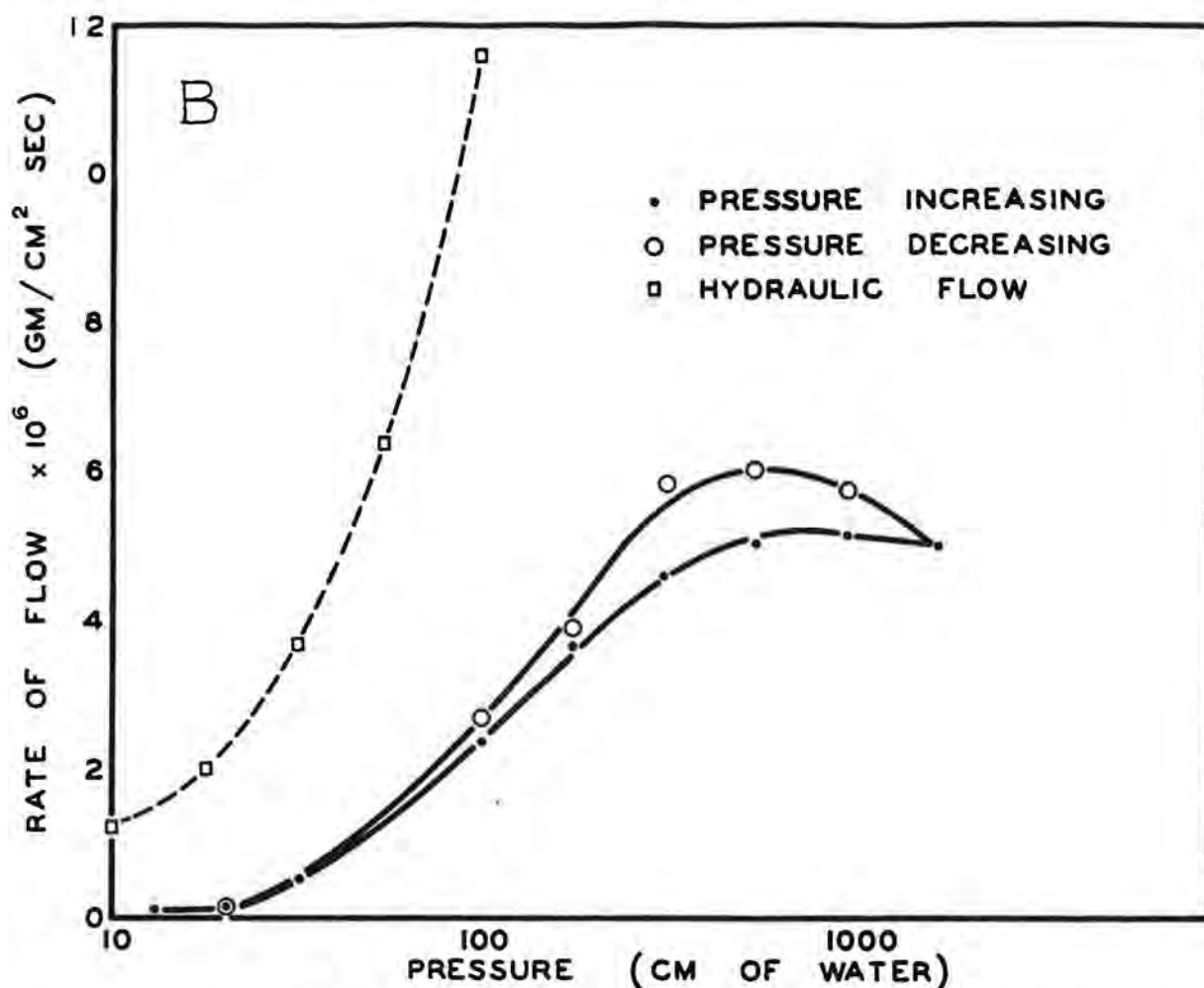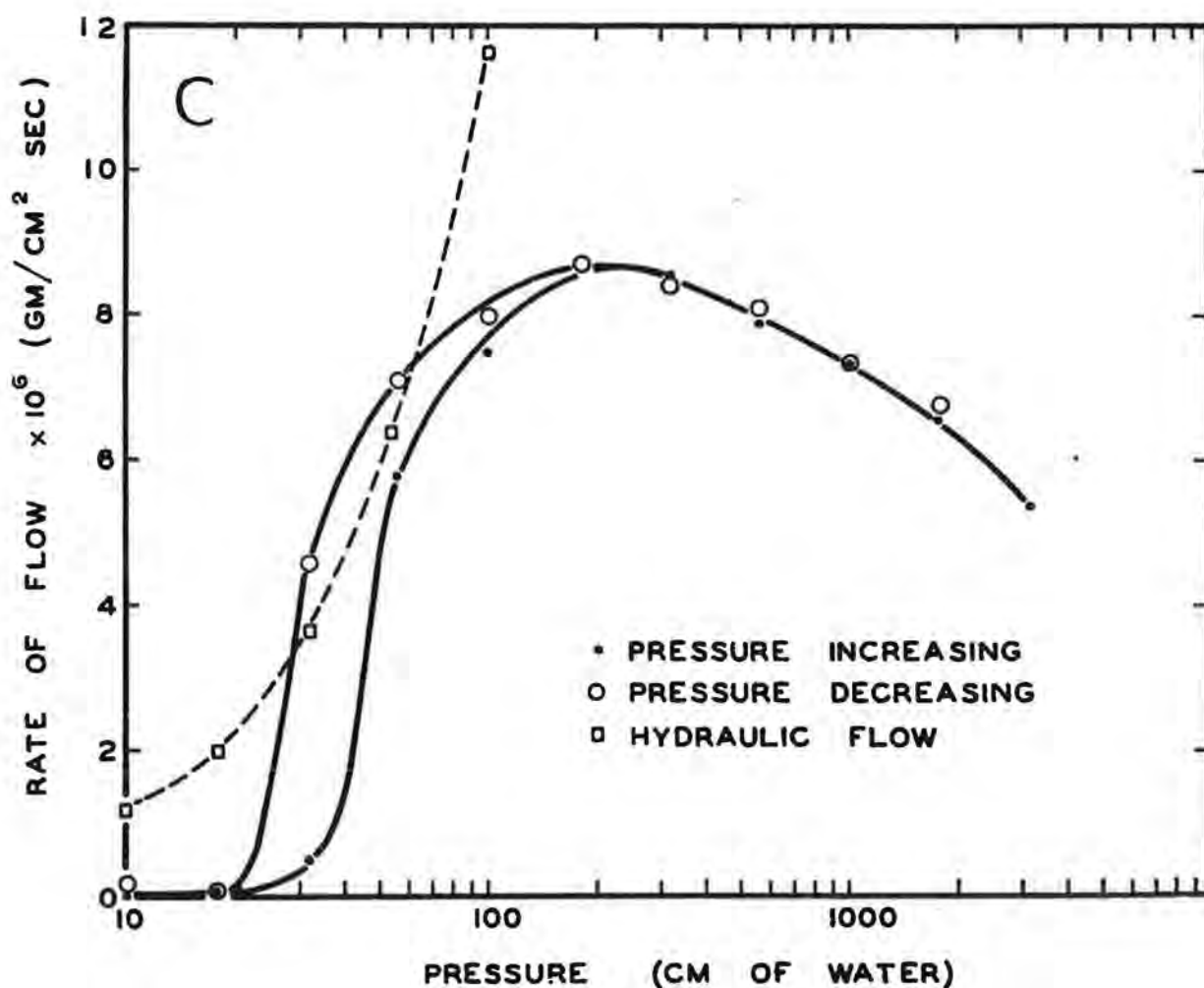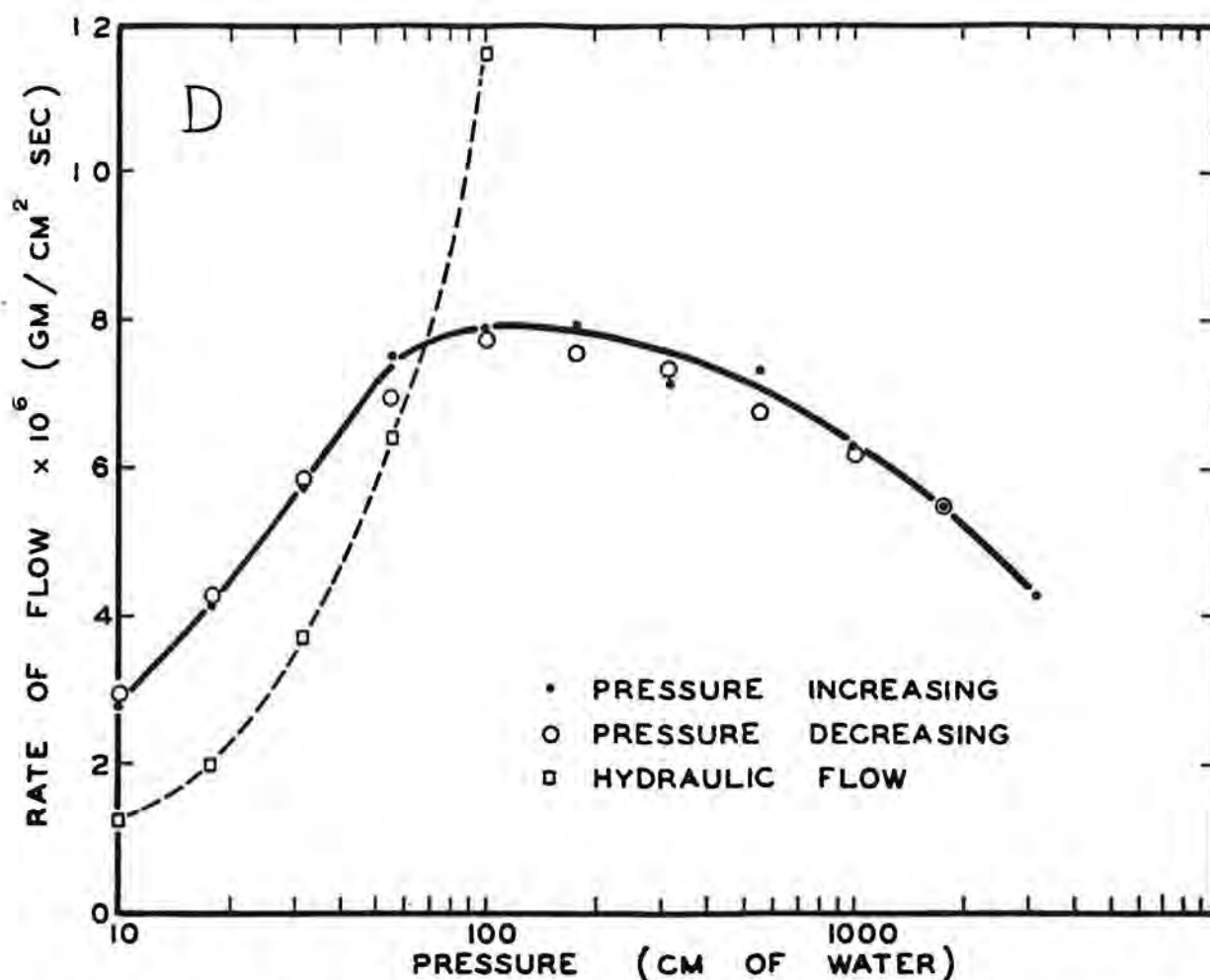
Figure 5. Flow due to the temperature gradient when the coarse-textured surfaces are in contact vs the pressure used to unsaturate the pore system at the interface.

The equation used was:

$$r = \frac{\gamma}{P} \tag{1}$$

where

r is the radius of curvature of meniscus, cm;
γ is the surface tension, dynes/cm; and
P is the pressure, dynes/cm^2.

The distance between the plates is 2r. Table I gives the relationship between the pressure and the space between parallel plates that the pressure will empty. From this table, it may be noted that the gap produced by 0.0025 cm shims will not empty until a pressure of about 56 cm of water is applied. Likewise, the lowest pressure used, a pressure of 10 cm of water, is more than enough to empty the gap produced by the 0.119 cm shims.

Considering Figure 7, if there was no temperature gradient across the 0.119 cm gap, it would empty when a pressure of 10 cm of water was applied. If now the temperature gradient is applied, vapor distills across the gap and condenses on the surface of the cold plate. Once the vapor has condensed on the cold plate, the pressure of 10 cm of water, acting as a hydraulic head, causes the liquid to flow through the plate. Two rates are

therefore involved: the rate of distillation across the gap and the rate of liquid flow through the plate due to the pressure acting as a hydraulic head.

TABLE 1

RELATIONSHIP BETWEEN PRESSURE AND THE SPACE BETWEEN
PARALLEL PLATES THAT THE PRESSURE WILL EMPTY

Pressure (cm of water)	Distance Between Plates (cm)
10.0	0.0146
17.8	0.0082
31.6	0.0046
56.2	0.0026
100.0	0.0015

Figure 6. Flow due to the temperature gradient when the fine-textured surfaces are separated by 0.0025-cm shims vs the pressure used to unsaturate this gap.

Figure 7. Flow due to the temperature gradient when the fine-textured surfaces are separated by 0.119-cm shims vs the pressure used to unsaturate this gap.

The curve showing the rate of flow through the porous plate due to a hydraulic head equal to the air pressures used is shown in Figure 7. The rate of flow at a pressure of 10 cm of water is seen to be 1.2×10^{-6} gm /cm^2 sec. By extrapolation, the rate of distillation across the gap at this pressure is about 8×10^{-6} gm /cm^2 sec. Because of the difference in the two rates, water must have accumulated on the surface of the cold plate. This accumulation would continue until the gap filled to the point where the water probably bridged the gap over a certain area. This reduced the area of the vapor phase and hence reduced the total flow of vapor to the point where the two rates were equal. Experimentally, the two rates were always equal at the steady state, and it is this rate which is plotted in the figures. At this pressure, therefore, the observed rate is governed by the rate of flow of liquid through the porous plate.

As the pressure is increased to a pressure of about 70 cm of water, the observed rate of flow increases, corresponding to the increase in the rate of flow through the porous plates. In the meantime, the rate of distillation decreases in agreement with the known fact that the rate of distillation varies inversely as the pressure in the space above the liquid. At a pressure of about 70 cm of water, the two rates of flow are equal. Therefore, at this pressure the gap becomes empty.

As the pressure increases beyond this value, the gap remains empty and the observed rate of flow decreases, corresponding to the decrease in the rate of distillation, which is now the rate controlling process. Therefore, the variation in the observed rate of flow over the entire range of pressure used is accounted for.

Theoretically, the portion of the curve to the left of the maximum for the experiment with the temperature gradient across the gap, should coincide with the curve showing the flow due to a hydraulic head. The reason for their failure to do so is not known. This peculiar behavior requires further study.

According to calculation, the 0.0025 cm gap remains saturated as the pressure increases to a value of about 56 cm of water. At this pressure the gap empties.

If the transfer of moisture takes place in the vapor phase, there should be no flow at the pressures at which the gap is saturated and maximum flow at the pressure at which it empties. In agreement with the prediction, Figure 6 shows that there is virtually no flow at pressures below 56 cm of water and a large flow at 56 cm. That the rate of flow at 56 cm is not the maximum is again accounted for by the rate of flow through the porous plate being the slower, and therefore the controlling rate at this pressure. The further rise, and then fall in the observed rate of flow as the pressure increases is accounted for in the same way as for Figure 7.

Because of hysteresis, the moisture content of a given porous sample at any given suction, over a certain range, is higher when the suction is approached from zero suction than when approached from the opposite direction (2, 3). This same hysteresis in the moisture content is shown by the 0.0025 cm gap, and is reflected by the hysteresis in the rate of flow. Figure 7 shows no hysteresis because the gap is too large to show this effect in this range of pressures.

In Figures 4 and 5, the rate of flow through the porous plates does not enter as a factor influencing the observed rate of flow. The observed rate of flow due to the temperature gradient is much lower at each pressure than the flow through the porous plates.

In Figure 4, for the fine surfaces in contact, the space between the plates is saturated below a pressure of 200 cm. of water and the flow is therefore zero. As the pressure is increased beyond this value, the space is progressively emptied and the rate of flow increases, corresponding to the increase in the area of the vapor phase. At a pressure of 1,000 cm of water, the space is completely empty and the flow is at a maximum. A further increase in pressure produces no further increases in effective area but does reduce the rate of distillation for the reason already mentioned. In Figure 5 the much larger gap between the coarse surfaces begins to empty at a pressure of 30 cm of water. Again, the hysteresis shown in Figures 4 and 5 is due to the hysteresis in moisture content.

When the gap between the plates separated by the shims is emptied, no film flow is possible. On the other hand, when the pore system at the interface of the two plates is emptied, film flow is possible at the points of contact. The curves in Figures 4 and 5, however, show no characteristic which would indicate appreciable film flow. For instance, if film flow occurs, one might expect that the maximum rate of flow would be highest when the surfaces were in contact since under this condition film flow becomes possible.

Comparing Figures 4, 5, 6, and 7, the shift of the maximum toward lower pressures occurs because the pressure required to empty a gap decreases as the width of the gap increases. The height of the maximum increases as the texture of the surface becomes coarser because of the increase in area for vapor flow brought about by a reduction in the area of the bearing surface. The maximum is highest when shims are used in agreement with the fact that the area of the bearing surface is at its smallest at this time. That the maximum for the 0.119 cm. gap is less than that for the 0.0025 cm. gap is in agreement with the requirement that, with other factors constant, the rate of distillation decreases with increasing distance between the plates.

By thermocouples placed on the plate surfaces, the temperature difference across the 0.119 cm gap was found to be 25 - 24 = 1 deg. C. Hence, the rate of distillation across this gap may be calculated using the equation:

$$W = \frac{M D P}{R T x} \left(\frac{P_o - P_c}{P} \right) \qquad (2)$$

in which

> W = the rate of distillation, gm./cm ^{2} sec ;
> M = the molecular weight of water, gm /mole;
> D = the coefficient of diffusion, cm ^{2}/sec ;
> R = the gas constant, ergs/deg. C mole;
> T = the absolute temperature of the evaporating liquid, deg A ;
> x = the distance between the evaporating liquid surface and the condensing surface, cm ;
> P = the pressure in the space above the liquid, dynes/cm.^{2};
> P_o = the saturation vapor pressure of the evaporating liquid, dynes/cm ^{2}; and
> P_c = the saturation vapor pressure at the condensing surface, dynes/cm.^{2}

Substituting the appropriate values in Eq. 2, for a pressure of 100 cm. of water, gives

$$w = \frac{18 \times 0.22 \times 83 \times 13.5 \times 980}{8.31 \times 107 \times 298 \times 0.119} \times \frac{2.375 - 2.238}{83}$$

$$= 2.43 \times 10^{-6} \text{ gm /cm}^2 \text{ sec.}$$

This value is about one-third the experimental value of 8×10^{-6} gm /cm ^{2} sec at this pressure. This is probably good agreement in view of the uncertainty about the temperature difference. The actual temperature difference was probably larger, in which case the agreement between the calculated and experimental rate would improve.

Conclusion

In this system of two porous plates and the gap between them, there was no flow due to the temperature gradient as long as the gap remained saturated. Flow began when the gap began to unsaturate. The flow attained its maximum when the gap was completely unsaturated. These results are in agreement with the theory that moisture movement due to a temperature gradient across a porous material takes place in the vapor phase.

THE SALT TRACER EXPERIMENT

Water flowing in the liquid phase may be expected to carry along dissolved salt. This experiment was carried out to detect flow in the liquid phase using a salt tracer.

Materials

The materials used were as follows:

1. Sand passing a 48-mesh screen, but retained on a 115-mesh screen;
2. Calcium chloride of commercial grade; and
3. Distilled water.

Procedure

The sand which passed a 48-mesh screen and was retained on 115 was cleaned in aqua regia and then washed in distilled water. Washing was continued until successive analyses indicated no chloride ion. The sand was then placed in the apparatus. It was held between the porous plates by a rubber ring and formed a cylinder 6.4 cm in diameter and 1.3 cm in length. A solution of calcium chloride (0.043 gm /ml) was placed in one side of the apparatus and distilled water in the other. To speed the adsorption equilibrium of the salt ions on the sand, the sand was saturated with the calcium chloride solution when it was placed in the apparatus.

The amount of water (or solution) in the sand was regulated in the usual manner by applying a controlled positive air pressure in the chamber containing the sand. Likewise the temperature gradient was applied as already described. In applying the temperature gradient, the side with the salt solution was made the hot side. Flow from the hot to the cold side was observed and measured.

The amount of calcium chloride passing through the sand and into the distilled water in a given time was calculated from a determination of the chloride ion content of the distilled water, by the Mohr method. The rate and total volume of movement of water were noted so that it was possible to calculate the quantity of salt that should have appeared in the distilled water if the total flow had taken place in the liquid phase.

Next, a constant temperature of 27 deg C was placed across the bed of sand. The rate of transfer of salt under these conditions was determined.

To observe the transfer of salt when the water moves due to suction, a suction gradient at a constant temperature of 27 deg C was placed across the bed of sand. A given air pressure applied in the chamber containing the sand produces the same pressure difference across each of the porous plates when the pressure of the water on the other side of the plates is atmospheric. By increasing the pressure on the other side of one of the plates, the pressure difference across that plate is lowered, and hence so is the suction. The two plates then exert different suctions and so create a suction gradient across the sample. In the present investigation, the suction gradients were applied to draw the water toward the side with the distilled water.

Results and Discussion

Two pressures, one of 1,050, the other of 20 cm of water, were used to partially unsaturate the sand during the temperature gradient experiments. The data obtained are given in Table 2.

From this table it can be seen that the experimentally measured rate of transfer of salt is much smaller than the calculated rate. The calculated rate is the rate at which the salt should have passed through the bed of sand if the observed flow of water had occurred entirely in the liquid phase.

The table also shows that the experimental rate of transfer of salt at constant temperature is the same as that in the experiment with the temperature gradient. The salt passes through the bed of sand at constant temperature by diffusing through the liquid films and lenses of the pores. During this diffusion process, no flow of water from the formerly hot to cold side was observed in the measuring system. Rather, there was osmotic flow in the opposite direction, that is, into the salt solution.

TABLE 2

TRANSFER OF SALT THROUGH PARTIALLY UNSATURATED SAND WHEN WATER MOVES DUE TO A TEMPERATURE GRADIENT

Suction (cm of water)	Temperature Gradient			Constant Temperature (27 deg C)	Transfer of Salt Due to Temperature Gradient (gm /hr)
	Rate of Flow of Water (ml /hr)	Calculated Rate of Transfer of Salt (gm /hr)	Experimental Rate of Transfer of Salt (gm /hr)	Experimental Rate of Transfer of Salt (gm /hr)	
1,050	0.2	0.01	0.0001	0.0001	0
20	0.2	0.01	0.0001	0.0001	0

TABLE 3

TRANSFER OF SALT THROUGH PARTIALLY UNSATURATED SAND WHEN WATER MOVES DUE TO A SUCTION GRADIENT

Suction of the Two Plates (cm of water)	Rate of Flow of Water (ml / hr)	Calculated Rate of Transfer of Salt (gm / hr)	Experimental Rate of Transfer of Salt (gm / hr)	Transfer of Salt (%)
454 and 10	0.12	0.0058	0.0056	97
597 and 10	0.15	0.0072	0.0066	92
800 and 10	0.19	0.0091	0.0093	102
1,000 and 10	0.21	0.0101	0.0106	105

The diffusion described occurs even when the temperature gradient is applied. Therefore, the flow due to diffusion must be subtracted from the flow observed in the temperature gradient experiment. The result, as shown in the last column of Table 2, indicates that there is no transfer of salt by water moving in the liquid phase during the experiment with the temperature gradient. It may therefore be concluded that the water passed through the bed of sand in the vapor phase.

As a further check, the increase in the concentration of the salt solution was calculated for the observed transfer of a given volume of water from the hot to the cold side. The concentration was also determined experimentally. The agreement between experimental and calculated values was within 2 percent.

In view of the small amount of salt transferred during the temperature gradient experiment, it seemed desirable to check the amount transferred during flow caused by suction gradients. The suction of the plate on the salt solution side was kept constant at 10 cm of water while the suction of the other plate was increased from 454 to 1,000 cm of water. The temperature was constant at 27 deg C. The concentration of the calcium chloride solution used was 0.048 gm /ml. The data obtained are given in Table 3.

The last column which gives the ratio, expressed as percent, of the experimental rate of transfer of salt to the calculated rate shows a scatter around the value 100 percent. The 100 percent transfer of salt indicates that the movement of water due to the suction gradients takes place in the liquid phase.

THE STREAMING POTENTIAL EXPERIMENT

These experiments were carried out in an attempt to detect flow in the liquid phase by measuring the streaming potential. To obtain more surface area per unit volume, sand passing a 250-mesh screen and retained on 325 was used. The sand was held between the porous plates of the apparatus as described for the salt tracer experiment. Platinum wire electrodes, 0.082 cm in diameter and 3.8 cm in length were placed at the ends of the bed of sand. The voltage was measured with a Rubicon potentiometer. Distilled water was used.

To observe the effect of temperature on the voltage between the electrodes when there was no flow through the bed of sand, the sand was saturated before the temperature gradient was applied. The steady menisci in the pipettes indicated no flow of water. The voltage was then measured and found to vary erratically between 0.01 and 0.1 volt. The polarity also was not consistent with the direction of the temperature gradient.

The sand was then partially unsaturated by applying various pressures, and the usual flow from the hot to the cold side was observed. The voltage was measured and found to vary over the same range as it did in the previous experiment when there was no flow. Therefore, flow in the liquid phase was not detected.

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Conclusions

The results of these experiments indicate that there is no flow in the liquid phase when water moves, due to a temperature gradient, from the hot to the cold side of a partially unsaturated porous material.

Therefore, it appears that the flow occurs in the vapor phase. On the other hand, when water moves due to a suction gradient, the flow occurs entirely in the liquid phase. These conclusions are in agreement with those of Gurr, Marshall, and Hutton (4) who used the salt migration method to study moisture movement in soils.

This investigation presupposes flow in a continuous film. If the flow in the liquid phase is not continuous but involves multiple evaporation condensation steps in series as suggested by Smith (6), then it cannot be detected either by salt tracer or by the measurement of streaming potentials in the manner attempted in the present investigation. Experiments devised to investigate this particular mechanism are planned.

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Physics of Water Movement in Porous Solids

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Introductory Remarks by Chairman

Water movement in porous systems is perhaps the most consequential phenomenon with respect to the life and activities of the human race. The movement of water to the plant roots and hence through the plant to the leaves enables the latter to utilize the sun's rays and the carbon dioxide of the air for the synthesis of the basic food materials for animal life. Proper irrigation of deserts and drainage of swamps adds to the areas available for food production and sites of habitation, while adequate drainage has been called justly the first principle of highway and airport engineering. Water may move out of saturated clay and silt layers underneath the foundations of heavy structures and cause their settlement; it may move into and through porous building materials and cause wet walls and cellars. On the other hand, porous building material may conduct water vapor created by human and animal life activity out of rooms and cells and help to keep their atmosphere comfortable and healthy. These are only a few of the myriad and multifarious examples that could be adduced about the importance of water movement in porous systems even if we should exclude such vital processes as the movement of water and of aqueous solutions into, through and out of all living systems. Water has been called the friend and enemy of the engineer and to do its friendly or hostile act, it moves largely through porous systems.

Considering this wide and vital importance in many different areas of human endeavor, it is to be expected that the phenomenon of water movement through porous solids has been studied from many different points of view and that since the dawn of humanity, specific problems deriving from this phenomenon have been solved more or less adequately by methods ranging from the crudely empirical to the most refined theoretical. Because of their specific nature, it is often difficult to apply the solutions thus found to analogous cases in other fields. The situation calls for a general theoretical structure from which specific solutions can be derived for specific conditions. The time has come when it is possible to establish such a theoretical structure at least for that large portion of the total problem which is predominantly physical in nature and in which physicochemical and chemical interactions between the water and the pore walls are sufficiently small to permit their exclusion from the theoretical treatment. In the light of this, we are extremely grateful to Dr. Philip of Australia for giving a comprehensive and most excellent survey on the Physics of Water Movement in Porous Solids.

● THE FIRST part of the paper treats the connections between the mechanics of fluids in saturated porous solids and classical hydrodynamics. It is shown that the permeability tensor may be expressed in terms of precise integrals of the internal geometry of the solid. Methods of using the Navier–Stokes equation to compute the permeability of a porous solid in this way are outlined. The limits to Darcy's law arising from the "inertia terms," and from variation in time of the applied potential, are discussed.

The remainder of the paper reviews recent studies of water movement (liquid and vapor phases) in unsaturated porous solids under the influence of gravity, and moisture and temperature gradients. Some attention is also given to the adsorbed phase, and to heat transfer in the solid. A coherent mathematical-physical theoretical framework has been developed, which is amenable to analysis. In the context in which it was con-

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structed, it has proved in good agreement with experimental observations of a diversity of phenomena. The theory is incomplete, in the sense that it does not deal adequately with all aspects of water movement in soils of high colloid content.

The aim of this paper is to review some recent developments in the study of water movement in porous solids. Much of this work has been done by soil physicists primarily concerned with microhydrological problems arising in connection with dry and irrigated agriculture. It may not, therefore, be well known to soil mechanicians and foundation engineers, who are equally interested in water movement in soils, though for rather different practical reasons.

The theoretical structure to be presented here has developed, and proved fruitful, in this agro-hydrologic context, and it is emphasized that there are limits to its applicability, as it stands, to foundation problems. In the sense that it does not deal adequately with all aspects of water movement in soils of high colloid content, the theory is incomplete. Nevertheless, it would seem that any more complete quantitative theory must incorporate within it many, if not all, features of the present theory.

Water in the soil and other porous materials may be present in three phases—liquid, vapor, and adsorbed phase. (Attention is restricted to unfrozen materials; ice does not therefore enter into consideration.) Concern in this case is with the transfer of moisture via all three phases, although treatment of the adsorbed phase is cursory. The liquid phase is considered initially and it is useful to introduce the concept of permeability (hydraulic conductivity) by first considering flow through a saturated system.

FLUID FLOW IN SATURATED SOLIDS

There is no need for an elaborate treatment of fluid flow in saturated solids here, as many recent reviews of this topic are available (e.g., Carman, 1956, Scheiddegger, 1957). These works, however, do not seem to recognize clearly the connections between the mechanics of fluids in saturated media and classical hydrodynamics. This is the aspect stressed in this compressed treatment. For the purposes of the later sections, however, all that is really required is that there should exist, in a given medium, a linear relationship between applied potential gradient and macroscopic flow velocity. In this sense the theoretical structure outlined in the succeeding sections is independent of this section.

Darcy's Law. From his experiments on water flow through filter beds, Darcy (1856) deduced

$$Q = KA(h+L)/L \tag{1}$$

where Q is the discharge through filter in unit time, A is the area of the filter, L is the thickness of the sand, h the water depth over the sand, and K "un coefficient dependant de la nature du sable." Later investigators have applied the equation to the flow of water in homogeneous isotropic media in forms such as

$$Q/A = u = KS \tag{2}$$

where u is the macroscopic flow velocity, and S the magnitude of the potential gradient. An extension of Eq. 2 to apply to any fluid may be made, provided the medium remains stable and does not react with the fluid:

$$u = (K/v)S \tag{3}$$

v is the kinematic viscosity. K, now the permeability, is a characteristic of the geometry of the medium, and is independent of the fluid. A vectorial form of Eq. 3 is

$$\overline{U} = -(K/v)\nabla\Phi \tag{4}$$

where $\overline{U}$ is the vector macroscopic velocity, and Φ is the potential defined by

$$\Phi = P/\rho + \Omega \tag{5}$$

Here P is the pressure, ρ the density, and Ω the potential of the external or body forces.

Eq. 4 holds for homogeneous isotropic media, the extension to anisotropic media being

$$\overline{U} = - (1/\nu) \; \underline{K} \; \nabla \Phi \qquad (6)$$

where $\underline{K}$ is the permeability tensor. In this general case vectors $\overline{U}$ and $\nabla \Phi$ differ in direction except for certain special directions in the medium.

The Capillary Bundle Model, and Its Limitations. Clearly, collections of capillary tubes can be constructed which form a special case of the porous solid. Naturally, these special media belong to the general class of porous solids, and, if the equations exhibited above are valid, they will, of course, hold for these special media. However, theoretical deductions based on this special model are not necessarily valid in the general case. Yet nearly all theoretical studies of porous media have been based on capillary models.

Some workers (e.g., Adzumi, 1937, 1939; Childs and Collis-George, 1950a; Flood, Tomlinson and Leger, 1952) have used quite complicated variants of the simple capillary bundle which involve series- or series-parallel-connected systems treated essentially as pipe networks with laminar axial flow in the pipes (with no allowance for the transitions at bends and changes of section). Even the sophisticated treatments of Scheidegger (1954, 1957) and Fatt (1956a, b, c) depend on the capillary model.

The objections to the capillary bundle model, and its variants, relate both directly to the failure of tube flow to bear much physical resemblance to flow in porous solids in general (hereafter called "medium flow"), and to the fact that, in any case, capillary models cannot give information on some aspects of the flow process which are quite important both to theory and practice.

The difference in character between tube and medium flow will be seen if the fate of a small parcel of fluid moving through each system is considered. In the tube the parcel possesses a constant linear velocity throughout, while in the medium it is subject to forces which continuously change not only the magnitude but also the direction of its velocity. This important difference finds quantitative expression in the 1,000 to 1 ratio of the critical Reynolds numbers of the two systems (cf. Muskat, 1937, p. 56; Goldstein, 1938, p. 319).

Obviously, many aspects of medium flow (e.g., effects of particle shape and spacing on permeability; the effect of particle orientation on the directional properties of permeability; the question of identity or non-identity of hydrodynamic and electrical "tortuosity") are unlikely to receive meaningful treatment when the actual medium geometry is discarded at the outset, as it is in the capillary bundle approach. However, it is possible to use classical hydrodynamics to study these questions in a precise way.

The Navier-Stokes Equation in a Porous Solid.

$$\partial U / \partial t - U \times (\nabla \times U) + \tfrac{1}{2} \nabla U^2 = - \nabla \Phi + \nu \; \nabla^2 U \qquad (7)$$

is the Navier-Stokes equation for an incompressible fluid. U is the microscopic vector velocity (as distinct from the macroscopic $\overline{U}$ introduced earlier) and $\nabla \Phi$ has a somewhat different significance than it had in the earlier macroscopic equations. There it was a smoothed potential gradient; here it denotes a vector point function which will generally vary in magnitude and direction from point to point. Textbooks (e.g. Lamb, 1932, p. 576) give the derivation of Eq. 7 from simple considerations about the mechanics of a fluid in motion. Essentially, the equation is established by relating the forces and accelerations on a small element of the fluid on the supposition (rigorous for Newtonian fluids) that the shearing stress sustained by the fluid is proportional to the velocity gradient normal to the plane of shear. The (constant) ratio of the shearing stress to the velocity gradient is the dynamic viscosity of the fluid, μ, which is equal to $\rho \nu$.

Navier obtained Eq. 7 as early as 1822, the theoretical basis being improved by Saint-Venant in 1843. Curiously enough, this general analysis of the motion of a viscous fluid preceded the much less general, but better known, studies of Poiseuille and Darcy. Apparently, it was not recognized that their results represented simple special cases of Eq. 7.

When

$$U \times (\nabla \times U) - \tfrac{1}{2} \nabla U^2 = 0 \qquad (8)$$

and the motion is steady in time, Eq. 7 reduces to

$$\nu \nabla^2 U = \nabla \Phi \tag{9}$$

For certain special motions and media (e.g., flow parallel to the generators of the generalized tube) Eq. 9 will hold exactly. However, in most media, and certainly in the porous solids which are of interest here, the validity of Eq. 9 depends on the reduction of Re, the Reynolds number of the motion, to sufficiently low values for the inertia terms (i.e., the terms of second degree in U) to be negligible. Both analysis (Lamb, 1932, p. 599) and experiment (Muskat, 1937, p. 56) suggest an upper limit of Re of order of magnitude unity, below which Eq. 9 holds to sufficient accuracy. Thus Eq. 9 is found to apply to almost all fluid motions in the porous solids of nature and technology, and certainly to all where the concept of permeability is valid.

Use of the continuity requirement

$$\nabla \cdot U = 0 \tag{10}$$

in Eq. 9 yields

$$\nabla^2 \Phi = 0 \tag{11}$$

The motions must satisfy Eq. 9 and Eq. 10 (or Eq. 11), together with appropriate boundary conditions. These will include the requirement that at all fluid-solid interfaces the fluid velocity is zero, i.e.

$$U = 0 \tag{12}$$

. The remaining boundary conditions are now noted. It is well known that in anisotropic porous solids the directions of the (macroscopic) potential gradient and the (macroscopic) flow velocity do not necessarily coincide. It follows that a permeameter test of a specimen may be erroneous if the axis of the specimen does not coincide with a principal axis of the permeability tensor; i.e., if the impermeable side walls exert an artificial restraint on the flow pattern which would not occur if the specimen were subjected to the same potential difference, but were surrounded by a large mass of the medium.

The same difficulty arises in deriving the permeability properties of a given medium from the Navier-Stokes equation, and it can be resolved exactly only when suitable planes of (reflective) symmetry exist in the medium. This may seem to limit the value of this approach. However, certain artificially constructed media do exhibit such symmetry, and most other media can be represented to a good approximation by the repetion in each dimension of some basic solid configuration. (There is, in principle, no need for the geometry of the basic configuration to be simple.) The degree of idealization is evidently very much less than that involved in the capillary bundle model, and it can be fairly claimed that most of the physical characteristics of the real system are retained.

The mathematical permeability test (for this is essentially what is being undertaken) shall be carried out for the case $\nu = 1$ and unit potential difference across the basic cell. These special values may be employed without loss of generality, since the linearity of Eq. 9 and the governing conditions ensure that flow velocities are directly proportional to the applied potential difference, and inversely proportional to ν. (Essentially, the linear form of Eq. 9 and the governing conditions comprise a derivation of Eq. 6, and the other forms of Darcy's law, via classical hydrodynamics. Strictly speaking, however, a statistical assumption concerning the uniformity of the medium in the large is also needed; but this is implicit in Eq. 6, etc., in any case.)

Therefore, specification of the problem is completed by imposing the boundary conditions:

$\Phi = 1$ at plane 1; $\Phi = 0$ at plane 2.
Velocity gradient at planes 1 and 2 is zero.
Velocity components parallel to planes 1 and 2 are
zero at these planes.
Velocity and potential gradients normal to planes
3, 4, 5, 6 are zero at these planes. (13)

Here planes 1 and 2, 3 and 4, 5 and 6, denote pairs of opposite planes of symmetry. It will be understood that the equations hold only in the region of fluid occupancy, and that conditions need be satisfied only on those parts of the planes of symmetry occupied by fluid.

The solution of Eq. 9 subject to these various conditions may be found in the form

$$U = U_{12} (x, y, z) \tag{14}$$

where x, y, z are Cartesian co-ordinates specifying position within the basic cell, the x-direction being normal to plane 1, the y-direction normal to plane 3 and z-direction normal to plane 5.

Similarly, by replacing Eq. 13 by corresponding boundary conditions for unit applied potential differences between planes 3 and 4, and between planes 5 and 6, two further solutions may be obtained

$$U = U_{34}(x, y, z) \qquad ; \qquad U = U_{56}(x, y, z) \tag{15}$$

Then, if K_x, K_y, K_z denote scalar permeabilities in the three respective principal directions,

$$K_x = \frac{l_x \displaystyle\int_{A_x} U_{12} dA}{A_x i} \qquad ; \qquad K_y = \frac{l_y \displaystyle\int_{A_y} U_{34} dA}{A_y j}$$

$$K_z = \frac{l_z \displaystyle\int_{A_z} U_{56} dA}{A_z k} \tag{16}$$

Here, A_x, A_y, A_z denote (any) cross-sections of the basic cell normal to the x, y, and z directions respectively; l_x, l_y, l_z denote the lengths of the basic cell in these same directions and i, j, k denote the corresponding unit vectors. The permeability tensor is then

$$\underline{K} = K_x\, ii + K_y\, jj + K_z\, kk \tag{17}$$

<u>Solution of Equation 9.</u> In principle, solution of Eq. 9 subject to these conditions can be obtained by relaxation. For two-dimensional media, a stream-function may be introduced and the problem reduced to solution of a bi-harmonic equation (Shaw, 1953, p. 196, Allen, 1954, p. 105; Southwell, 1956, p. 251). An alternative procedure involving relaxation solution of Laplace's equation and Poisson's equation is needed in three-dimensional problems, and may be better in two-dimensional cases also. Three-dimensional relaxation is a formidable process, and real progress here will probably require use of a high-speed computer. Nevertheless, although real media are three-dimensional, the more tractable two-dimensional problem retains many of the physical aspects of interest, and is worthy of some study. Some two-dimensional solutions have been obtained (Philip, 1957g), and illustrate such facts as the non-identity of hydrodynamic and electrical "tortuosities" in porous solids.

It is not likely that this hydrodynamic approach can be applied in detail to a specific field problem. The internal geometry of the solid is unlikely to be known sufficiently accurately, or, if it is known, it will almost certainly be so complicated that the computations become very intricate.

It has been seen, however, that this approach enables fitting the mechanics of fluids in porous solids into the theoretical framework of classical hydrodynamics, and expressing permeability in terms of precise integrals of the internal geometry of the solid. Furthermore, the study of flow through simple configurations by the methods outlined here can do much to fill out understanding of permeability—in particular its relationship to the shape, size, and orientation of pores and particles.

It will be noted that this method of analysis does not resolve the differences between

the "particle" approach to permeability, as exemplified by the Kozeny-Carman equation, and presented in the work of Kozeny (1927), Carman (1937, 1938, 1956). Wyllie (undated; Wyllie and Gregory, 1954) and others, and the "pore" approach of Childs and Collis-George (1950), Purcell (1949) and others. Both are based on the capillary bundle model, and claims for the superiority of one approach or the other within some defined range of technological application must depend primarily on appeal to experiment. However, the methods outlined here can provide soundly based checks on such matters as the supposed constancy of the Kozeny-Carman "constant," and the validity of the "tortuosity" concept in structured solids.

The Limits to Darcy's Law. (a) The "inertia terms." It has been shown that Eq. 9 depends on the validity of Eq. 8. For tube flow Eq. 8 is exact, and Eq. 9 holds until Re is about 2,000, when the laminar flow develops instability, and the flow becomes turbulent. On the other hand, the inertia terms Eq. 8 cannot be neglected in general medium flow above some "critical" value of Re, usually in the range 1 to 5. Often one finds in the literature the suggestion that the failure of Darcy's law with increasing Re is due to the onset of turbulence. It is clear that this is incorrect, and that the non-linearity which signals the failure of Darcy's law arises, in the general medium, from the inertia terms. The recent computations of Tamada and Fujikawa (1957) of drag on an array of cylinders demonstrate this very well, and similar results would apply to the case of flow through a porous solid.

This effect was recognized by Lindquist in 1932. It is emphasized here because, even in very recent publications, the mistaken idea persists that turbulence determines the upper limit of validity of Darcy's law. (Note that, as the flow rate is increased, turbulence may ultimately develop. The point is that there exists, between the Darcy and the turbulent regimes, a non-linear but laminar regime.)

(b) Flow unsteady in time. Darcy's law, and the hydrodynamic analysis given above, are for motions steady in time. Darcy's law has often been applied to problems in which the flows and the potential gradients are not steady in time. Philip (1957b, 1) has examined the problem of unsteady flows, applying the Navier-Stokes equation in some simple cases, and developing an approximate analysis in general media. The general result is that, when the applied potential, S, is a function of time, Eq. 3 must be replaced by

$$u = u_0 \, e^{-\beta t} + (\beta K/\gamma) e^{-\beta t} \int_0^t S(T) e^{\beta t} \, dT \qquad (18)$$

Here u_0 is the value of u at t = 0, and

$$\beta = p^2 \nu / \gamma K \qquad (19)$$

where p is the porosity and γ is a numerical constant dependent on the internal geometry. Usually it will be about 1.25.

Eq. 18 may be regarded as the appropriate generalization of Darcy's law. For the case $u_0 = 0$, and S suddenly changed from zero to a constant non-zero value at t = 0, Eq. 18 yields the result that the instantaneous "permeability" at time t, K_t, is given by

$$K_t = K(1 - e^{-\beta t}) \qquad (20)$$

It is seen that the error produced by using the unmodified Darcy's law will be negligible in most practical applications. In periodic systems, however, the differences can be important (Philip, 1957b). It is also possible that perceptible deviations from Darcy's law may occur during the very early stages of absorption or infiltration into unsaturated systems (Philip, 1957h).

MOVEMENT OF THE LIQUID PHASE IN UNSATURATED SOLIDS

Hydraulic Conductivity in Unsaturated Solids. When the solid is not saturated with the liquid, a gaseous phase is also present. In the case which is of interest here the liquid is water, and the gas is air containing water vapor in equilibrium with the liquid

water. (In the petroleum industry other multiphase systems arise—e.g. oil-gas, oil-brine, oil-gas-brine. The physical problem is rather similar to that treated in this and following sections. However, there are some important differences, which cannot be discussed here.)

It has long been assumed (cf. Richards, 1931), and was confirmed experimentally by Childs and Collis-George (1950), that Darcy's law may hold in unsaturated systems in a more general form in which the permeability is now a function of the moisture content of the solid. Analytical proof of this generalized form of the law depends on the assumption that the drag between the phases is negligibly small (Philip, 1957j). This is certainly true of the systems to be considered here.

Since water is the only concern, it is now convenient to introduce the term "hydraulic conductivity" (Richards, 1952), K', to denote the quantity K/v, which appears in equations such as Eq. 4. Anticipating the next sub-section, express Φ in units of length, so that K' has the dimension (length x time $^{-1}$). The unit cm sec^{-1} is commonly used for K'. This and the following sections are limited to isotropic solids.

Introduced here is the volumetric moisture content, θ. This is the fractional volume of the solid which would be occupied by the water it contains, if all this water were in the liquid phase. This is almost exactly the volume fraction occupied by liquid water, but the definition takes care of ambiguities which might arise concerning the vapor phase.

Except at the dry end of the moisture range, where the experimental difficulties are great, the general behavior of the $K'(\theta)$ function is now well established, thanks to the work of Richards, Moore (1939), Childs and Collis-George, other soil physicists, and a number of investigators in the petroleum industry. K' is found to decrease very rapidly as θ decreases from its saturation value. This is not surprising since:

1. The total cross-section available for flow decreases with θ.

2. The largest pores are emptied first as θ decreases. Since the contribution to permeability per unit area varies roughly as the square of the pore radius, K' may be expected to decrease much more rapidly than θ. (This is an instance where argument from the capillary model is probably permissible.)

3. As θ decreases, the chance of water occurring in pores or wedges isolated from the general three-dimensional network of water films and channels increases. Once continuity fails, there can be no flow in the liquid phase, apart from flow through liquid "islands" in series-parallel with the vapor system (Philip and de Vries, 1957). The latter type of flow is more appropriately treated as "vapor flow" for reasons indicated below.

It is difficult to locate the maximum value of θ at which K' is zero for a given soil. An experiment in which (isothermal) liquid and vapor transfer in dry media are distinguished unequivocally is needed, but does not seem to have yet been made.

"Moisture Potential" and Total Potential of Water in an Unsaturated Porous Solid.
The water in unsaturated porous solids is not "free" in the thermodynamic sense, due to capillarity (dominant in moist media) and adsorption (dominant in "dry" media) (Edlefsen and Anderson, 1943). The energy state of the water is commonly expressed by the quantity Ψ (variously known as the "moisture potential," "capillary potential," "moisture tension," "moisture suction," "negative pressure," etc.; see, for example, Richards, 1949, 1953; Childs and Collis-George, 1950b; Croney et al., 1952). It is often convenient to express this quantity as a length, rather analogous to the concept of head in hydraulics. Specifying Ψ in centimeters here, so that $g\Psi$, where g cm sec^{-2} is the acceleration due to gravity, may be identified with the differential specific Gibbs function of the soil water. It follows that the liquid and vapor systems are connected by the relationship

$$h = \exp\left[g\Psi/RT\right] \tag{21}$$

where h is the relative humidity, R (erg gm^{-1} deg. C^{-1}) is the gas constant for water vapor ($= 4.6.5 \times 10^6$), and T deg. K is the absolute temperature. Note that in unsaturated solids Ψ is negative.

The total potential Φ may be regarded as comprising Ψ and the gravitational component z, where z is the height above some datum. That is

$$\Phi = \Psi + z \tag{22}$$

Φ, rather than Ψ, should enter Eq. 21 when h is expressed in terms of saturated vapor density at the datum level $z = 0$, instead of that at elevation z. However, on the occasions when it is necessary to use Eq. 21, there will be very little numerical difference between the two results.

At any fixed temperature, Ψ is a well-defined function of θ for any given porous solid. The variation of Ψ with T is not so well established. It appears that, to a fair approximation, the $h(\theta)$ relationship is independent of T in the region where adsorption is dominant ($h < 0.6$) (McBain, 1932; Carman and Raal, 1951; Carman, 1953; Philip and de Vries, 1957). In the region where capillary condensation is dominant it has sometimes been provisionally assumed that Ψ at a given value of θ is proportional to the surface tension σ (cf. Philip and de Vries, 1957). However, the experimental data (Richards et al., 1938; Gardner, 1955) suggests that, in rather moist soils, the temperature coefficient of Ψ exceeds that of σ. The explanation seems to be that, as T increases, the volume of totally entrapped air bubbles expands, leading to an altered configuration of the meniscal surface between the liquid water in the medium and the external atmosphere. Experimental study of this effect is in progress in the Australian C.S.I.R.O. Division of Plant Industry.

(The presence of soluble salts somewhat complicates this picture of the energetics of water in a porous solid. Gradients of solute concentration can be expected to have a more important influence on vapor transfer than on liquid transfer. This matter will not be considered further here.)

The General Equation Describing Liquid Flow of Water in a Porous Solid. Many of the concepts of the two previous sub-sections were largely implicit in the work of Buckingham (1907). The following half-century saw first neglect, and then gradual rediscovery and exploration of the implications of his study. In 1931 Richards developed a general partial differential equation describing isothermal liquid flow in porous media, but he took as the dependent variable Ψ, though he recognized the possibility of an alternative formulation in terms of θ. This was unfortunate, since the equation in θ is somewhat more tractable than that in Ψ. In 1936 Childs suggested that moisture movement in porous solids was a diffusion phenomenon, but he confined his attention to the case of constant diffusivity, which does not accord well with observation (cf. Kirkham and Feng, 1949). In 1948, however, Childs and George applied Darcy's law to the isothermal movement of water down a potential gradient produced by a moisture gradient, and deduced a concentration-dependent diffusivity. This work implied the existence of a general partial differential equation describing isothermal liquid flow in porous media, when Ψ was a single valued function of θ. Klute (1952 a, b) derived this equation explicitly. As it shall be shown here it has subsequently been possible to incorporate in this approach moisture transfer in the vapor and adsorbed phases, and the effects of temperature gradients. Also of importance has been the development of numerical methods of solving equations of the diffusion type in which the diffusivity is concentration-dependent.

Eq. 4 may then be written in the form appropriate to unsaturated solids:

$$q_{liq} / \rho_w = - K' \nabla \Phi \qquad (23)$$

Here q_{liq} is the vector flux density in the liquid phase (gm cm^{-2} sec^{-1}) and ρ_w gm cm^{-3} is the density of liquid water. Then, combining the continuity requirement

$$\frac{\partial \theta}{\partial t} = \frac{1}{\rho_w} \nabla \cdot q_{liq} \qquad (24)$$

and Eq. 23 yields

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (K' \nabla \Phi) \qquad (25)$$

Eq. 24 neglects vapor (and any adsorbed phase) transfer. (This is quite unimportant in many applications. However, it will be shown later how the other phases may be included in a more precise formulation.) Use of Eq. 22 in Eq. 25 yields

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (K' \nabla \Psi) + \frac{\partial K'}{\partial z} \qquad (26)$$

When the motion is isothermal, and Ψ is a unique function of 0, Eq. 26 reduces to

$$\frac{\partial 0}{\partial t} = \nabla \cdot (D_{\theta \, liq} \nabla \theta) + \frac{dK'}{d\theta} \cdot \frac{\partial \theta}{\partial z} \qquad (27)$$

where

$$D_{\theta \, liq} = K' \frac{d\Psi}{d\theta} \qquad (28)$$

This is essentially the equation derived by Klute (1952).

Where temperature gradients exist, and Ψ depends on both θ and T, Eq. 26 may be written as

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (D_{\theta \, liq} \nabla \theta) + \nabla \cdot (D_{T \, liq} \nabla T) + \frac{dK'}{d\theta} \cdot \frac{\partial \theta}{\partial z} \qquad (29)$$

(cf. Philip and de Vries, 1957). Here $D_{T \, liq}$ is given by

$$D_{T \, liq} = K' \frac{\partial \Psi}{\partial T} \qquad (30)$$

$D_{\theta \, liq}$ again has the value given in Eq. 28, though now one should write the differential as partial, not total.

In this way the right hand side of Eq. 25 is split into three components—that due to moisture gradient, that due to temperature gradient, and that due to gravity. $D_{\theta liq}$ and $D_{T \, liq}$ are called the liquid moisture diffusivity and the thermal liquid diffusivity of the medium. Both these quantities vary markedly with θ. Strictly, they vary also with T, but the variation with T is relatively slow, and in most practical applications it will suffice to treat $D_{\theta \, liq}$ and $D_{T \, liq}$ as purely θ-dependent.

The Variation of $D_{\theta liq}$ with θ. It has already been remarked that K' decreases rapidly as θ decreases from its saturation value. On the other hand, d $\Psi/d\theta$ increases fairly markedly as θ decreases. The net effect is that $D_{\theta liq}$ tends to decrease as θ decreases, though not so rapidly as does K'. $D_{\theta liq}$ is of course zero in solids so dry that K' is zero. Typical $D_{\theta liq}(\theta)$ functions will be found in Childs and Collis-George (1950a), Klute (1952a, b), Staple and Lehane (1954), and Philip (1955b, 1957f). Maximum values of $D_{\theta liq}$ may range from 10^2 cm^2 sec^{-1} or more for sandy soil down to 10^{-2} cm^2 sec^{-1} or less for fine-textured soils. The shape of the curve can also be expected to vary with the texture of the solid.

The Variation of $D_{T liq}$ with θ. As is noted above, there is some uncertainty as to the precise behavior of $\partial \Psi / \partial T$, especially for values of θ close to saturation. Philip and de Vries (1957) computed $D_{T liq}$ for a fine-valued soil, and found a marked peak close to saturation. It is possible that for the reasons noted earlier, the peak should be even more pronounced. In this particular work the maximum value of $D_{T liq}$ was about 2×10^{-7} cm^2 sec^{-1} ^{0}C^{-1}. Both at saturation and in solids so dry that K'=0, D_{T} liq will be zero.

MOVEMENT OF THE VAPOR PHASE IN UNSATURATED SOLIDS

Simple Theory of Vapor Transfer. The simplest way to treat the recent developments in understanding of vapor transfer in porous solids is to first present what is, essentially, the classical theory, and then to indicate where the assumptions of the classical theory fail. Then consider a modified theory, recently put forward, which is based on more real assumptions than the classical theory, and which gives quantitative agreement with observed transfer under temperature gradients. The simple theory gives values for the transfer which are only about one-tenth to one-fifth of the observed values.

The classical equation of vapor diffusion, modified so as to apply in porous solids

(Penman, 1940; Krischer and Rohnalter, 1940; van Bavel, 1952; Rollins et al., 1954) may be written

$$q_{vap} = -D_{atm} \; m \; \alpha a \; \nabla \rho \qquad (31)$$

where

q_{vap} is the vector vapor flux density $(gm \; cm^{-2} \; sec^{-1})$

D_{atm} is the molecular diffusivity of water vapor in air $(cm^{-2} \; sec^{-1})$

α is a tortuosity factor allowing for the additional path length

a is the volumetric air content of the medium $(cm^3 \; of \; air/cm^3)$

ρ is the density of water vapor $(gm \; cm^{-3})$

m is the "mass flow factor" introduced to allow for the mass flow of vapor arising from the difference in boundary conditions governing the air and vapor components of the diffusion system (m may be taken as very close to unity in the systems of interest here.)

Now

$$\rho = \rho_0 h \qquad (32)$$

where ρ_0 is the density of saturated water vapor $(gm \; cm^{-3})$. It follows that

$$\nabla \rho = \rho_0 \nabla h + h \nabla \rho_0 \qquad (33)$$

If the approximation mentioned earlier is now made, and justified in more detail in Philip and de Vries (1957), that h is a function of θ only, Eq. 33 may be rewritten

$$\nabla \rho = \rho_0 \frac{dh}{d\theta} \nabla \theta + h \frac{d\rho_0}{dT} \nabla T \qquad (34)$$

Using Eq. 34 in Eq. 31 gives

$$q_{vap}/\rho_W = - D_{\theta \, vap} \nabla \theta - D_{T \, vap} \nabla T \qquad (35)$$

where

$$D_{\theta \, vap} = \frac{D_{atm} \; m \alpha a \rho_0}{\rho_W} \frac{dh}{d\theta} = \frac{D_{atm} \; m \alpha \; ag \rho}{\rho_W RT} \frac{d\Psi}{d\theta} \qquad (36)$$

$$D_{T \, vap} = \frac{D_{atm} \; m \alpha a h \beta}{\rho_W} \qquad (37)$$

Here the final expression for $D_{\theta \, vap}$ depends on Eq. 21. β in Eq. 37 denotes $d\rho_0/dT$. β is, of course, temperature dependent, but a value of $10^{-6} \; gm \; cm^{-3} \; C^{-1}$ is typical for temperatures occurring naturally in soils.

Isothermal Water Vapor Transfer. Observations in the field (Staple and Lehane, 1954) and the laboratory (Philip, 1955b) suggest that this theory is adequate in the comparatively unimportant case of isothermal vapor transfer. That is, values of $D_{\theta \, vap}$ computed from Eq. 36 appear to be fairly reliable. Just why the simple theory should be adequate for isothermal transfer, but fails badly for transfer under thermal gradients is a question which will be returned to later.

Water Vapor Transfer Under Thermal Gradients. Quantitative determinations of vapor transfer under temperature gradients (e.g. Gurr et al. 1952; Taylor and Cavazza, 1954; Rollins et al., 1954) have shown that the transfer rates are of the order of five to ten times that predicted by the simple theory. Furthermore, the moisture content at which the maximum vapor transfer is observed to occur is somewhat greater than the simple theory predicts.

Philip and de Vries (1957) have pointed out that the simple theory neglects the interaction of the water vapor with the liquid and solid phases in the medium, and takes no account of the difference between the temperature gradients in the air-filled pores and of the medium as a whole.

They put forward the concept that in a medium in which liquid continuity has failed,

the transfer occurs as a series-parallel process of flow through regions of vapor and liquid. They show that, whereas the classical theory treats the liquid "islands" as obstacles blocking the passage of diffusing vapor, these are in fact regions of very rapid transport of water. Condensation at the upstream end of the island and evaporation at the downstream end produce changes in the curvature of the meniscus at each end, which result in a virtually zero resistance to liquid flow through the island.

Furthermore, when the heat transfer through the various phases of the medium (solid, liquid and gaseous) was examined in detail by methods due to de Vries (1952a, b), it was found that the temperature gradients across air-filled pores could be of the order of twice the mean temperature gradient in the medium as a whole.

The combined effect of these two considerations is to yield a modified theory which predicts values of $D_{T\,vap}$ varying from about eight times that predicted by Eq. 36 in wet soils to about three times the value predicted by Eq. 36 in very dry soils. As it stands, the theory is admittedly approximate, especially in the moisture region where liquid continuity is established. Nevertheless, it appears to clarify the understanding of this phenomenon.

Similar complicating factors do not enter the case of isothermal vapor transfer, since: (a) the vapor pressure gradient is now due solely to gradients of moisture content, so that, in general, even very small changes of meniscus curvature produced by condensation and evaporation would be sufficient to reverse the direction of vapor transfer; and (b) the whole matter of differential temperature gradients in different phases does not arise.

One interesting implication of this work concerns the detection and definition of "vapor transfer." The usual experimental means of separating liquid and vapor flow has been to use a soluble "tracer." It is now obvious that such methods cannot distinguish between pure vapor transfer and vapor transfer in series-parallel with transfer through a discontinuous liquid phase in the form of "islands." Clearly, any solute would remain anchored in a particular island; there could be no net transfer of solute even if considerable liquid transport through the islands were taking place. Methods using air gaps are even more obviously fallacious.

Since one of the main practical reasons for distinguishing between liquid and vapor transfer is to gain insight into solute transfer problems in soils, there is a good case for the operational definition of "vapor transfer," proposed by Philip and de Vries (1957), as describing all flows in which there is no liquid continuity. A consequence of this definition is that transfer distinguished as "vapor" by soluble tracer methods would continue to be called "vapor" transfer, even though it is not so in the sense of the classical theory.

The recently published work of Kuzmak and Sereda (1957 a, b) lends further substantiation to the view of thermally induced moisture transfer outlined here.

POLYPHASE TRANSFER IN POROUS SOLIDS

Adsorbed Phase. It seems probable that, in soils, moisture transfer in the adsorbed phase can be significant only under rather special conditions, such as where the soil is very dry and possesses a large specific surface. Here this matter cannot be dealt with adequately. Theoretical studies such as that of Babbit (1950) and Philip (1955b, 1957c) indicate that transfer in the adsorbed phase is also a concentration-dependent diffusion phenomenon, which may be represented by the equation

$$q_{ads}/\rho_w = - D_{ads} \nabla \theta \qquad (38)$$

(Here q_{ads} is the vector flux density in the adsorbed phase ($gm^{-2} sec^{-1}$) and D_{ads} is a function of θ.) Possibly a second, thermal, term should be added on the right hand side of Eq. 38, but its neglect is consistent with the approximation that h is a function of θ only.

General Equation of Polyphase Transfer. Using Eq. 22 in 23, and adding Eqs. 35 and 38, the following is obtained

$$q/\rho_w = - D_\theta \nabla\theta - D_T \nabla T - K'k \qquad (39)$$

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where

$$q = q_{liq} + q_{vap} + q_{ads} \qquad (40)$$

$$D_\theta = D_{\theta\,liq} + D_{\theta\,vap} + D_{ads} \qquad (41)$$

$$D_T = D_{T\,liq} + D_{T\,vap} \qquad (42)$$

It will be recalled that k is the unit vector in the z-direction. Combining the continuity requirement in its more exact form (cf. Eq. 24)

$$\frac{\partial\theta}{\partial t} = -\frac{1}{\rho_w}\,\nabla\cdot q \qquad (43)$$

with Eq. 39 the following is obtained

$$\frac{\partial\theta}{\partial t} = \nabla\cdot(D_\theta\,\nabla\theta) + \nabla\cdot(D_T\,\nabla T) + \frac{dK'}{d\theta}\cdot\frac{\partial\theta}{\partial z} \qquad (44)$$

Comparing this equation with Eq. 29, it can be seen that, in this way, it is possible to incorporate vapor and adsorbed phase transfer into the formulation without complicating the mathematical form. D_θ and D_T may be taken as functions of θ. Note that the $D_{T\,vap}$ appearing in Eq. 42 should be the value given by the modified (Philip and de Vries, 1957) theory, not the value found from Eq. 36.

HEAT TRANSFER IN POROUS SOLIDS

Adequate study of the simultaneous heat and moisture fields in porous solids requires some attention also to the matter of heat transfer in such solids. The general heat-conduction equation for this case may be written (Philip and de Vries, 1957; Philip, 1957f):

$$C\,\partial T/\partial t = \nabla\cdot(\lambda\,\nabla T) + \rho_w L\,\nabla\cdot(D_{\theta\,vap}\,\nabla\theta) \qquad (45)$$

λ, the thermal conductivity (cal sec^{-1} cm^{-1} C^{-1}), includes the contribution to apparent conductivity arising from transport of latent heat by thermally induced vapor transfer (de Vries, 1952a). Both λ and the volumetric heat capacity, C (cal cm^{-3} C^{-1}), may vary with θ. L cal gm^{-1} is the latent heat of vaporization of water. It will be noted that Eqs. 44 and 45, both equations of the diffusion type involving θ - (and, strictly, T-) dependent diffusivities and conductivities as well as gradients of θ and T, together govern the simultaneous moisture and heat fields in the soil. De Vries (1958) has recently developed a more refined analysis of simultaneous heat and moisture transfer, which avoids certain simplifications in the formulation which leads to Eq. 45. The more precise approach promises, unfortunately, to be very complicated.

DISCUSSION

The preceding outlined results would be of limited interest if it were not possible to solve the equations developed. Fortunately, the equations can be solved in the cases of a number of phenomena of fundamental interest in microhydrology. The solutions are in conformity with experimental observations, and have proved serviceable in providing insight into the physics of such diverse phenomena as absorption (Klute, 1952a, b; Philip, 1957c, h, k, 1958a, b), infiltration (Philip, 1954, a, b, 1957c, d, e, h, i, k, 1958a, b), capillary rise (Philip, 1957c, 1958a), evaporation from soils (Philip, 1954b, 1957d, f), drainage and water retention by soils (Staple and Lehane, 1954; Day and Luthin, 1956, Philip, 1957d) and extraction of soil-water by plants (Philip, 1957d).

Typical results of this approach include the prediction of the various zones of the moisture profile during infiltration observed in the classical work of Bodman and Colman (1944; Colman and Bodman, 1945), prediction of the (experimentally well-established) "falling-rate" and "constant-rate" phases of evaporation from an initially saturated porous solid in a constant environment [and of a final phase of the drying process in which the heat flux in the solid influences the evaporation rate, which explains certain observations of Penman (1941)], and quantitative explanation of data of Richards and Moore (1952) on the effect of the quantity of water applied to a soil on the subsequent drainage and retention of the water. These matters cannot be elaborated here, and the reader is referred to the original papers. Youngs (1957) has recently published work which provides more detailed experimental confirmation of this approach, as applied to the problem of infiltration.

It will be noted that the Ψ, D, K', and other θ-dependent functions entering the preceding analysis are experimentally determined, and are not readily or reliably represented as analytical functions of θ. Even if they were, the equations will usually be so complicated that numerical methods of solution would still be required. This has meant that appropriate numerical methods have been needed. Rapid and accurate methods of solving concentration-dependent diffusion equations have been developed in this connection (Philip 1955 a, 1957 a, e).

The analysis of unsteady state phenomena by this means has been limited to problems which are one-dimensional (or exhibit radial symmetry) and in which the initial and boundary conditions are relatively simple. The study of more complicated cases will not be as readily accomplished, and there is definite scope for applying a simpler approximate model of moisture transfer. In cases where water is made available at the surface of a solid, and information is desired on its rate of entry (i.e. problems of absorption or infiltration) such a simple model is available (Philip, 1954a). The connection between the simple model and the detailed diffusion theory has been explored (Philip, 1957 i, k, 1958b) and it is found that the model corresponds to the limiting case (approximated in coarse-textured or dry media) where D_θ and K' assume very large values close to saturation, and are virtually zero throughout the rest of the moisture range. The approximate model has been used to illustrate the magnitude of the effects on infiltration dynamics of vertical heterogeneity of initial moisture content and of permeability characteristics (Philip, 1958c).

An important aspect of the theoretical structure outlined in prior sections is that it provides a coherent scheme which connects an (apparent) diversity of phenomena. Even quite recently each of these phenomena received its own empirical explanation, but now they can be regarded as particular solutions of the general equation 44 (plus Eq. 45, in cases where heat flux is important). This appears to be a definite step towards the establishment of the study of moisture transfer in porous solids as a quantitative physical science.

A limitation in the present approach is that many of the equations, including those which may be usefully solved, depend on the assumption that such characteristics of the soil as K', Ψ, and D_θ are unique functions of θ. Many of the difficulties arising in this connection are more apparent than real (Philip 1957h, 1958 a, b). However, some matters are beyond the scope of the analysis in the present form. For example, the variation of K' with electrolyte concentration in soils of high colloid content (Quirk and Schofield, 1955) means that such soils cannot be adequately dealt with when gradients of electrolyte concentration are present. Again, in deep soils of high colloid content, the $\Psi(\theta)$ relationship may well be influenced by overburden pressures, and the problem falls outside the field of the present approach. For all that, there remains a wide range of agricultural soils for which this theoretical framework is relevant.

It is scarcely necessary to point out that this approach does not depend on any special geometrical model of the solid (e.g. capillary tubes, packings of spheres). Clearly, the theory, in its isothermal form, holds for any solid which can be characterized by a moisture-potential- and a conductivity-function. The more general theory requires additional characteristics to be uniquely determined by θ and T, but this is no more restrictive.

The task of integrating into this structure the additional complications of colloidal

behavior, and of mechanical effects such as the influence of surface and foundation loads remains largely untouched. This seems to be the major theoretical problem yet to be faced in modern soil water studies. It demands an intimate combination of the skills of many disciplines—mathematical physics, thermodynamics of irreversible processes, physical chemistry of colloids, soil mechanics, and rheology—to name but the most obvious ones.

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Water Movement in Soils Under Pressure Potentials

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Introductory Remarks by the Chairman

During recent years a great deal of emphasis has been given to moisture conduction in soils under suction, thermal and electric potentials. From this, the impression might be gained that either all there is to know on water movement under pressure potentials, or that such movement is of lesser importance in soil engineering than movement caused by other potentials. Nothing could be farther from the truth on both counts. In the over-all picture, pressure potentials are still the most important water-moving agents in soil engineering and certainly there is still much to learn about the physics of pressure flow in porous media. Professor Schmid has prepared a brief and precise account of the historic development and present state of knowledge in this all-important area. While he traces with sure hand the essential role played by mathematics in the quantitative evaluation of flow conditions, he gives due consideration to the material-physical aspect of flow through porous hydrophilic systems as exemplified by soils.

● PRESSURE potentials were the first driving forces recognized to cause movement of water through soils, and originally they were believed to be the only driving forces for such movement. It is not surprising then that the problem of water movement under pressure potentials has received extensive treatment, and the existing literature is tremendous. An attempt will be made to review—as far as this is at all possible—some of the more important aspects of the problem in the following paragraphs and to summarize in a general way the present state of knowledge.

SINGLE PHASE FLOW

The first quantitative insight was achieved by Darcy experimenting with filter sands in the water works of Dijon (1), and his empirical law states that the filter velocity is proportional to the first power of the pressure gradient:

$$V = \frac{Q}{A} = -K \frac{\Delta p}{\Delta L} \tag{1}$$

Where V is the filter—or seepage velocity, Q the permeation discharge, A the permeated area, K the proportionality coefficient which can be resolved into permeability and viscosity: $K = \frac{k}{\mu}$, and $\Delta p = p_2 - p_1$, the pressure dissipated along the flow path ΔL. The minus sign indicates flow in the direction of decreasing pressures.

Equation 1 describes the movement of a liquid through an isotropic porous medium in the absence of an exterior force field or for horizontal flow. If the velocity V has a vertical component, the gravitational force must be included and Eq. 1 now reads:

$$V = -K \frac{\Delta p + \rho g \Delta Z}{\Delta L} \tag{2}$$

where ρ is the density of the liquid, g the gravitational acceleration and ΔZ the difference in vertical coordinates. Darcy's law in the form of Eq. 1 or 2 is of very restricted use since it describes only uniform conditions over a finite length. A more general expression is the differential form of Eq. 2:

$$\bar{V} = -\frac{k}{\mu}(\text{grad } p + \rho g) \tag{3a}$$

Here $\bar{V}$ is the local filter velocity vector. Eq. 3a can be simplified by the introduction of a force potential ϕ where

$$\phi = g \cdot Z + \int_{p_0}^{p} \frac{dp}{\rho(p)} \tag{3b}$$

and then

$$\bar{V} = -\frac{k}{\mu} \text{ grad } \phi \tag{3c}$$

Since any solution of a flow problem under pressure potentials requires the determination of three unknowns, namely $\bar{V}$, p, and ρ, Darcy's law alone is not yet sufficient for complete specification of the problem. The additional conditions are supplied by the relation between fluid density and pressure:

$$\rho = \rho\ (p) \tag{4}$$

and by the continuity condition:

$$n\frac{\partial \rho}{\partial t} = \text{div } (\rho\bar{V}) \tag{5}$$

where n is the porosity and t the time.

Combination of Eqs. 3, 4 and 5 yields:

$$n\frac{\partial \rho}{\partial t} = \text{div}\left[\frac{\rho k}{\mu}\ (\text{grad } \phi)\right] \tag{6}$$

Thus, if the water movement through the soil is described by Eq. 3c, the solution of Eq. 6 for the given boundary conditions constitutes the solution of the flow problem. The solution may be sought for the following conditions:

    (a) Steady state flow with geometrically prescribed boundary conditions.
    (b) Steady state flow with a free boundary (free surface gravity flow).
    (c) Unsteady state flow.

For cases (a) and (b), the time derivative vanishes and Eq. 6 is reduced to

$$\text{div}\left[\frac{\rho k}{\mu}\ (\text{grad } \phi)\right] = 0 \tag{7}$$

Assuming the water to be incompressible (ρ = const), and the soil to be homogeneous,

$$\nabla^2 \phi = 0$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial Z^2} \tag{8}$$

is the Laplace operator.

METHODS OF SOLUTION

A. Steady State Flow with Geometrically Prescribed Boundary Conditions

1. Analytical Solutions. In all cases where the flow is fully determined by the geometry of the boundaries, the boundary conditions can be defined by:

$$\bar{V}_n = 0 \tag{9}$$

along the boundary, where $\bar{V}_n$ is the component of the velocity vector normal to the boundary. Two dimensional solutions of Eq. 8 for the boundary conditions, Eq. 9, are relatively simple if the geometry of the boundary is such that it can be conveniently expressed analytically. This can be achieved by the use of complex variables and their conformal mapping, since it is known that solutions of the Cauchy-Riemann differential equations:

$$\frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial y} \; ; \quad \frac{\partial \phi}{\partial y} = -\frac{\partial \psi}{\partial x}$$

$$\frac{\partial x}{\partial \phi} = \frac{\partial y}{\partial \psi} \; ; \quad \frac{\partial x}{\partial \psi} = -\frac{\partial y}{\partial \phi}$$

(10)

satisfy also the Laplace Eq. 8. This procedure applied to the two-dimensional problem of Figure 1 gives

$$\frac{x^2}{d^2 \cos^2 \phi} - \frac{y^2}{d^2 \sin^2 \phi} = 1$$

(10a)

and

$$\frac{x^2}{d^2 \cos^2 h\psi} + \frac{y^2}{d^2 \sin^2 h\psi} = 1$$

(10b)

For constant values of ϕ and ψ, Eqs. 10a and 10b give the equipotential and streamlines respectively for the flow around a sheet pile wall in a semi-infinite soil mass. These two families of curves are confocal ellipses and hyperbolas with their common focus at the tip C of the wall. The components of the velocity vector are given by:

$$\bar{V}_x = K \, \frac{H-h}{\pi} \, \frac{\partial \psi}{\partial y}$$

(10c)

and

$$\bar{V}_y = K \, \frac{H-h}{\pi} \, \frac{\partial \psi}{\partial x}$$

(10d)
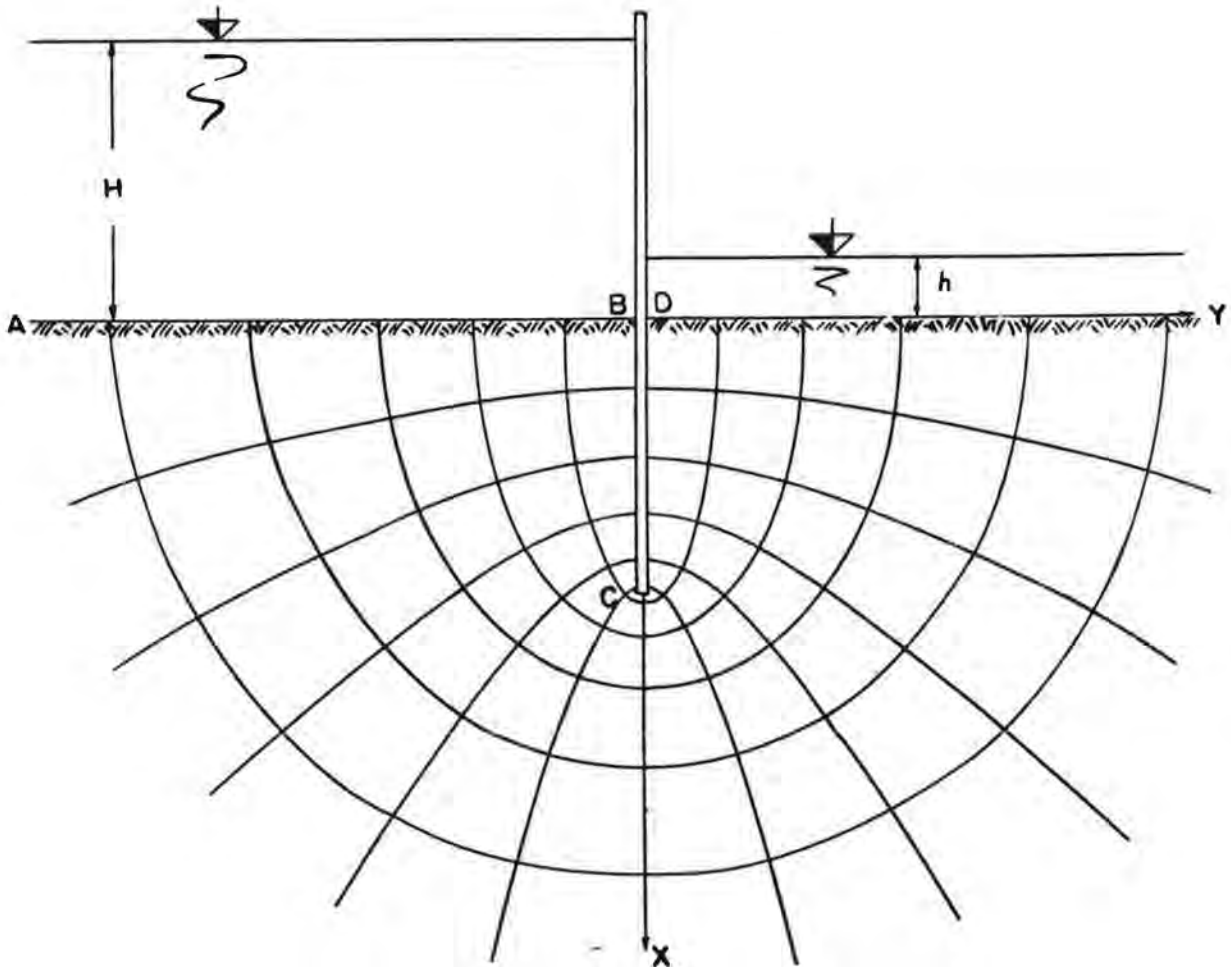
Figure 1. Flow around a sheet pile wall.

Of particular interest is the exit velocity at the down-stream surface of the soil, since it will indicate the safety against a quick condition. With

$$\frac{\partial \psi}{\partial y} = \frac{1}{d\sqrt{1 + (\frac{y}{d})^2}} \qquad \text{(for x = 0)}$$

gives

(10e)

$$\bar{V}_x = K \frac{H - h}{\pi d \sqrt{1 + (\frac{y}{d})^2}}$$

which has a maximum for y = 0: $\max \bar{V}_x = K \frac{H - h}{\pi d}$.

Since according to Eq. 3c grad $\phi = \frac{\bar{V}}{K}$ the maximum gradient thus will be

$$\frac{\max \bar{V}_x}{K} = \frac{H - h}{\pi d}$$

This maximum gradient must be smaller than the critical hydraulic gradient $S_{cr} = \frac{G_S - 1}{1 + e}$ to prevent the soil from "boiling" out. Here G_S is the specific gravity of the solids and e is the void ratio. Thus:

$$\frac{G_S - 1}{1 + e} > \frac{H - h}{\pi d} \qquad (10f)$$

This condition determines the minimum depth of penetration which is possible. This type of problem is frequently encountered where an excavation pit has to be maintained in the dry. Hence, a condition such as Eq. 10f would give the height H to which the groundwater level has to be depressed by well points to safeguard against boils.

Of further interest is the distribution of the velocity $\bar{V}_x$ between point C and D as well as the horizontal velocity $\bar{V}_y$ below point C. Using Eqs. 10c and 10:

$$\frac{\partial \psi}{\partial y} = \frac{\partial \phi}{\partial x} = \frac{1}{d\sqrt{1 - (\frac{x}{d})^2}}$$

Thus $\quad \bar{V}_x = K \frac{H - h}{\pi} \frac{1}{d\sqrt{1 - (\frac{x}{d})^2}} \quad$ (10g)

for x = d: $\bar{V}_x = \infty$

and

$$\bar{V}_y = K \frac{H - h}{\pi} \frac{1}{d\sqrt{(\frac{x}{d})^2 - 1}} \quad (10h)$$

for x = d: $\bar{V}_y = \infty$

The variations of $\bar{V}_x$ and $\bar{V}_y$ are shown in Figure 2.

At point C, $\bar{V}_x$ as well as $\bar{V}_y$ become infinite. However, because of Eq. 3c this would require grad ϕ to become infinite. Since the upper value of ϕ is finite and more or less determined by H. The condition grad $\phi = \infty$ would require an infinite negative pressure in the vicinity of C. This is, of course, physically not possible. Point C thus is a singular point where the solution of the potential theory is impossible. It must be concluded that there the boundary streamline separates from the
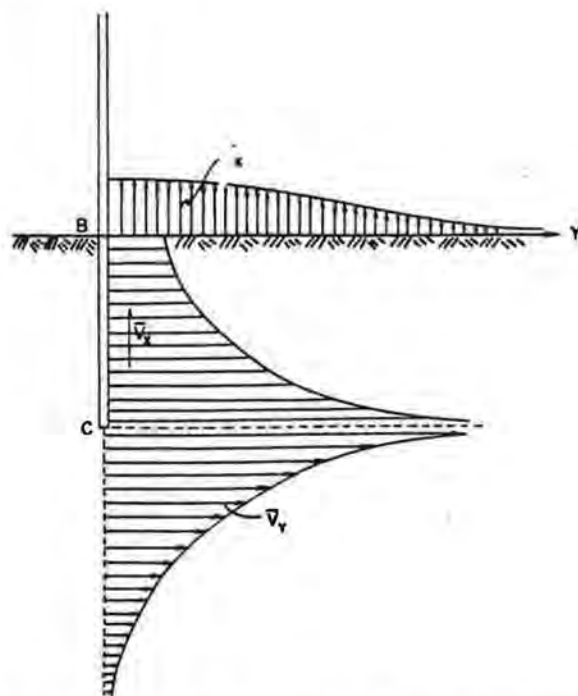
Figure 2. Velocity distribution along sheet pile wall.
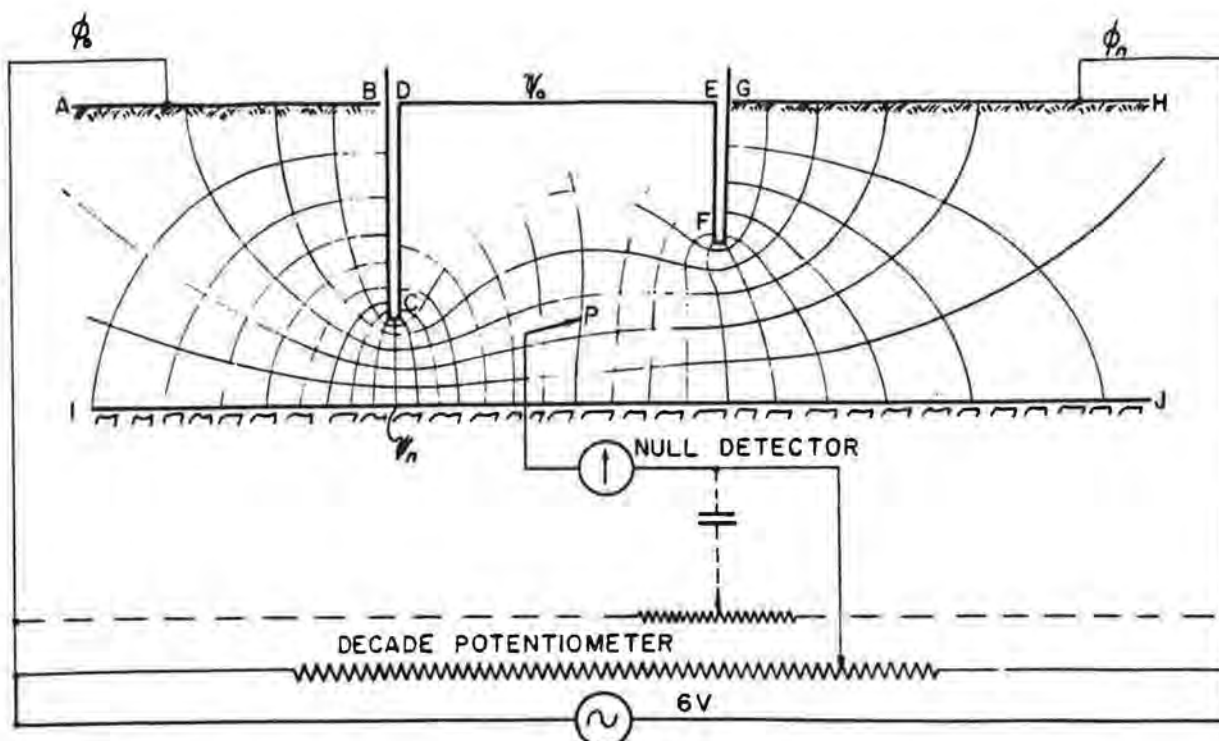
Figure 3. Solution of flow problems by electrical analog.

sheet pile wall and a small pocket is formed in which the absolute pressure is zero (vacuum). The situation at C is similar to the problem of laminar flow over a sharp crested weir.

Besides using the method of conformal transformation of complex variables, solutions for Eq. 8 may be obtained by using Green's function or by relaxation techniques. Many problems will require a reasonable amount of mathematical sophistication and for general methods appropriate mathematical texts should be consulted since the solutions are essentially a problem of mathematics.

A large number of frequently encountered problems have been treated in the foregoing fashion and their solutions are given in the literature notably by Muskat (2) and Polubarinova-Kochina (3). Scheidegger in his excellent recent book (4) gives a comprehensive bibliography.

2. Analog Solutions Whenever the boundary values are too complicated for obtaining solutions by the above mentioned methods, the use of analog models and analog computors may prove to be advantageous. The method is based on the principle that the differential Eq. 6 describing the force potential for water seepage through soil is analogous to the differential equations defining a number of other physical processes or phenomena. Among those are the electrical potential field, the magnetic potential field, the thermal potential field, as well as the trace of a two-dimensional stress tensor. The idea is by no means new and was used probably for the first time by G. Kirchhoff in 1845 (5). In contrast to analytical solutions which manipulate with numerical quantities, the analog solutions operate with physical quantities. These methods use the experimental determination of such physical quantities as magnetic flux, electric current and potential, temperature and stress which by their analog interpretation then give the velocity and force potentials for the seepage flow problem. Since the accuracy of such solutions depends on the precision of the measurement, the electric potential analog is most widely used, because electrical quantities such as resistance, potential and current can be measured easily with high precision by simple equipment. The discussion, therefore, will be confined to electrical analogs.

The differential equation for the electric potential field is given by:

$$\text{div } (g \cdot \text{grad } E) = 0 \tag{11}$$

where g is the conductivity and E the electrical potential. Substituting $E = A \cdot \phi$; $g = B \cdot K$ into Eq. 11, the equation becomes identical to Eq. 7. A and B are scaling constants. Thus, the drop in electric potential between two electrodes in a conducting medium corresponds to the drop of the force potential between the extreme equipotential lines of the flow problem. Figure 3 demonstrates the solution of the two-dimensional flow below a dam with cut-off walls by an analog model. The flow field ABC . . . J is cut out from a sheet of conducting paper and the boundaries $AB = \phi_0$, and $GH = \phi_n$, which are the extreme equipotential lines are drawn with a conducting paint as well as the extreme flow lines $B C D E F G = \psi_0$ and $I J = \psi_n$. By applying an ac potential difference between ϕ_0 and ϕ_n as shown, the equipotential lines $\phi_1 \phi_2 \phi_3$ . . . can be traced using the probe P and the null detector. Similarly, by impressing the potential along ψ_0 and ψ_n, the streamlines $\psi_1 \psi_2$ . . . can be found. The conducting paper technique is simple and cheap, but is only suitable for two-dimensional problems. Three-dimensional problems can be solved by applying the same principle to a model in an electrolytic tank, where an electrolytic solution serves as the conducting medium. The shape of this tank is modeled after the boundaries of the flow problem.

A third type of electric analog model is the resistance network. Here the continuous flow field is approximated by a grid system of resistors. This is permissible if the grid distance "h" is made sufficiently small. The method corresponds to the numerical solution of Laplace's Eq. 8 by a finite difference relaxation method where the field is divided into small square lattices. In this case, Eq. 8 can be written:

$$\nabla^2 \phi = \frac{\phi_1 + \phi_2 + \phi_3 + \phi_4 - 4\phi_0}{h^2} + \frac{h^2}{12}\left[\frac{d^4\phi}{\partial x^4} + \frac{\partial^4\phi}{\partial y^4}\right] \tag{12}$$

The term in the bracket is small of higher order and may be neglected. In terms of the electrical analog Eq. 12 corresponds to

$$\frac{\phi_1 + \phi_2 + \phi_3 + \phi_4 - 4\phi_0}{R} = 0 \qquad \text{where R is the resistance between the node}$$

points of the grid. A detailed description of such an analog computer is given by S.C. Ling (6).

3. Graphical Solution. An alternate procedure for solving Eq. 8 is due to Forchheimer. Here the flow pattern is obtained by a trial and error method. The derivation is given by Tschebotarioff (7), see also Taylor (8). The stream- and equipotential lines are sketched by watching the boundary conditions as well as the Cauchy-Riemann conditions, and the pattern is subsequently corrected such as to satisfy these conditions at every point. These conditions will be satisfied if the following rules are observed:

    (a) The flow boundaries are at the same time the extreme streamlines.
    (b) Lines of equal head are the equipotential lines.
    (c) Streamlines and equipotential lines intersect at right angles. (This applies also to the boundaries.)
    (d) All figures should approximate squares.

This procedure often gives a quick and sufficiently accurate solution which would be tedious to obtain analytically. It becomes impracticable, however, for the solution of three-dimensional problems unless there is radial symmetry.

4. Mechanical Models. Since for homogeneous isotropic coarse grained soils, the force and velocity potentials are independent of the permeability k, the problem could also be solved by direct model tests as long as the geometric relations are maintained. This method, however, is subject to relatively large experimental errors caused by capillary tension, air bubbles, etc. and will yield only qualitative results.

B. Steady State Flow with a Free Boundary

1. Analytical Solutions. Rigorous analytical solutions are very difficult and tedious to obtain and are based on the assumption of a sharply defined free surface along which the fluid pressure is constant and equal to the pressure in the gas above it. The most

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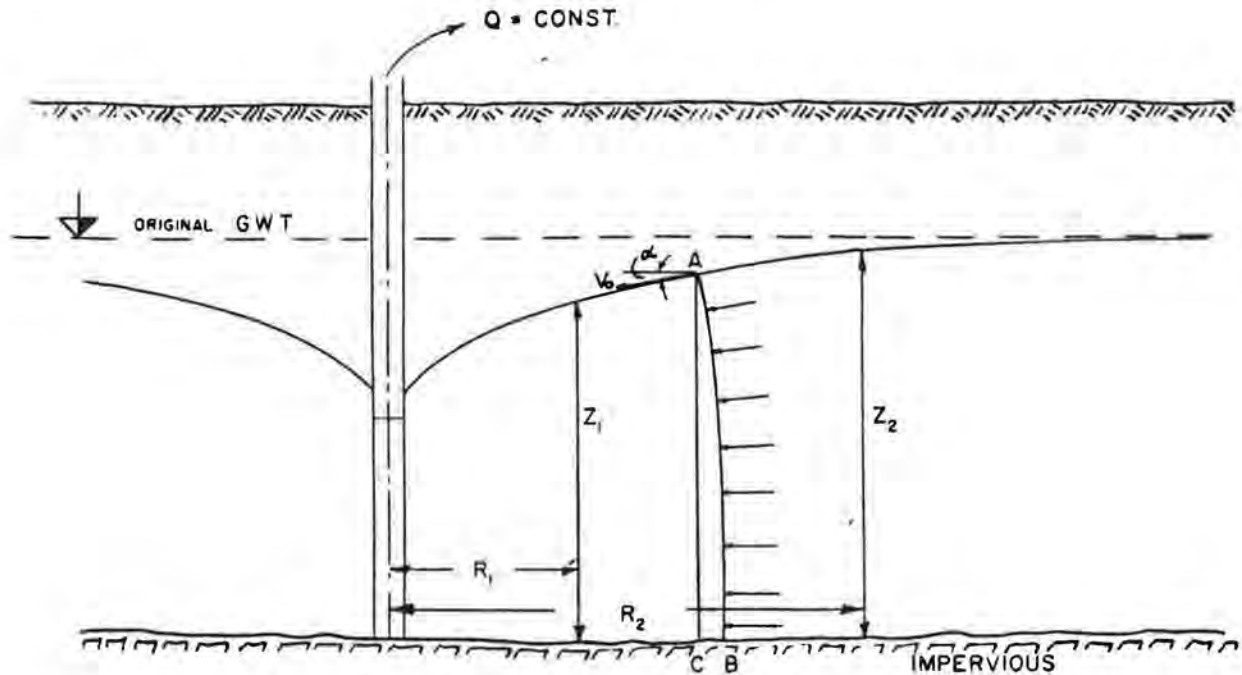
(STEADY FLOW WITH A FREE SURFACE)

Figure 4. Flow towards a well.

promising method is one using a velocity potential ψ such that with the previous notation

$$\psi = K (p + \rho g z)$$

$$\bar{V} = -\text{grad } \psi$$

and

$$\nabla 2 \psi = 0$$

using again a complex number representation and the hodograph transformation $u = \frac{\partial \psi}{\partial x}$, $V = \frac{\partial \psi}{\partial y}$ the free surface is determined in the hodograph (u, V) plane. Once the free surface is known, it can be treated like a geometric boundary. The method was pioneered by Hamel (9) and a series of solutions are given by Muskat (2) and especially by Polubarinova-Kochina (3).

A much simpler and, for many engineering purposes, sufficiently accurate, approximate solution can be obtained using Dupuit's assumption (Fig. 4).

Let V_0 be the tangential filter velocity at the point A of the free surface which has an inclination of α with the horizontal. Then Dupuit's assumption is that the horizontal component of the filter velocity along the line AC is uniform and equal to $K \frac{dZ}{d\gamma}$. Although this assumption has been questioned (2), it seems to give results in good agreement with rigorous solutions whenever the slope α of the free surface is not too large. Applying this assumption then to the problem of flow towards a well

$$Q = V \cdot A = K \frac{dz}{dr} \cdot 2 r \pi \cdot z \tag{13}$$

After integrating this separable differential equation and solving for the constant of integration

$$Q = \pi K (Z_1^2 - Z_2^2) \cdot \ln \frac{r_2}{r_1} \tag{14}$$

This equation now gives the yield of a well on a horizontal impervious layer under steady flow conditions.

2. Analog Solutions. In view of the difficulty of obtaining rigorous analytical solutions, the electrical analog method may be particularly useful whenever high accuracy is required. Because the free surface boundary is not known, it must be determined first by trial and error. With the conducting paper technique, it amounts to using a trial shape and check whether the electric potential at the free surface is equal to zero. The correct shape can be found by successive approximations. The resistance analog computer can also be used in a similar manner to great advantage.

3. Graphical Solutions. The graphical method described under A could only be used if a guess is made with respect to the free surface boundary. The quality of the solution depends on the accuracy of this guess. There is unfortunately no direct way of checking the results.

C. Unsteady State Flow

In the general case, the continuity Eq. 5 together with Darcy's law, Eqs. 3c and 4, leads to a non-linear partial differential equation which makes an analytical treatment rather difficult. However, Shchelkachev (10, 11, 12) by using the assumptions of fluid, as well as soil being compressible, and following Hook's law succeeded in developing the linearized equation:

$$\nabla^2 \phi = \frac{\mu}{K} (\alpha n + \beta) \frac{\partial \phi}{\partial t} \tag{15}$$

where $\phi = \int_{p_0}^{p} \frac{dp}{\rho(p)}$; and $\alpha = \frac{1}{\rho} \frac{d\rho}{dp}$, $\beta = \frac{dn}{dp}$ are the compressibility coefficients

of liquid and soil which are assumed constant. It should be noted that in the force potential ϕ the gravity term is neglected. Eq. 13 is of the same type as the transient heat flow equation and methods for its solution are given by Carslaw and Jaeger (13) and Courant and Hilbert (14).

D. Anisotropy

In 1948, Ferrandon (15) derived formulas for the flow through anisotropic porous media which led to the notion of permeability as a tensor quantity. Ferrandon's theory has been substantiated by Scheidegger who checked the permeability tensor concept, comparing directional measurements of permeability. As a consequence, it can be stated that in the general case, the direction of the filter velocity $\overline{V}$ and the force potential gradient grad ϕ do not coincide except in three orthogonal directions in space. These three directions may be called the principal axes of the permeability tensor. A flow problem in anisotropic soil can be reduced to the case of isotropic flow by a geometric distortion with respect to the principal axes of the permeability tensor. In the case of two-dimensional flow, for example, by a reduction in scale in the direction "2" by the amount $\sqrt{\frac{k_1}{k_2}}$ where k_1 and k_2 are the permeabilities in the principal directions.

E. Permeability

The discussion above might suggest the idea that the water movement in soils under pressure potentials is a solved problem from the scientific point of view except for possibly some isolated questions at the periphery. Nothing could be farther from the truth. All the considerations so far were made under the tacit assumption that the permeability of the soil was a known and constant material property. While it is not too difficult to measure the permeability in the laboratory under a given set of conditions, the problem remains how a variation of these conditions will influence the permeability and also, how to appraise the conditions likely to be encountered in the field.

Of course, the problem of changing soil properties in stratified deposits as well as the lack of uniformity within an individual layer itself always will be with the soil engineer. He is often dealing with natural soil deposits which have been formed in quite an erratic way. Yet, even if he should fine—in a rare case—a completely uniform, homogeneous soil, it often will be practically impossible to duplicate the field conditions

in a laboratory permeability test. This holds particularly for sands, because undisturbed sampling of sandy and gravely soils is not possible without excessive costs. Disturbed samples, however, have a different structure, aggregation and porosity and hence a different permeability. Therefore, the influence of these factors on the permeability must be known.

It seems logical that some relationship should exist between the geometry of the pore space in the soil and the permeability. Because of the irregularity of the particle shapes, the lack of uniformity of the grain size in most soils and because of the inumerable possibilities for particle aggregation into some more or less pronounced structure, no parameter defining the geometry of the voids in a unique way has as yet been discovered.

Attempts to correlate soil permeability with such other physical quantities as porosity n, grain diameter d, capillary diameter D, surface area S, are almost as old as Darcy's law.

Hazen, for example, related permeability to an effective grain size diameter: $k \approx C\, d_{10}^2$ where d_{10} is the sieve opening passed by 10 percent of the sample. It is frequently overlooked that the formula is valid only for clean, uniform filter sands.

The relationship between porosity and permeability in particular has been discussed and investigated extensively in the past 60 years. Today there are at least ten conflicting formulae (16) giving a relationship between permeability and porosity. Some of them were derived from theoretical considerations, others from experimental results or a combination of both.

The porosity alone can never completely specify the geometry of the voids. It is obviously possible for any one particular soil to have quite different structural arrangements and thus to have a different pore geometry at the same porosity. The most promising approach appears to be the use of an equivalent or effective capillary diameter D_e. This diameter is introduced if the permeate (soil) is replaced by an idealized capillaric model consisting of a system of capillary tubes through which flow occurs according to the Hagen-Poiseulle equation. Unfortunately, this effective capillary diameter D_e cannot be measured directly by independent means, but it can be determined from permeability tests. The author has shown recently (17) that above a critical porosity D_e may be considered constant.

A modification of the capillaric model theory was made by Kozeny who introduced the notion of the hydraulic radius. His formula

$$k = \frac{C\, n^3}{S^2} \qquad (16)$$

as well as several modifications of it so, for example, the Kozeny-Carman equation:

$$k = \frac{n^3}{5\, S_0^2\, (1 - n)^2} \qquad (17)$$

still enjoy wide popularity at present, but they have been severely criticized recently (4, 17) and their validity is questionable. In these formulae, C is the Kozeny constant varying between 0.5 and 0.667, S is the surface area per unit volume, S_0 is Carman's "specific" surface, that is, surface per unit volume of solids and n is the porosity.

One reason for the discrepancies and contradictions between the various proposed permeability relations may be derived from the fact that with the exception of Baver (18) and Winterkorn (19), all investigators are concerned with the full porosity of the soil. This is unrealistic. It has been known for some time that water is adsorbed at the particle surfaces by surface forces resulting in a complete fixation of several layers of water molecules and, some distance farther away, these surface forces cause an increase in the viscosity of the water.

Also, in the complex system of the inter-connected pore space there will be dead ends, side pockets, and cross capillaries without an appreciable pressure gradient. None of these will contribute to the flow, yet all of them do contribute to the porosity. Although several investigators mention these facts, they fail to consider them in the derivation of their formulae.

On the basis of these arguments, the author has derived the following permeability relationship (17):

$$K = \frac{\gamma}{32\,\mu}\,D_e^2\,(n - n_0) \qquad (18)$$

where γ is the unit weight of the water, μ the viscosity, D_e the effective capillary diameter, n and n_0 is the total and the ineffective porosity, respectively. Experimental results are in good agreement with this equation. Figures 6 and 7 show permeability data giving values for D_e and n_0 computed from Eq. 18. D_e is constant above a certain porosity and thus may be a function of the granulometry of the particles, whereas n_0 appears to be a function of the structure or aggregation of the soil. Winterkorn (19) under somewhat different conditions also found a limiting or specific porosity analogous to Eq. 18.

The fact that the permeability values when plotted against the porosity "n" show a deviation from the straight line as n approaches n_0, suggests that in this range D_e is no longer constant but becomes a function of the pressure. A functional relationship between permeability and pressure was found indeed empirically by Tiller (21, 22) who established that

$$k = k_0\,(\delta - p)^{-m} \qquad (19)$$

Figure 5. Porosity vs permeability after Equation 18.

where δ is the total—or overburden pressure on the soil and p is the porewater pressure. This relationship holds above some experimentally determined value for $(\delta - p)$. A similar relationship between permeability and pressure was found by Fatt and Davis (23). Another interesting phenomenon in this connection is the existence of an initial pressure gradient in clays demonstrated by Derjaguin and Krylov (24) and supported by recent measurements of residual pore water pressures in consolidated clays (25). Since Eqs. 16, 17, 18, and 19 give the soil permeability as a function of the porosity n or as a function of the total pressure δ on the soil, permeability values determined in the laboratory can be reduced to the conditions of the soil in situ, provided the structure of the test sample has been relatively undisturbed. It is always necessary, however, to determine the permeability at least at two different porosities, and it is advisable to determine k at three or more different values for n and plot the diagram k vs n.

Permeabilities can be measured in the laboratory by either the constant head test, the falling head test, or indirectly from consolidation test data. In the former two tests, particular care is required to avoid the formation of air bubbles which would influence the results. This may be achieved by either assembling the test setup under vacuum and using de-aired water or by running the permeability tests under sufficient back pressure that any air present remains in solution. The latter can be done most conveniently in a triaxial test chamber. The indirect determination of the permeability from consolidation test data is open to some criticism because of the simplifying assumptions of the consolidation theory. In some cases, it may be advantageous to determine the permeability directly in the field, namely, whenever a high reliability of the results is required, or, when the integrity of the samples will be questionable, or, when a laboratory determination would be of little value because of the non-uniformity of a particular deposit. In all these cases the permeability may be determined by a pumping test. After the subsoil conditions have been ascertained by borings, the appropriate well equation can be used to compute the permeability. For the ground water
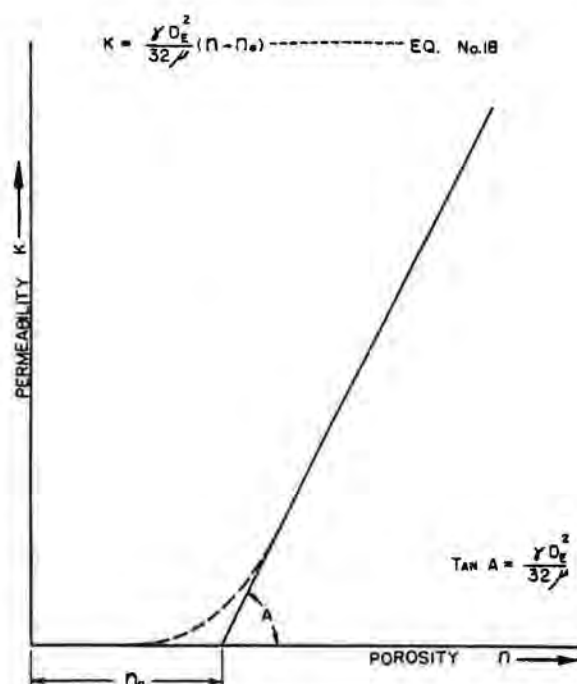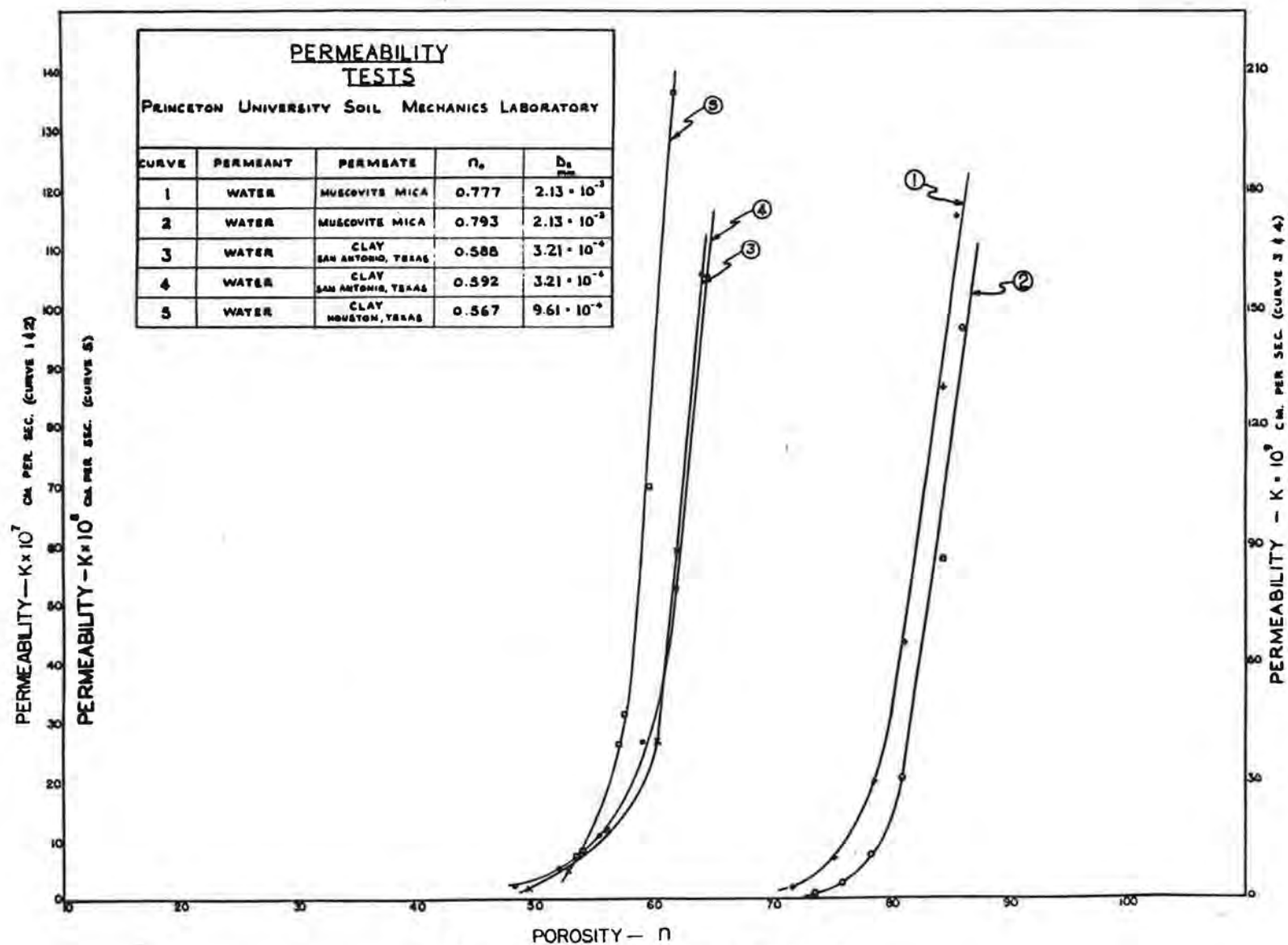
Figure 6. Permeability vs porosity.

Curve	Investigator	Permeate	Permeant	n_o	D_E mm
1	Michaels and Lin	Kaolinite	Methanol	0.483	9.52×10^{-4}
2	"	"	Water	0.544	10.33 "
3_A	"	"	Nitrogen	0.547	8.73 "
3_B	"	"	Nitrogen	0.568	8.00 "
4	"	"	Cyclohexane	0.568	6.67 "
5	Howe and Hudson	Quartz Sand and Clayslip	Air	0.173	3.64×10^{-1}
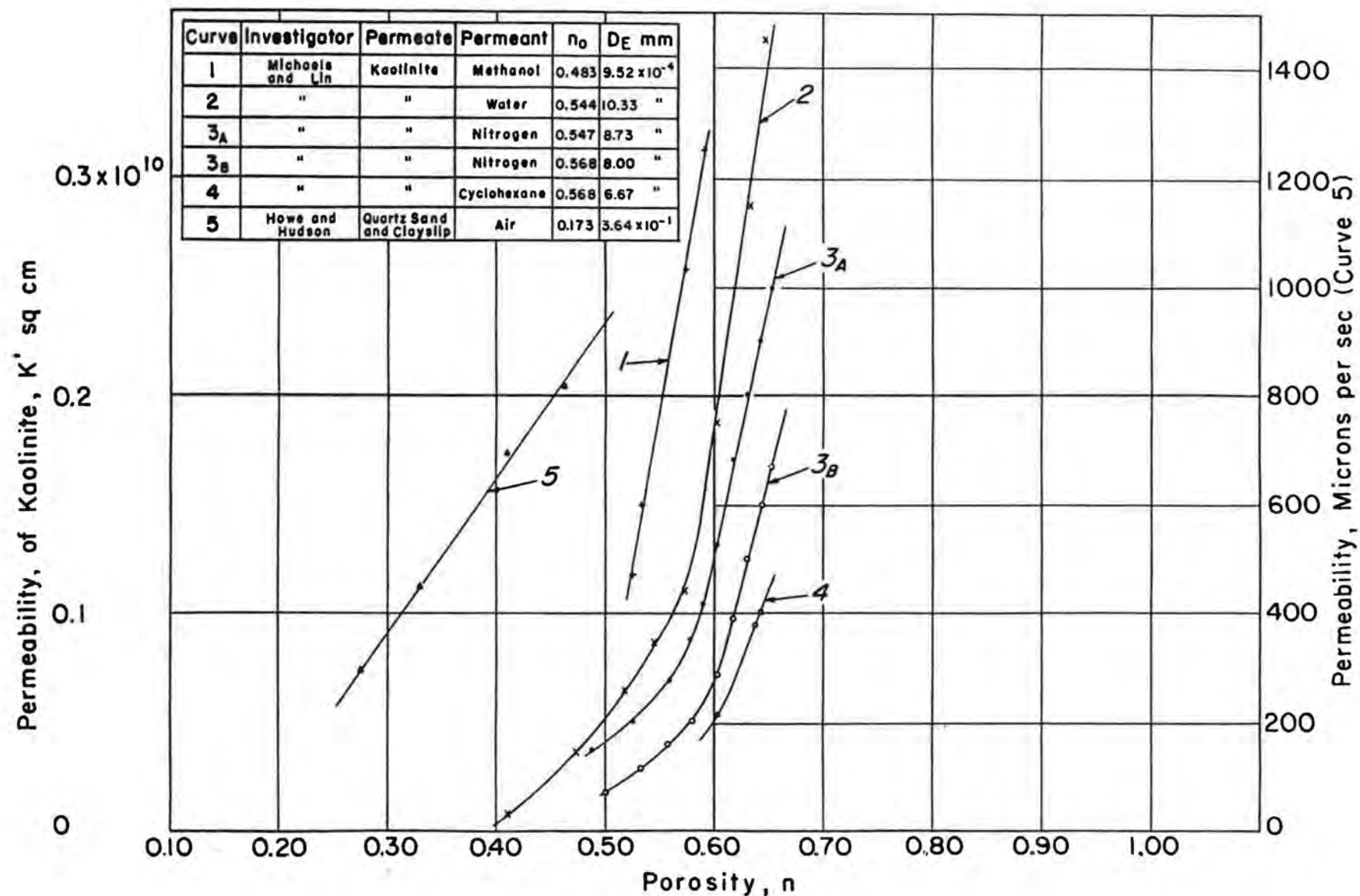
Figure 7. Permeability vs porosity.
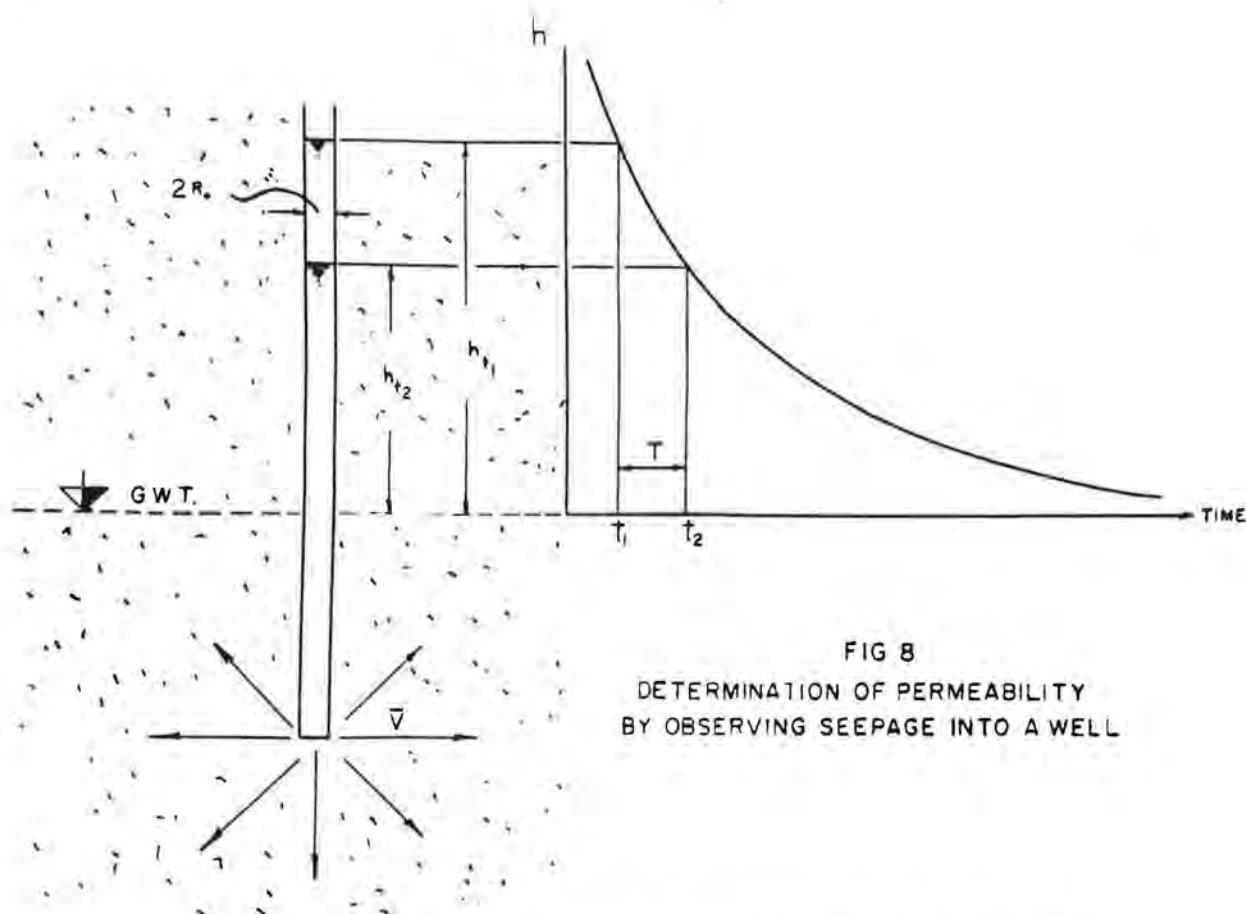
FIG 8
DETERMINATION OF PERMEABILITY
BY OBSERVING SEEPAGE INTO A WELL

Figure 8. Determination of permeability by observing seepage into a well.

conditions of Figure 4, for example, Eq. 14 may be rewritten as follows:

$$k = \frac{Q}{\pi} \frac{\ln \frac{r_1}{r_2}}{(Z_1^2 - Z_2^2)} \tag{20}$$

Thus, a well can be driven into a pervious layer and pumped at a constant rate Q. After steady conditions have been reached, the water levels Z_1 and Z_2 in two observation wells a distance r_1 and r_2 from the pumped well can be measured and Eq. 20 yields the over-all permeability. It should be noted that the distances r_1 and r_2 should be sufficiently large as to be outside the immediate cone of depression in the vicinity of the pumped well. Otherwise, the Dupuit assumption under which Eq. 14 was derived, namely that the slope of the water table is small, would no longer be a good approximation. This method eliminates most of the uncertainties discussed earlier, but it is relatively expensive.

A somewhat simpler method which requires only one well and also does not require steady conditions is possible by the use of Maag's equation:

$$k = \frac{R_0}{4T} \ln \frac{ht_1}{ht_2} \tag{21}$$

which gives the permeability of a soil in terms of the drop of the water level in a well projecting into the ground water table. The meaning of the symbols is shown in Figure 8.

While this method is cheaper and quicker than the previous one, it naturally allows the determination of the permeability only in the vicinity of the well. In contrast, the previous method allowed the determination of the over-all permeability of a relatively large area.

In summary it may be stated that much is still to be learned regarding the factors

which influence the permeability of soils for water transport under pressure potentials. Particularly, the influence of soil aggregation and structure and the influence of the surface forces are yet little understood. Because of the large numbers of variables, the problem is a rather complex one. In this area there still is a wide field for future investigations and it is hoped that these questions will be resolved in due time.

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Some Concepts Pertaining to the Freezing Soil Systems

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Introductory Remarks by the Chairman

Aristotle wrote about the necessity for stopping once in a while and looking over the path traversed or the material or mental possessions accumulated. This necessity of stopping and looking is especially important if one deals with complex systems and phenomena. Professor Jumikis, who has worked long and intensively on the frost problem in soils, is taking such a stop and is relating what he sees from the perspective of his own research in this field and that of others. The situation is indeed complex, but it is a system and not chaos; and while the intertwining and coupling of many processes occurring simultaneously in the system can as yet be traced only qualitatively, such tracing is the first step toward ultimate clarification of the picture and the desired quantitative treatment of the processes involved. We are grateful to Dr. Jumikis that he has taken the time to stop and look.

● THIS ARTICLE pertains to the subject of soil thermodynamics. In preparing it the author tried to give proper emphasis to some of the important concepts and processes which take place in a soil system upon freezing. Basic physical concepts such as the process, the system, primary and induced potentials, and some modes of possible soil moisture transport in a freezing soil system are presented.

The contents of this article are intended primarily as a guide for those who are not yet familiar with the various physical concepts used in engineering soil thermodynamics in connection with frost action research. However, it is hoped that it may also be of some benefit to others interested in this subject as review material; that it may assist in the consolidation of the framework of engineering soil thermodynamics as a scientific and technological method; and that it will stimulate constructive discussion concerning a subject of great importance.

NEED AND PURPOSE FOR RESEARCH IN FROST ACTION IN SOILS

Purpose

The purpose of frost action research in soils is to study the interrelationships of the various factors involved in damaging roads by frost in interaction with soil moisture, and how to combat effectively frost in highway engineering. As the amount of theoretical and experimental facts gained in frost action research increases in volume, there arises a need for generalization and consolidation of the knowledge, as well as for a generalized review on this subject. It is believed that such a review can be accomplished briefly by presenting a description of some fundamental concepts pertaining to the freezing soil system. It is also hoped that the generalization, although picturing an ideal condition, will differ but little from the real, natural conditions.

Effects of Freezing upon Soil

Freezing causes the soil moisture to translocate from warm regions to the cold ones. The freezing process in soil and the heat and moisture transfer in soil induced by freezing are very complex phenomena. Indeed, some of the processes which take place upon and during freezing of a soil system are not yet well understood, or are even unknown.

Observations, experiments and studies show that a variation in any one of the factors partaking in the soil freezing process influence to a greater or lesser extent the other factors, such as the properties of soil, water and ice. This is to say that the whole system "soil-water-temperature" is influenced by the application of a freezing thermal potential. In other words, energy in the form of heat is applied to or abstracted from this system. This implies that, because of the variation in properties effectuated by temperature and moisture in it, soil is a difficult engineering material to deal with and to study, particularly when subjected to freezing temperatures.

Methods of Study

Because the soil freezing problem in highway technology in the United States and elsewhere is of national importance, much effort is being spent at the present time and much more is still to be spent in trying to solve several problems. These involve an attempt to learn and understand the basic phenomena relative to frost action in soils and to use several lines of attack and methodology in attacking these problems. Some engineers and scientists pay more attention to the interior of the freezing soil system; some others—for reasons that will be pointed out later—study the freezing soil system in its entirety, evaluating the performance of the freezing soil system by its total net end result.

Work done hitherto by other authors and by the author of this article reveals that the studies of the interior, or the details, of the freezing soil system are very difficult and complex. This is partly because of the many factors involved, and partly because of the many independently or mutually interacting processes these factors induce when subjected to thermal potentials. For example, an effort was made to solve many problems relating to the details of the interior of the soil system strictly by means of thermodynamics alone. But, although very useful in many ways, by its very nature thermodynamics ignores the internal structures of the system. However, thermodynamics permits the treatment of the freezing soil system in its entirety, between the entrance of energy and its exit of the system, giving a net end result which then can be evaluated practically. Of course, the processes which take place in the interior of the freezing soil system are then masked out, but they are there.

To understand the soil freezing process, it is, of course, necessary to understand each of the partial processes and their effects on the total end result. Algebraic summation of the results of the singular processes should give a check for, or balance out, the total net performance of the entire system. These are then the primary reasons why the details of the interior of the freezing soil system, as well as the total performance of the entire freezing system should be studied. This detailed knowledge will then be basic for practical application in highway and airport engineering. It seems now that the unknown and obscured factors and their associated processes in a freezing soil outnumber the known ones. And this, in its turn, challenges the studies and justifies the efforts in pursuing frost action research in soils to learn all the factors and processes involved, and to understand more fully the freezing phenomenon as a whole.

Need for Experimental Studies of Frost Action Research

There are certain things which can be studied theoretically within the scope of a frost action research program. However, because of the complexity of the system "soil-water-temperature, " and because of the even more complex factors in the freezing process involved as well as induced, there exists a great need for their experimental elucidation. Judging from the amount and variety of the experimental work that has been done so far, and from the published results on the various phases of frost action research, one gets the impression that such studies have now received a great impetus, and that some day the "grain by grain efforts" will fit together nicely, giving the engineering profession a framework so necessary in dealing with freezing soils. The knowledge of the performance of a soil system under freezing conditions in its entirety is necessary in designing and constructing highways, airports and other earthworks. The knowledge of the details of the interior of a freezing system, however, is an absolute necessity if frost in highway soils is to be combated effectively.

Until more definite knowledge becomes available as to what actually happens inside the freezing soil system in detail, and what are the various reasons and causes for a factor or process, or for changes in properties of the soil matter (soil, moisture, ice, air or gas) under freezing conditions, the author is at present trying primarily to detect the end result on soil caused by a freezing thermal potential as a driving energy for the upward transfer of soil moisture from the ground-water to the freezing ice lenses.

CONCEPTS

Process

A process is here defined as any event in nature and in the laboratory soil freezing experiment in which a redistribution of energy (heat energy), and moisture transport takes place.

In order to transfer moisture between two points within the soil system there is needed a driving pressure, or more generally, a potential difference between these two points, for example, entrance and exit of the system.

System

The soil system which is subjected to freezing for study purposes is a separated, free finite part of matter (imagine free body) such as the soil sample separated from its surroundings by its container and insulation material. Thus, the system is clearly defined by spatial boundaries. For a detailed description of a soil system and its surroundings see Jumikis (1). In the system changes in the state of matter (for instance water) and transfer of energy and mass, for example heat and water, respectively, upon freezing can be studied. The soil system to use in the experimental frost action research is an open one to correspond to the conditions as they prevail in nature. According to De Groot (2), an open system is one which can exchange matter as well as heat and energy and work with its surroundings. A closed system is one which cannot exchange matter, but can exchange heat, energy and work.

Referring to Margenau (3), "completely closed systems, however, are never found in nature . . .," although he admits that under certain circumstances closed systems can exist.

Potential

In engineering and in science, the term "potential" has many meanings. In some branches of science, such as in physics and the engineering sciences, this term, commonly used as an adjective, means "available." Thus, one speaks of potential energy or energy of state or position. In contradistinction, in soil science dealing with moisture migration in soil, and in thermal soil mechanics dealing with frost action in soils, the term "potential" is traditionally used as a substantive—for example, thermal potential, capillary potential, electric potential, concentration potentials (solvent, density, moisture potentials), gravity potentials, and other possible potentials. In this sense, "potential" at a point, or "potential difference" between two points of a freezing soil system would mean the energy, measured by work done, necessary to transfer a unit mass of soil moisture through the porous soil medium from a given position in reference to another particular point within the system, as for instance, from the ground-water table to the downward penetrating cold front, or any other coordinate point within the system. The potential as the energy or driving pressure for the moisture transport in soil, hence, must be capable of being expressed by means of a certain function from which the intensity of the driving pressure, and/or the velocity and amount of the upward-migrating soil moisture passing a horizontal cross-section of the system in question at any point can be mathematically defined. From this, one immediately realizes that in the evaluation of frost penetration depths, where it is necessary to know the rate of the upward flow of soil moisture (4), the latter must be expressed as a well-defined function of the driving pressure if quantitative results in frost action research are to be obtained. It is to be remembered that among the many
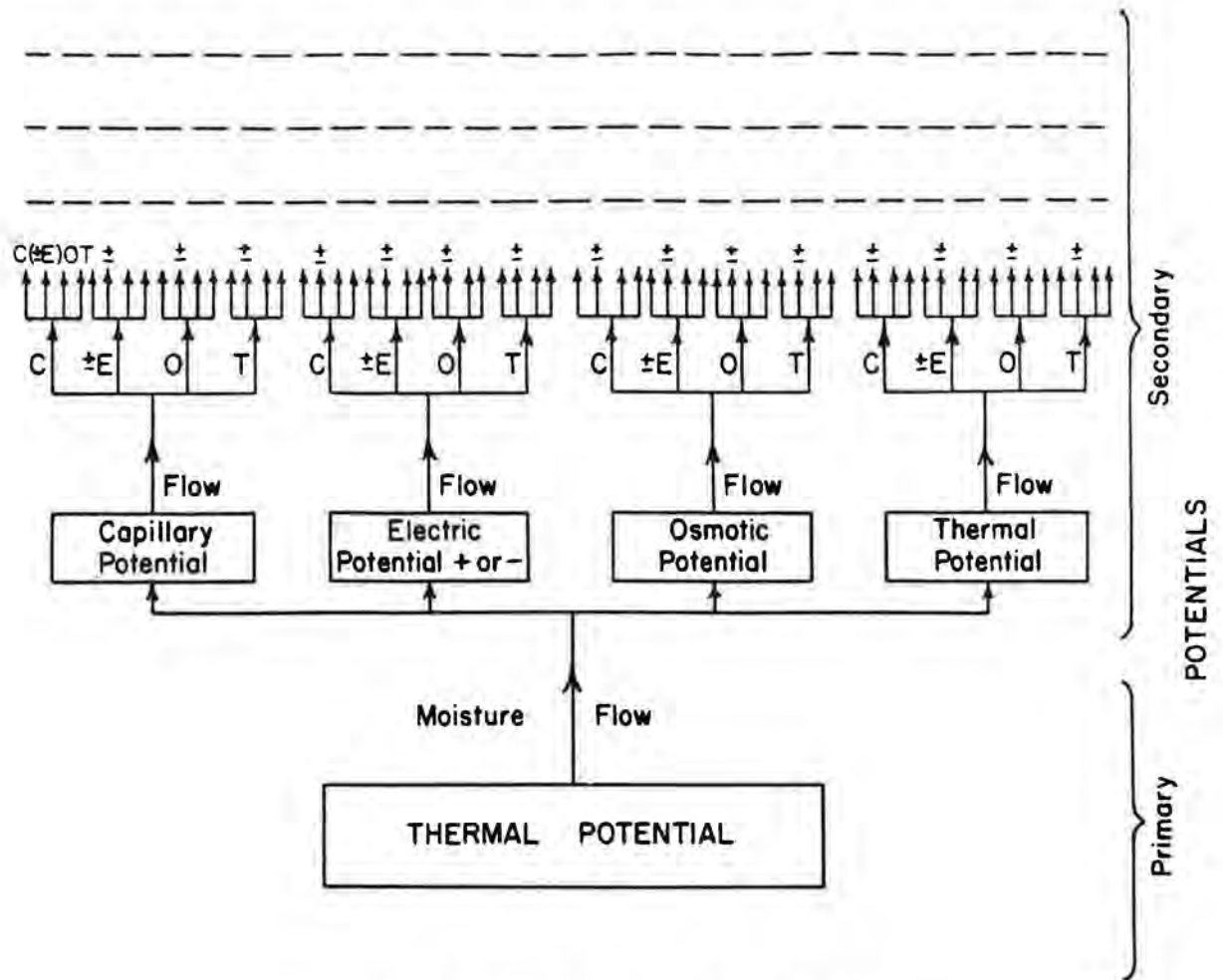
Figure 1. Primary and secondary potentials.

factors, temperature and position (coordinates) of the points between which the pressure difference is to be measured, are of very great importance. Sometimes the driving pressure is also termed the driving force, pressure deficiency (relative to atmospheric pressure), subatmospheric pressure, soil suction, suction pressure, soil moisture tension, capillary tension and suction force. Because of the negative characteristic of the capillary water suspended at its meniscus (negative pressure or tension), the stress in the capillary water is called suction pressure, pressure deficiency, soil moisture tension, and other terms as above. Now, the tension of the soil moisture is not just an externally applied constant like that which can be produced, for example, by means of Beskow's capillarimeter, which is of the hydraulic type and can be operated with water or mercury (5). On the contrary, the moisture tension is an intrinsic property of the soil system. This property, in its turn, depends upon the mutual affinity of the water to the surfaces of the solid soil particles, or rather to the adsorbed, static or immobile, stressed moisture films around the soil particles. Quantitatively, thus, the soil moisture tension would manifest the total joint and net action of all the system's internal forces in displacing an elementary or differential volume of soil moisture.

The energy potential is a simple concept and easily applied in studying freezing soil systems.

Classification of Potentials

For the purpose of convenience and simplicity, the various potentials which might occur under varying conditions in the freezing soil system may be classified into two

broad groups as follows (6): (a) primary potentials, and (b) secondary, or induced potentials.

A primary potential is one applied externally to the system. For instance, a primary potential may be a thermal potential, an electrical potential (causing the phenomenon known as electro-osmosis), a gravity potential, and other possible potentials.

A secondary potential is one which is induced within the soil by an externally applied primary potential. Any primary potential may induce one or several secondary potentials as new processes or mechanisms for the translocation of soil moisture (7), such as new heat potentials, electric potentials, concentration potentials, .(moisture, soluble salts), but probably no gravity potentials. These conditions are illustrated in Figure 1. For example, a primary thermal potential may cause the change in soil moisture densities, which in their turn, may induce hydro-dynamic pressure differences. Or, a concentration gradient may induce an energy flow, which in its turn induces a temperature difference. Thermal potentials in a freezing soil system, according to the author's observation induce electric potentials. The magnitude of the induced electromotive force depends largely upon the strength of the concentration of the electrolyte (viz., soil moisture containing some amount of soluble salts) in the soil present. Induced electromotive forces in freezing soil systems composed of Dunellen soil (glacial outwash material) were measured in the laboratory by the author from 40 to 120 millivolts.

Induced potentials may act and contribute to moisture flow in the same direction as the flow which is caused by a primary potential, or it may act in the opposite direction, depending upon the properties of the porous material or membrane, and other factors still not clearly known (8). This reference source (8) contains also a note that the phenomenon of thermo-osmosis was discovered by Lippmann in 1907.

Hence, the net amount of the upward moisture transport in a soil system upon freezing, or the end result of the entire system, is an algebraic one. This once more points out the convenience of working with an entire thermal system. The effects of a secondary or induced potential are called by De Groot "cross-phenomena" or "cross-effects" (2, p. 2); De Groot, Winterkorn (9), and Bosworth (10) term the induced potentials also the "coupling effects."

It is here pertinent to note that the many terms now in circulation and used to designate one and the same thing (for instance the driving pressure, or the induced potentials, or many other descriptions) merely indicate that in the progress in frost action research in soils the point has been reached where revision, re-evaluation and coordination in the corresponding terminology is in order.

PREPARATION OF SYSTEM

Preparation

Before the freezing experiment, the soil sample must be prepared and the type of the system—open or closed—provided. The preparation consists of ascertaining the grading and weight of the dry soil, the density obtained by means of the standard compaction test at its optimum moisture content, determination of porosity of the soil packing and, in the case of an open system, permitting the soil sample to come into moisture equilibrium by taking in water from the "ground-water." Obviously, the soil sample is not fully saturated, but this condition would correspond very nearly to the field conditions which exist in the soil just before the freezing season sets in. This is in accord with Winterkorn's opinion that "for engineering purposes the most suitable type of test is one in which the soil system is permitted to saturate itself in capillary contact with free water" (meant ground-water) (11). By doing so, the adsorption process of soil moisture on the surfaces of the soil particles is already accomplished and the moisture films around the particles and the connecting of the ground-water table are established under natural conditions before the freezing of the soil system begins. Again, one should see that the soil system is prepared for the freezing experiment in such a way as to simulate natural field conditions as nearly as possible.

Depending upon the texture of the soil, the state of packing, the configuration, that is, geometry and surface topography of the soil particles, the voids within the soil
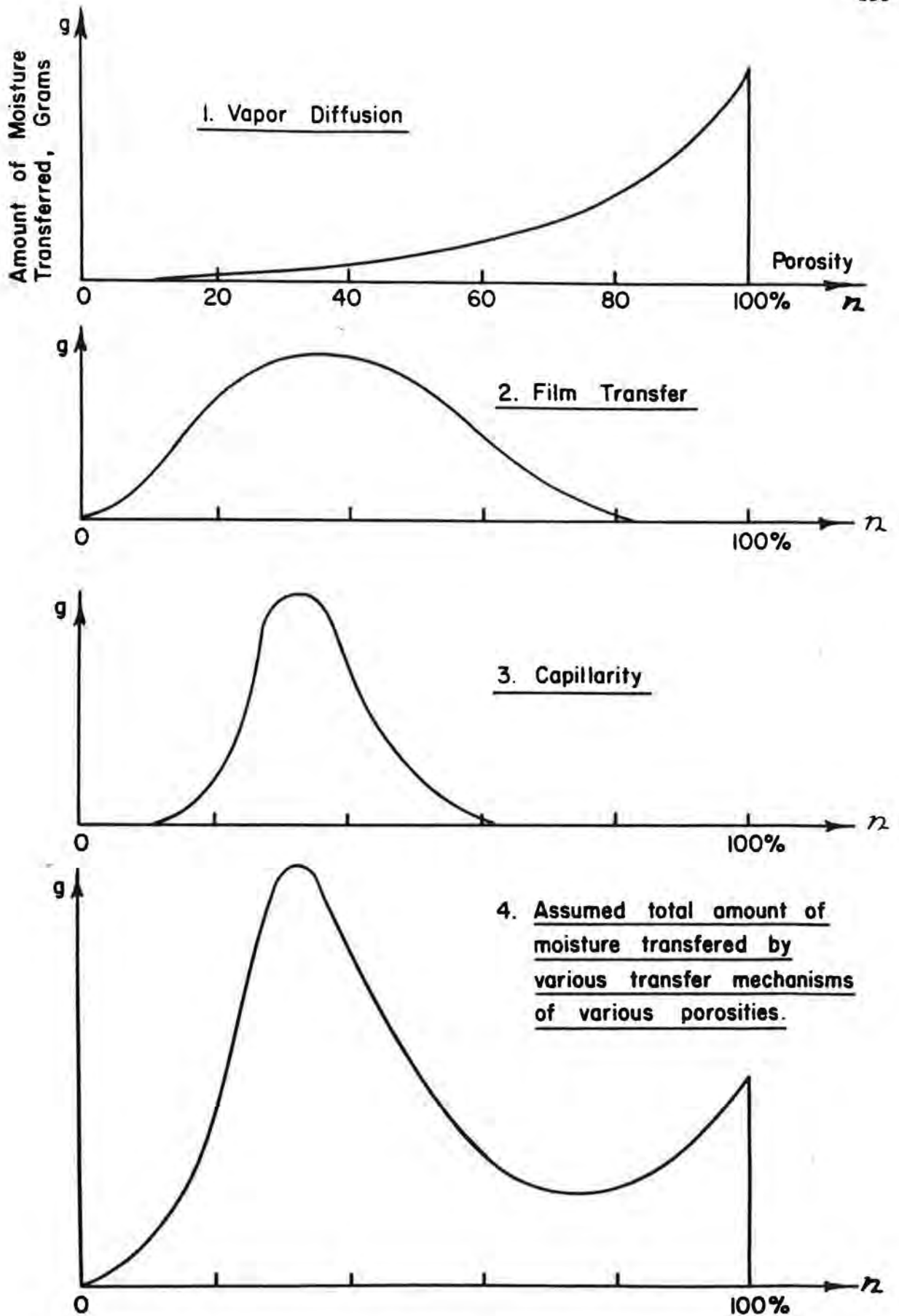
Figure 2. Various moisture transfer mechanisms and their assumed effects on the amounts of moisture transferred.

system form interconnecting channels of various sizes, shapes, and roughness for the passage of moisture and air. Thus, the soil moisture flows upward through poorly defined flow paths in a zig zag-like motion, also dispersing sideways through the constrictions of the void network.

Packing

The degree of packing is very important to know and to report, as this gives a clue as to what kind of mechanism in the upward soil moisture transfer in the freezing system would be most likely to take place: film flow, film-capillary flow, film-vapor flow or pure vapor flow (6). These conditions are illustrated in Figure 2. Under certain conditions, however, a combination of all the afore-mentioned moisture transfer mechanisms may take place simultaneously, depending upon the changing temperature and vapor pressure conditions, or the type of electrolyte present, the freezing soil and the distribution of the variously sized voids.

A pure capillary moisture flow (capillary water in direct contact with the bare surfaces of soil particles) within a soil medium is in all probability to be ruled out because it is difficult to imagine such an ideal porous medium, which usually consists of voids of various shapes and sizes, where absolutely all voids would be filled with water. In a capillary system, there whould be no discontinuities in the system of capillary water channels and passages. According to capillary

Figure 3. Instruments attached to the soil system: P - pressure measuring devices, H - frost heave measuring devices, T - temperature measuring devices, E - electrodes for measuring induced electric potentials, and G - connection to ground-water supply.

theory, all voids should be fully saturated with soil moisture at every point between the ground-water table and the freezing ice lenses. If there are plugs or air gaps, or bubbles of gas in these flow channels, and yet upward supply of soil moisture is observed, then the flow is not a pure capillary one, but takes place by way of other mechanisms: film, film-vapor transfer, or pure vapor diffusion, or in combination with capillary flow. Since the soil particles in the soil are in a humid environment, they are already, before freezing more or less coated with a moisture film. If the porosity of the soil is such as to give rise to capillary moisture transfer, and all void-channels are filled with water, then the capillary moisture flows through channels, the walls of which are covered with film moisture. In other words, the capillary water would not touch the bare surfaces of the soil particles directly. In such an instance a combined flow, namely film-capillary upward flow of soil moisture upon freezing, would take place, the velocity of the capillary flow being then greater than that of the stressed film on the surfaces of the soil particles. Simple as these conditions can be imagined to be, there is, however, a quite good agreement among engineers and scientists that up to now the various modes of mechanisms of the upward migration of soil moisture upon freezing are not, unfortunately, yet fully understood, and that much study is still to be devoted to elucidate these processes.

After the films are established within the soil system, the instruments are attached to the soil system for the measurement of temperature within the soil and its environ-

ment, driving pressure differences, electromotive forces, consumed supply of ground-water during freezing, and for the measurement of frost heaves (Fig. 3). The soil system is insulated laterally and finally subjected to freezing from its top downwards (Fig. 4).

FREEZING THE SOIL SYSTEM

Application of Thermal Gradient

After the soil system has been prepared and laterally insulated against transverse flux of heat, it is subjected to freezing. Freezing is accomplished by applying cold to the upper horizontal surface of the vertical soil cylinder, the lower end of which is inserted in a water bath (T = 8C) to simulate the source of ground-water or perched ground-water. Upon freezing the upper part of the soil system, after releasing the latent heat of the soil water, freezes, that is. changes phase from liquid to solid, and, in general, temperature change takes place within the system. This means that across the soil system, from top down, a curvilinear temperature gradient is set up. If so, then an upward heat transfer from a region of higher temperature in the soil system (ground-water) towards a region of colder temperature (frozen layer of soil) takes place. Thus, the application of a thermal gradient to the soil system means that heat energy is applied to the system. The source of heat, after full establishment of the thermal gradient, is the ground-water in the soil freezing experiment as well as in the field in winter. The soil receives its heat from the radiation of the sun and also partly by the conduction from the interior of the earth. The heat, as has been said, flows upward in such a soil system as is dealt with here. The transfer of the thermal energy in its turn, starts the upward migration of moisture in the porous soil system (12). During the course of the upward migration, the flowing water loses some of its driving
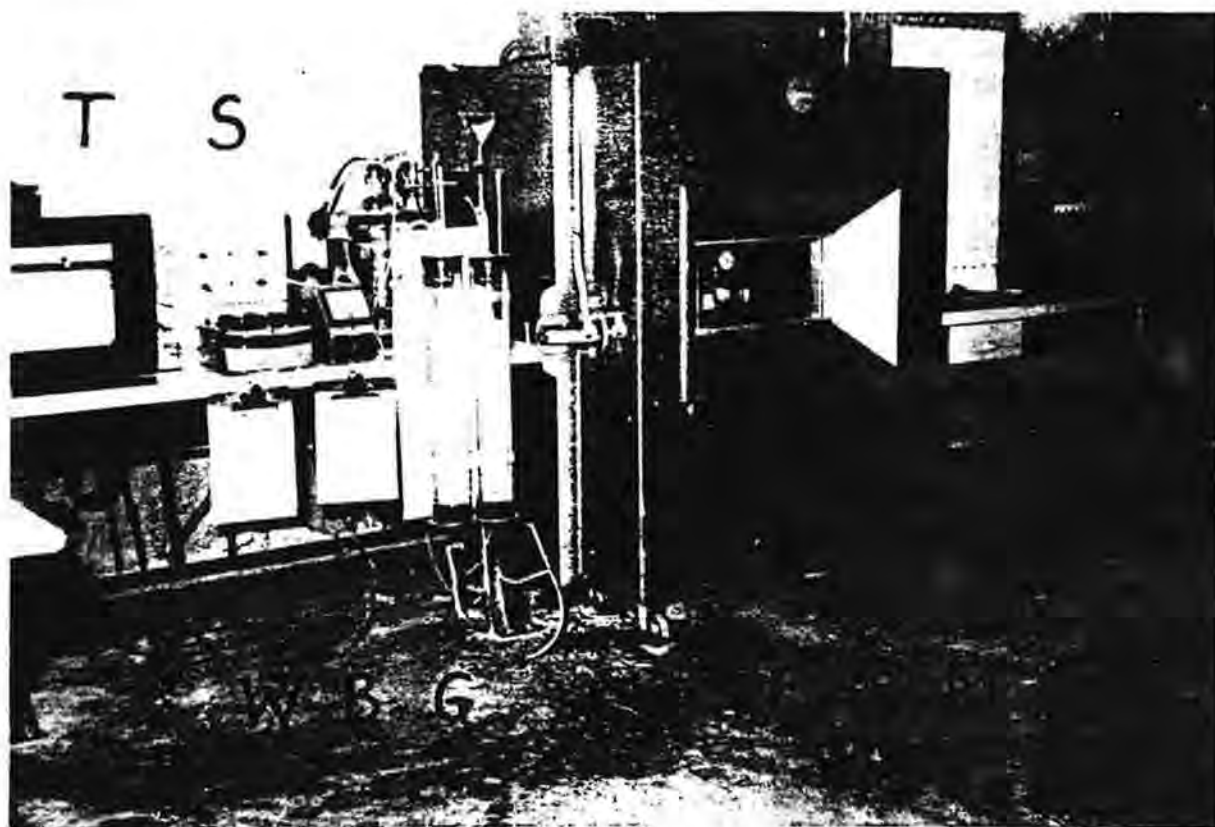
Figure 4. The soil system is subjected to freezing in a freezing chamber. T - temperature recorder; S - switches; W - Wheatstone bridge; B - bridge balancing apparatus; G - devices for maintaining constant ground-water level, and for measuring the amount of ground-water supplied to the freezing soil system; F - freezing chamber; M - manometer board; and P - pressure recorder.

pressure. This means that the driving pressure performs some mechanical work which becomes lost. In doing external, over-all work, the entire soil system loses some of its energy, so that the system in nature does not work with 100 percent efficiency. Here it has to be said that depending upon the state of packing, the soil moisture may first undercool, and then freeze.

During the freezing process in soil a good many other changes than those outlined take place, namely, changes in thermal properties of the various matters present in soil, undercooling of water (in proper environment), change in density and viscosity of water, change in the dielectric constant of water, changes in the structure of the double layer around the soil particles. The resulting frost heaves, frost penetration depth and thawing of the frozen soil are also changes within the soil ultimately contributing to the damage to roads.

SOME PRINCIPAL MODES OF MOISTURE TRANSPORT UPON FREEZING

Basically, soil moisture can be transported upward through the porous medium of soil upon freezing (a) as a liquid (bulk or film), (b) as a vapor, or (c) as liquid and vapor.

Vapor Transport

If the voids are relatively large, and there is no continuous moisture in the liquid form in the voids connecting the ground-water with the downward freezing ice lenses, the moisture from the ground-water is transported upward by way of vapor diffusion. The driving pressure is here the vapor pressure difference between the partial vapor pressure at the warmer end (the free water surface = ground-water table) and the partial vapor pressure in the upper region of the soil system just below the frozen ice where it can be very small, or even negligible as compared with that at the free surface (13). This is to say that moisture migration takes place in the direction along the drop of the thermal gradient. The vapor pressure decreases from the ground-water table up to the freezing isothermal surface.

Vapor diffusion in soil upon freezing along soil particles coated with film moisture is difficult to comprehend analytically because of the difficulty in expressing mathematically by an equation the geometry of the voids of the system or the surface topography of the soil particles.

If soil is fully saturated with water, the moisture migration cannot take place in the vapor phase. If the packing of the soil is very dense, moisture transfer in the vapor phase is ineffective.

If there is no ground-water present (approximately a closed system), the soil freezing is then a drying process until all of the soil moisture has been transferred into the freezing zone.

Film-Capillary Transport

The moisture migration process determines the moisture distribution in soil, and thereby the so-called drying out of the soil. Upon this the thermal properties (heat conductivity, viz., diffusivity) of the moist soil change, and the frost line penetrates deeper into the soil.

If the state of packing is such that the soil moisture can occupy absolutely all voids, then, upon freezing, an upward motion of film-capillary soil moisture from the ground-water table takes place. Because of the temperature difference between the warmer ground-water and the downward freezing isothermal surface, the driving pressure for the upward-directed capillary moisture flow is again the difference in the vapor pressure at the free water surface and the one at the curved surfaces or menisci at the freezing ice lenses, plus the flow pressure (molecular, or viscous, or both) caused by molecular motion of the warmer particles of water from the ground-water upward toward the cold front. Under certain temperature conditions, and surface topography and configuration of soil particles and the ice lenses, the magnitude of the vapor pressure at the freezing isotherm might be negligible, or even non-existent (13, 14).

It has been reported that M. Faraday (1850) and J. Tyndall (1858) presented a theory which is plausible even today, in which it is assumed that ice is coated by a mobile, noncrystalline film of water which is stable even below the freezing point (15). The surface film on ice represents a gradual transition layer from the rigid structure of the bulk of the ice crystal to the double layer of soil moisture on the surfaces of the soil particles.

Nakaya and Matsumoto (16) performed experiments on the adhesive force between two ice particles and observed a phenomenon which seems to show the existence of a liquid water film around two small ice spheres. This liquid-water film is not super-cooled water but is in equilibrium with its vapor phase on one side and with the ice crystal on the other.

To continue the discussion on film-capillary transport, it is assumed that the ice lenses are connected via the ice water films and further via the soil moisture films and capillary moisture (where such exists) with the ground-water (1). In such a case the film-capillary water supply to the freezing ice lenses is secured uninterrupted. Because the capillary water is less stressed by molecular forces attractive to the soil particles than the films surrounding the particle, the capillary moisture transport mechanism seems to be more effective in the combined film-capillary flow than the moisture transport via the capillary moisture and films surrounding, viz., separating the soil particle. One remembers that stressed film water has properties different from those of moisture in bulk.

Film Transport

In a very dense, close packing of soil (for which there is a theoretical and practical limit), where the soil particles are packed so close to each other (small porosity) that the moisture around and between the soil particles forms uninterrupted liquid films through the entire soil system down to the ground-water supply, then, depending upon the texture of the soil (whether silt, silty clay, clayey silt, or clay) the film transport mechanism becomes more effective than the capillary one (Fig. 2). The moisture transport in the vapor phase is then very ineffective as compared with the movement of liquid. Of course, the process of the upward moisture migration via the films in the freezing soil is slow. However, a considerable amount of soil moisture can flow from the ground-water upward during a relatively long period of time, for example, during the winter months. It is the slow flow process indeed, which often is overlooked and forgotten, and which contributes to the danger of damage to highways and runways.

In the film transport mechanism, the ice lenses are thus connected via the moisture film at the ice surface and via the soil moisture films with the source of ground-water supply. The driving pressure is the pressure difference between two points under consideration effected by thermo-viscuous flow of the film moisture plus possible other potentials. These may be differences in density of moisture at different temperatures, concentration differences in electrolyte at different elevations in the soil column (temperature), induced secondary electrical potentials effecting additional flow of soil moisture up or down, depending upon the properties of the porous material, and other possible conditions. The film seems to be two-dimensional, that is, it is immobile perpendicular to the surface of soil particle, but is mobile parallel to the surface. The movement of the film moisture is hence a slip, by overcoming the shearing resistance of the liquid.

The amount of moisture transferred by means of film flow, it can be understood, is proportional, among other things, to the specific surface area of the soil particles in a unit of volume. The increase in density of the soil means more soil particles packed within a unit of volume, which in its turn means more specific surface, more moisture films, and consequently more film moisture transferred.

Combination of Various Modes of Transport

Depending upon the texture and gradation of the soil, and the degree of the packing, or the presence of a multi-layered soil-system, a combination of the various soil moisture transport mechanisms may exist simultaneously upon freezing. For example,

with large porosities, it is more likely that upward soil moisture transport in the vapor phase will be more effective than a film flow. In a densely packed clayey silt or silty clay the film transport mechanisms will be more effective than vapor flow. Between the maximum possible and minimum possible densities, and for different textures of soil, and in various combinations, other than gravel and clay, several upward soil moisture transport mechanisms, and in various proportions may set in. There are no sharply defined boundaries between the various modes of transport mechanisms and processes. It is quite reasonable to assume, rather, that a transition from one mode to another constitutes the combination of the simultaneously acting various modes of transport. One deduces that in reporting research results on moisture transfer in soils upon freezing, it is essential to report also the porosity of the soil, because for each degree of packing there may be a different moisture transport mechanism in action.

ICE SEGREGATION

The amount of segregated ice in a frozen soil system (number, thickness and distribution of visible ice layers or lenses) depends very much upon the intensity and rate of freezing. When the soil system is frozen quickly, say 8 in. frost penetration in three days at a temperature difference between surface and ground-water of 45 F, no ice layers are visible. The whole soil sample may be frozen through solid. Upon splitting the soil sample longitudinally immediately after the test, examination of the frozen sample by eye or with the aid of a magnifying glass does not reveal any ice segregation in layers, although the moisture content in the soil after the freezing test is larger than before the test, and the moisture content is larger at the ends of the soil cylinder than at its midheight. Slow freezing, on the contrary, brings about clearly visible ice layers of various thicknesses, for example from one-half of a millimeter to about 12 millimeters in thickness. If there are layers in the soil with layered voids or with air gaps, and combination of moisture transport mechanisms are active, segregated ice layers of about 4 in. in solid thickness are observed at midheight of a 12 in. high cylindrical soil sample.

Ice segregation in soil takes place also under cyclic freezing and thawing conditions when the thawed ice waters freeze again. This also occurs when the frozen soil thaws from the bottom and then the thawed section freezes again. This can happen when the freezing surface temperature on the top of the soil sample remains constant for several days (thus, frost would not penetrate deeper than its established position, but the temperature of the ground-water increases for one or another reason to such an extent that the upward flowing soil moisture can thaw the frozen soil from below).

Of course, ice segregation is influenced by differing thermal properties of the soil material and by the various types of soil moisture and electrolyte, as well as the ice in soil, or rather the properties of the frozen soil itself. Heat conduction through unfrozen and frozen soil particles is different from that through unfrozen water, chilled water and ice. Thus, ice lenses develop in the downward freezing soil in jump-wise layers, leaving unfrozen water between two separately spaced ice lenses. This phenomenon is analogous to the rhythmic precipitation of the Liesegang Rings as brought out by Winterkorn (17). Hence, in a frozen soil there may be ice as well as unfrozen water at the same time. As the temperature conditions may change to the negative, some of the unfrozen water may also freeze as time passes or the frost intensity increases.

CONCLUSIONS

Soil systems are most difficult to treat where various modes of upward soil moisture transport are active. Such systems, however, are encountered very frequently in nature and, although the heights of the upward transported soil moisture in such systems may not be large, they cause enough trouble relative to the performance of roads to become of real concern, and to warrant the effort to do something about them.

Study of the freezing soil system in its entirety and of the net end result of the performance of the entire system by means of the energy concept is thus seen to

be very advantageous for its simplicity and practical application, particularly as related to combined moisture transport mechanisms. This method comprehends all the factors and potentials—although some of them may be masked out—which might contribute to the net amount of the upward flow of soil moisture upon freezing and the total performance of the soil system. Any flow in the system is the result of all of the contributing factors. And, because the soil system in nature does not work with 100 percent efficiency, it is most appropriate that such freezing soil systems be studied experimentally.

This review of the various concepts used in the soil freezing experiment and the many factors with their associated and induced processes strengthens and consolidates the theory on the freezing soil system, and indicates that much frost action research is to be done along many lines and in all phases.

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Pressures Developed in a Porous Granular System as a Result of Ice Segregation

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Introductory Remarks by the Chairman

The great French mathematician and philosopher, Poincaré, has pointed out on a number of occasions that even in mathematics true pioneering advance is usually made by the geometric and intuitive mind. This advance is subsequently rendered "secure" for science by the analyst or logician. Unfortunately, as Poincare also points out, this "securing" by the logician may often be likened to building a complicated scaffold around the simple intuitive creation, obscuring its beautiful lines and diminishing also its inspiratory power for further intuitive creation. In the present age, scientific and engineering education is becoming more and more analytical with the deplorable result that present college curricula often deprive engineering students of an opportunity to develop geometric and intuitive creative thinking. It is hoped that the fine example of geometrical thinking shown in the paper by Edward Penner and in other important contributions to this symposium will help to restore the needed balance between geometrical and analytical approach not only in this field, but also in other areas of engineering science.

● FROST ACTION in soils has been studied for a number of years by the Division of Building Research with a view to developing more adequate frost action criteria for soils engineering in regions of seasonal frost. The normal pattern of events that leads to the destruction of roads and airports is heaving of the soil when it freezes and loss of supporting strength when it thaws. The displacement of shallow foundations and the damage to cold storage warehouses due to frost action normally involves only the frost heaving aspect, the loss of supporting strength being of little consequence.

The expansion of water when it freezes accounts for a small fraction of the total heave. Although this in itself may be particularly destructive in many building materials, a large percentage of the displacement in soils is rightfully attributed to the formation of ice lenses at the freezing plane. The flow of moisture is normally assumed to be largely in the liquid phase under the influence of a so-called "suction" gradient. As a consequence, the development of this suction at the ice/water interface is the most essential element in the mechanism of frost heaving since it must precede and continue during the growth of ice lenses. In a closed system the suction increases to a maximum when ice lensing stops.

Recent experiments by the author (1) showed that the magnitude of the suction (soil moisture tension) at the ice/water interface, when the growth of the ice lens stops, depends upon the dimensions of the pore system in the soil. Such measurements were made in the absence of any appreciable external pressure on the ice phase which, however, exists in nature and its effect is therefore of significance in the formation of ice lenses. This paper gives the experimentally determined relationships between overburden pressures and the magnitude of the soil moisture tension when the ice lens growth has decreased to zero, that is, under equilibrium conditions. Some thermodynamic aspects of the freezing of moist soils have been described by Edlefsen and Anderson (2) and the ice lensing system has been described by Winterkorn (3), Powers (4), and Gold (5). Based on somewhat similar treatment the mechanism of ice lensing is discussed in the light of the experimental results.

EXPERIMENTAL

Material and Specimen Preparation

The granular system used consisted of powdered quartz known in the ceramic industry as potter's flint. The grain-size distribution based on the hydrometer analysis is given in Figure 1. Selection of this material was on the basis of chemical purity and fineness.

The specimens were prepared at various densities in a Harvard Miniature Compaction Apparatus by controlling the moisture content and compactive effort. The dimensions of the specimens were $1^5/_{16}$ in. in diameter and approximately 3 in. long. In preparation for compaction, uniform moisture distribution was attained by applying water with a fine spray and subsequently storing the material in a sealed polythene bag. Uniformity of moisture content was ascertained by sampling and determining the moisture content at various locations in the moist material.

After molding in the compaction apparatus in $1/_4$-in. layers the specimens were

Figure 1. The grain-size distribution of the potter's flint used in these experiments.

oven-dried at 105 C. Upon placement in the sample holder of the frost cell (Fig. 2) almost perfect saturation was achieved by permitting de-aired water to enter the specimen at the base and to spread unidirectionally. When the saturation of the specimen was complete the external source of water was cut off (closed system). Using this method of preparation the specimens showed no tendency to swell when saturated or shrink when desaturated. The specimens also had sufficient strength to resist deformation at the overburden pressures used in the freezing experiments. It may be noted here that the sample holder of the frost cell was designed to accommodate specimens prepared in the Harvard compaction apparatus.

Method of Freezing

The specimens were frozen unidirectionally, similar to the freezing of soils in nature. Antifreeze mixtures were circulated in the outer compartments of the frost cell to control the temperature of the specimen. In the bottom two compartments the circulating fluid was maintained at $+1\frac{1}{2}$ C. The temperature of the fluid circulating through the top compartment was -3 C. The variation in temperature was approximately ± 0.05 C in the conditioning fluid but was a small fraction of this within the specimen. Temperature measurements were made with a specially built, high precision millivolt recorder, using copper-constantan thermocouples. To avoid any disturbance in the material after preparation thermocouples were placed so that they would not coincide with the location of the equilibrium ice/water interface.

The method of freezing was first to temperature condition the lower end of the saturated specimen to $+1\frac{1}{2}$ C and then start the circulation of the -3 C fluid. This would freeze the specimen unidirectionally from the top, leaving at the completion of the experiment approximately 2 in. of unfrozen material beneath the ice lens. Ice crystallization was mechanically induced at about 2 C of supercooling. Greased lucite rings were provided around the specimen to reduce the side friction caused by heaving. It must also be emphasized that the freezing of the specimens did not comprise of a gradual lowering of temperature of the conditioning fluid. No further changes in the temperature were imposed on the specimen after the -3 C conditioning fluid was introduced.
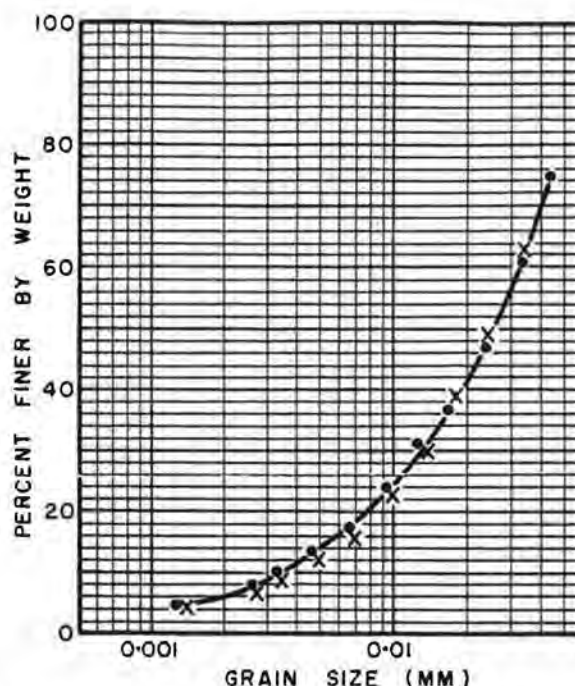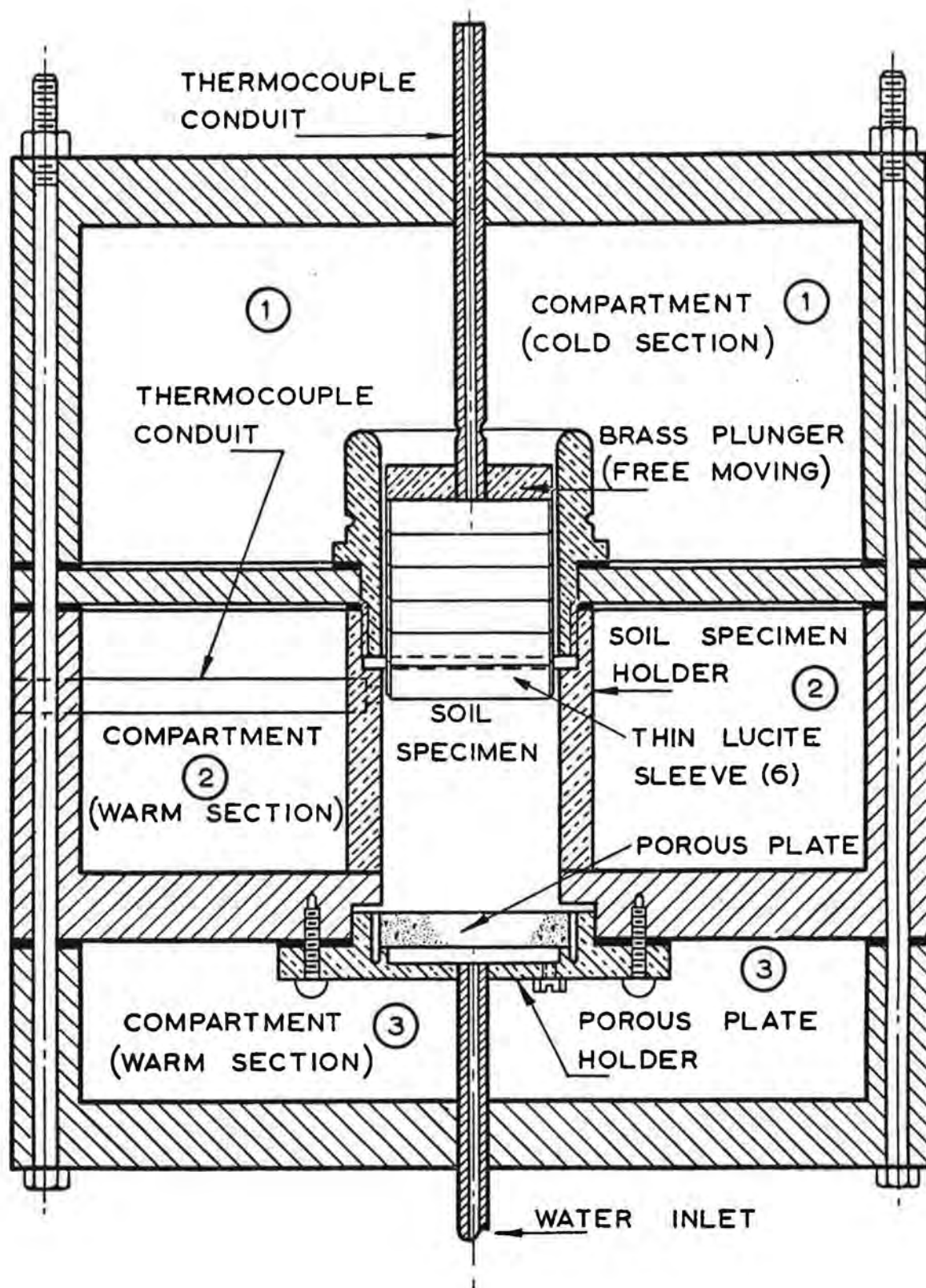
Figure 2. Section through frost cell.

Soil Moisture Tension Measurements and the Application of Positive Pressures

Heaving normally continued for several days depending largely on the overburden pressure. At the completion of heaving the unfrozen portion of the specimen was quickly removed from the frost cell and sliced in $\frac{1}{2}$ in. lengths for moisture content determinations.

Two methods were used to determine the soil moisture tension induced in the unfrozen portion of the soil due to ice lens growth. From separately determined moisture content/soil moisture tension curves the induced tension could be evaluated from the moisture contents of the unfrozen portion. More details of this method may be found in an earlier publication (1).

In the second method a mercury manometer with a water connection to the base of the unfrozen portion of the specimen was used to give continuous moisture tension readings throughout the experiment. This second method was considered superior to the first since it did not involve the separate determination of the moisture tension curve. It is also considerably more accurate in the region where the moisture content change is small with increasing tension. One drawback of the second method is that it is limited by a maximum of about one atmosphere of tension.

RESULTS

The maximum soil moisture tensions induced by the growth of the ice lens were determined for three different overburden pressures: 23, 229, and 535 gm per sq cm. The lowest overburden pressure used represents the weight of the plunger only and the highest pressure was low enough so that some ice segregation would be permitted. The freezing experiments were carried out with specimens prepared at various dry densities ranging from 1.592 to 1.750 gm per cu cm. When heaving ceased, the degree of saturation was calculated from the moisture contents of the unfrozen soil. The degree of saturation was plotted versus dry density for the three different overburden pressures as shown in Figure 3. The quantities beside the plotted points in the figure give the amount of water lost per 100 gm of unfrozen soil. Knowing the relationship between percent saturation and moisture tension (Fig. 4) the moisture tensions induced at various densities and overburden pressures could be determined. These data have been plotted in Figure 5, curves A, B, and C.

To determine in a more direct way the relationship between moisture tension and overburden pressure a further series of experiments was conducted using the same type of material. These experiments were similar to those already described with the exception that a mercury manometer was used to measure the moisture tension in the unfrozen soil. This permitted direct readings of tensions as the experiment progressed. The final moisture tensions at various overburden pressures are plotted in Figure 5, curve D. The results were similar to those obtained by the former method.

From the results shown in Figure 5 the equilibrium conditions with respect to overburden pressures and soil moisture tensions may be summarized as follows for the particular granular material used: (a) the maximum moisture tension induced in the unfrozen portion due to ice segregation decreases with increasing overburden pressures; (b) the greater the packing density of the granular material the higher the moisture tension induced
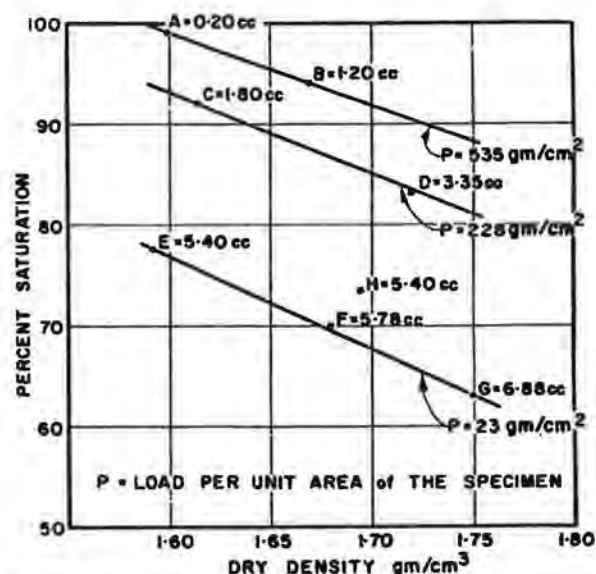
Figure 3. The relationship between dry density, overburden pressure and percent saturation beneath the freezing zone when heaving is reduced to zero in a closed system.

at the same overburden pressure; (c) frost heaving due to ice segregation can be limited either by the development of a sufficiently high moisture tension, by applying overburden pressures, or by a combination of both; and (d) expressed in gm per sq cm the limiting moisture tension is about half the limiting overburden pressure. (The overburden pressure was calculated in terms of load per unit area of the specimen.)

DISCUSSION OF THEORY

To facilitate the discussion a diagram (Fig. 6) has been constructed showing the relative position of the ice/water interface and ice lens with respect to the structure of the pore system.

The size of a stable spherical crystal of a solid in its own melt depends on temperature and may be expressed in the form used by Sill and Skapski (6). Using the subscripts i for ice and w for water:

Figure 4. The relationship between moisture tension and percent saturation.

$$\Delta T = \frac{2\,T\,\sigma_{iw}}{r\,\rho_i\,Q_f} \tag{1}$$

where:

r = radius of the crystal, cm
ρ_i = density of the ice, gm per cu cm
σ_{iw} = interfacial energy, ergs per sq cm
Q_f = latent heat of fusion, ergs per gm
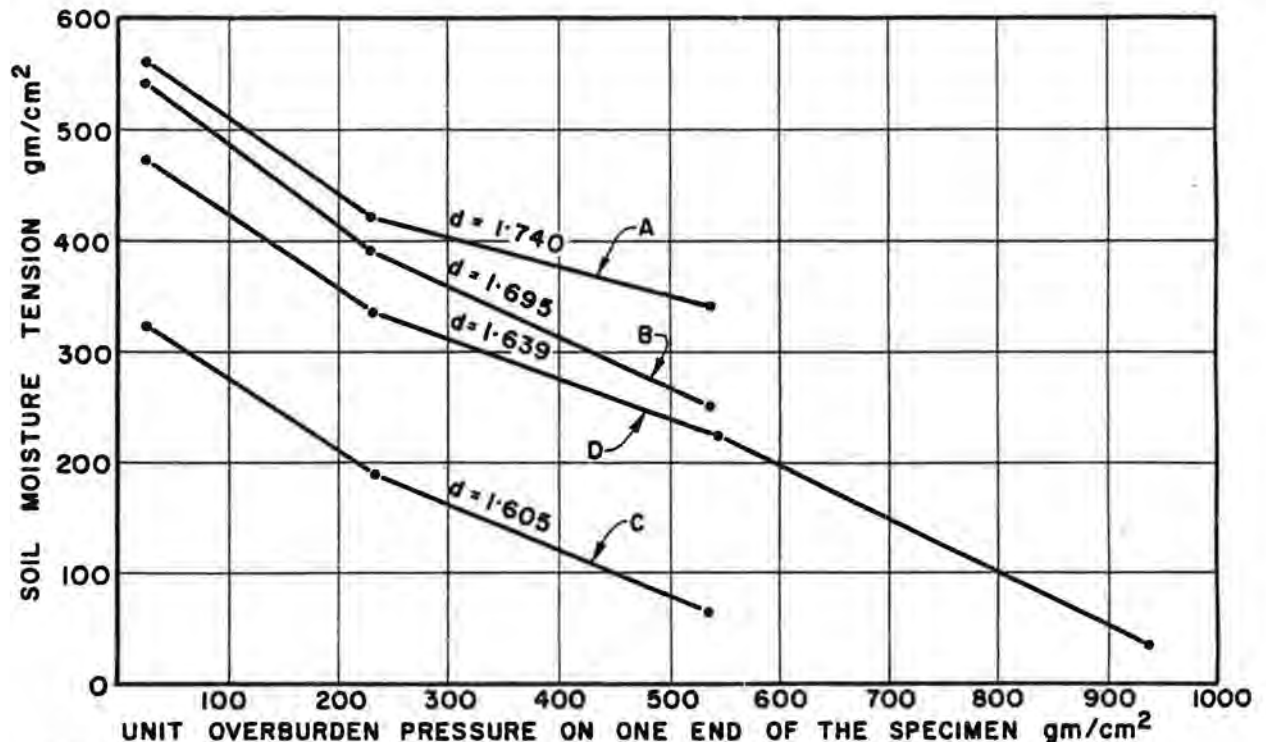
Figure 5. Relationship between soil moisture tension and overburden pressure when heaving ceased.

T = temperature of melting at zero curvature of the solid/liquid interface, K

ΔT = freezing point depression below T

Assuming that this relationship holds for the freezing of water in small spaces, it follows that the temperature at which ice will propagate through a soil depends on the pore dimensions. By freezing a saturated soil specimen unidirectionally the advance of the ice is impeded as predicted by Eq. 1. This mechanism is believed to bring about the freezing point depression of such a system but the reaction of all parts of the system to this is not the same and brings about the growth of ice phase which results in the phenomenon of ice lensing.

The conditions in a saturated salt-free porous system immediately after crystallization is induced are as follows: (a) the pressure in the pore water is zero and the adsorbed layer is essentially fully developed; (b) the overburden pressure is small, since the ice lens has just begun to grow; (c) the temperature along the ice/water interface
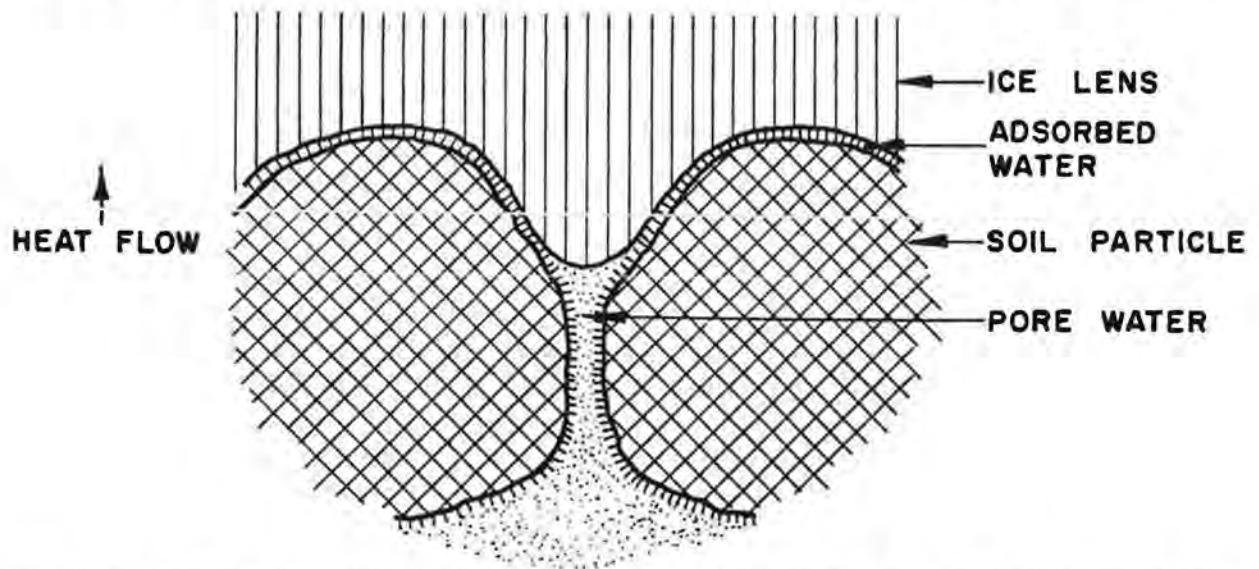
Figure 6. An enlarged schematic diagram showing a section of the ice lens with respect to the soil particle and soil pore.

is everywhere the same and has been lowered as predicted by Eq. 1.

In the pore the ice/water interface has assumed a critical radius and the rate of melting and freezing here is equal. Above the soil particle, however, the ice/water interface is either flat or has assumed a negative curvature. The freezing point of the water at the ice/water interface above the soil particle is close to that of free water, since the adsorbed phase is considered to be fully developed, but the freezing point of the pore water is given by Eq. 1. Consequently, the ice phase will grow above the soil particles at the expense of the adsorbed phase. If such a system is kept saturated, an external pressure must be applied to stop the growth of ice above the soil particles. To fix the thermodynamic equilibrium condition, two variables, in this case temperature and pressure, are considered simultaneously. If the two phases are to be in equilibrium the free energy of the ice must be equal to the free energy of the water, that is, $f_i = f_w$. This means that when any change occurs in the system the free energy of each phase changes by an equal amount: $df_i = df_w$. It follows that:

$$v_i \, dP_i - s_i \, dT = w_w \, dP_w - s_w \, dT$$

where:

v_i and v_w = specific volume of ice and water, respectively,

dP_i and dP_w = change in pressure on the ice and water, respectively,

s_i and s_w = specific entropy of the ice and water, respectively,

dT = freezing point depression below that of bulk water.

Rearranging the terms and dividing by dT:

$$\frac{v_W\, dP_W}{dT} - \frac{v_i\, dP_i}{dT} = s_W - s_i$$

Substituting $\frac{Q_f}{T}$ for $s_W - s_i$, where Q_f is the latent heat of fusion and considering finite changes, the expression becomes:

$$\frac{v_W\, \Delta P_W - v_i\, \Delta P_i}{\Delta T} = \frac{Q_f}{T} \tag{2}$$

Since the ice above the soil particle is postulated to be in direct contact with the adsorbed phase, any change in total pressure is felt equally by both the ice and water phases. As a consequence, $\Delta P_W = \Delta P_i$ and Eq. 2 in terms of the total pressure becomes:

$$\Delta P_i = \Delta P_W = \Delta P_{iW} = \frac{Q_f\, \Delta T}{T(v_W - v_i)} \tag{3}$$

ΔP_{iW} is the pressure required to bring about equilibrium expressed in terms of the freezing point depression. Eq. 3 predicts that for a freezing point depression, ΔP is positive, since Q_f is positive and the quantity $v_W - v_i$ is negative. The equation holds equally when ΔP is negative but in this case ΔT is positive.

Example 1. Ice Lensing Stopped with a Positive Pressure by Loading the Specimen

A sample calculation will illustrate the maximum pressure required to stop ice lens growth when the system remains saturated, assuming a pore radius r with a freezing temperature of -0.01 C compatible with Eq. 1. Substituting the following values into Eq. 3:

$$Q_f = (79.8)\ 4.184 \times 10^7 \text{ ergs per gm}$$
$$T = 273\text{ K}$$
$$v_W = 1.00 \text{ cu cm per gm}$$
$$v_i = 1.09 \text{ cu cm per gm}$$
$$\Delta T = -0.01 \text{ C}$$

gives a pressure of 1.356×10^6 dynes per sq cm. Applying this pressure to the system causes the temperature of freezing of the pore water and the ice/water interface above the soil particle to be equal.

Stating this in another way, before the pressure was applied to the ice/water interface the freezing point at that location was T_1 which, according to the moisture conditions imposed, was approximately 273 K. In the pore water the freezing point was T_2 as predicted by Eq. 1, so that $T_2 < T_1$. Since the influence of the pressure is not felt by the pore water T_2 does not change but T_1 decreases by an amount Δt with increasing P until $T_1 - \Delta t = T_2$. As a consequence there is no further tendency for the ice lens to grow.

In the above example the case has been considered where ice lensing is stopped by applying a positive pressure to the ice/water interface. This load is not transmitted to the pore water because the porous system is considered sufficiently rigid to resist deformation.

The growth of the lens can also be stopped by applying a suction to the water in the pore system. When suction is applied to the water in the system some of the larger pores may empty but the water in those that remain filled is under tension. At the same time the films of water that surround the individual particles decrease in thickness. Returning to Figure 6, applying a suction to the water has the effect of drawing the ice/water interface into the force field of the particle and can then be considered to be under compression. As a result of this pressure the temperature of freezing at the ice/water interface above the soil particle decreases as the soil grain is approached.

Eq. 3 predicts that the freezing point increases when water and ice together are placed under tension. As a consequence the water in a pore of size r which freezes normally as predicted by Eq. 1 now has a higher freezing temperature. The opposite

is true at a position above the soil particle because here the tension tends to draw the ice/water interface into the adsorptive field and the resulting pressure lowers the freezing point. The maximum tension is developed when the resulting freezing point of the pore water and the water at the ice/water interface above the soil particle are equal. If the influence of the tension were not considered to place the ice/water interface above the soil particle in a state of compression and thus lower its freezing point, one would arrive at the false conclusion from Eq. 3 that the tension necessary to stop ice lens growth would be numerically equal to the pressure given in Example 1. Restating this, in the case where ice lens growth is permitted to induce a tension in the pore water (closed system), the freezing point of the water at the ice/water interface above the soil particle and of the pore water are again T_1 and T_2, respectively, where $T_2 > T_1$. T_1 is approximately 273 K and T_2 is set by Eq. 1. As the tension increases in the pore water its freezing point increases to some value equal to $T_2 + \Delta t_2$. At the ice/water interface above the soil particle the freezing point decreases due to the reasons given above to some value equal to $T_1 - \Delta t_2$. When $T_2 + \Delta t_2 = T_1 - \Delta t_1$, no further ice growth can take place and describes the equilibrium condition. The case where $\Delta t_2 = \Delta t_1$, describes the situation where the positive pressure in the ice/water interface above the soil particle is equal to the tension in the pore water. In fact whether this is a special case or if equilibrium conditions arise where Δt_2 and Δt_1, are not equal but have values such that $T_2 + \Delta t_2 = T_1 - \Delta t_1$, is not known. In any case when $\Delta t_1 = \Delta t_2$ the theoretical magnitude of the maximum tension is one half that given in Example 1 for a sample of similar pore dimensions.

Curve D in Figure 5 shows that in a saturated system the external pressure required to stop ice lens growth is approximately twice as great as the tension when no external load is applied. Although this is supporting evidence it is still too limited to be accepted as complete confirmation of the theory.

There are two additional complicating features of the system which must also be considered. Firstly, the area of the ice/water interface is not known in the experimental determinations of pressure. Pressures are expressed in this paper as loads applied per unit area of sample. Secondly, a pressure applied at one point in the ice, for example, above the soil particle, is not fully transmitted to the section of the ice above the pore, in fact, it tends to decrease. It is thought that adjustments in the ice are accomplished by the ice assuming changes in the curvature and, consequently, in the internal pressure, both above the particle and above the pore. Further, a granular system which is heterogeneous with respect to particle size such as was used in these experiments adds to the complexity of the system, in particular because of the emptying of the larger pores as the moisture tension in the pore system is increased.

In spite of these uncertainties there is general agreement between the theory and experimental results. It follows from the theory that the maximum moisture tension or suction induced becomes less if any external overburden pressure is applied. This is also shown by the results in Figure 5.

If the freezing point depression in such systems is related to the dimensions of the pores compatible with Eq. 1 the maximum heaving pressures or the maximum soil moisture tensions induced should be greater if the density of the granular material is increased. The curves relating overburden pressures and corresponding moisture tensions determined experimentally fall in the order predicted by the theory. This was shown in another way in previous experiments with respect to soil texture and maximum moisture tension. In coarse-grained soil the moisture tension developed was much less than in fine-grained soils.

Experimentally, the limiting overburden pressure expressed in grams per unit area of sample is approximately double the limiting tension in curve D, Figure 5. Theoretically the magnitude of tension when ice lens growth stops can be shown to be less than the external pressure required when the system is kept saturated. Whether the 2 to 1 relationship shown in Figure 5 holds for all soils is not known. Further substantiating proof would involve determining pressure versus tension relationships at equilibrium for soils with different grain-size distributions. At present, no way is known of evaluating the area of contact between the ice phase and the soil particle, consequently the overburden pressures for the experiments are expressed in load per

unit area of sample. There are also thought to be important factors unaccounted for by using the relationship between ΔP_{iw} and ΔT. These involve the adjustments in the curvature of the ice resulting from difference in overburden pressure at a point above the particle to a point above the pore.

The theory predicts that ice lensing may be halted by overburden pressure, by tension in the pore water, or a combination of both. This has been shown to be possible experimentally.

Finally, attention is drawn to the different relationships that may be derived between ΔP_i and ΔT, ΔP_w and ΔT, and ΔP_{iw} and ΔT from Eq. 2. A detailed discussion may be found in the publication "Thermodynamics of Soil Moisture" by Edlefsen and Anderson (2). In an earlier paper (1) the author tended to be in agreement with the theoretical treatment by others. This treatment, however, appears valid only when the ice and water phases are considered to be isolated from each other in the system. Experience with the model described in this paper, in which the ice and water phases are in intimate contact, supported by the experimental results, suggests that there is no way in which either phase can be independently subjected to tension or pressure in a system where ice lens growth is possible. Nevertheless, since only general agreement between the theory and the experimental results can be claimed, complete confidence in the ice lensing mechanism discussed is at present not possible.

ACKNOWLEDGMENTS

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Importance of Water in Formation of Soil Structure

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Introductory Remarks by the Chairman

Modern science is based on observation either of naturally occurring phenomena or under the controlled conditions of the experiment. Interestingly, the French word for experiment is the same as for experience. The first step in natural science is to determine the "how" by observation; then follows the second step of finding out the "why," and of establishing a logical theoretical system that allows prediction of natural phenomena as functions of pertinent factors. Czeratzki and Frese have greatly enriched this symposium by careful and ingenious photographic studies of the morphology of soil structure formation as a result of wetting and drying and of freezing and thawing of moist soil systems. The mechanisms of soil structure formation, so beautifully demonstrated by the work of these authors, can be easily tied to physico-chemical and geometric factors brought out by other contributors to this symposium. As a matter of fact, these morphological studies aid in the recognition of those of the numerous physico-chemical factors involved that are the most significant with respect to the actual behavior of natural soils and of those that play only secondary and lesser roles. Giving morphology its just due in this area of interest, it is not amiss to do the same to some of the great morphologists to whom this science is deeply indebted, but whose names are largely unknown to the present engineering generation. First, should be mentioned D'Arcy Wentworth Thompson, the father of Biophysics and his magnum opus "On Growth and Form." With respect to the morphology of natural ice formations, honors are justly due to Elliot (1827), Herschel (1833), Le Conte (1850), von Mohl (1860) and Sachs (1860-61). May we learn again the art of observation which these men possessed and may we utilize to the utmost the newer, better and easier means of recording.

● THE SIGNIFICANCE of soil structure for the growth of plants and proper development of animal life in soil and also for many problems of soil and hydraulic engineering gives special importance to the problem of the causes and mechanism of structure formation. In view of the numerous factors involved and their mutual interrelations which often can be discerned only with difficulty, it is indicated to treat this problem in separate parts. Accordingly, this contribution is limited to the presentation of phenomena that in the formation of soil structure can be observed with the unaided eye.

In these dimensions, the soil structure may appear as coherent, that is, without specific structural units that are separated from each other, or it may be subdivided into individual structural units or elements. The latter are called aggregates. However, this name is correct only in the case that primary soil particles are aggregated to form a larger unit. In macroscopic dimensions, this aggregation differs from flocculation insofar as it is the result of fragmentation and splitting of a coherent soil mass rather than due to primary particles approaching each other closely and subsequently sticking together. Such a phenomenon can be caused essentially only by forces that act on the soil from the outside. The respective forces can originate from human activity in soil cultivation, from the boring and digging of soil animals, from the root activity of plants and from metereological influences. In a cultivated soil, the above named factors act independently and with varied intensities. They aid each other in structure formation, but they may also destroy structure formed by other factors. Most of the

soil animals and also the plant roots affect soil structure favorably; on the other hand, human activity, depending on the cultivation system, chosen mainly from economical considerations, may destroy or improve soil structure.

Of widely varying importance for the soil structure is the climate since it is composed of factors that act in markedly different ways. Neglecting the extremes of wind and water erosion, which usually destroy the soil itself, and considering only the phenomena taking place in the much milder processes of structure formation, the following main climatic factors are found: temperature, precipitation and evaporation. The importance of these factors with respect to soil structure derives from their effect on the amount and condition of soil water. The main effect of temperature on soil water is the change of its physical state. Since in this presentation the change of water from liquid to vapor is included in the evaporation factor, the treatment of the temperature effect shall be restricted to change of soil water to ice and vice versa, as in freezing and thawing. Precipitation and evaporation increase or decrease the water content; hence, they are two important counter-players in the water economy of the soil.

The changes in amount and condition of soil water caused by the continuous change of the climate or meteorological factors influence the structure of soils susceptible to these factors. They are the cause of a more or less well marked dynamics of soil structure, understanding of which is of great importance in soil research. This dynamics of structure formation leads to a better explanation of morphological phenomena in soils, which latter permit the drawing of conclusions with respect to the physical properties of soils. Knowledge of the dynamics of soil structure is also an important basis for agricultural research, especially with regard to tillage operations. Soil structure obtained by working with agricultural implements is closely related to the structure formed naturally in the soil; hence, understanding of soil structure dynamics is an essential prerequisite for rational soil working, especially under difficult circumstances. Of course, economic reasons limit the cultivator to enter actively in the interplay of these relationships. As a rule, he must try to adapt his measures to the natural phenomena in the soil in a manner that the effect on the soil structure of his own efforts is aided by the action of the natural forces. Even though the dynamics of the structure of a given soil is markedly determined by meteorological and climatic influences, it is of great importance that the soil be worked in a suitable manner and that a large specific soil surface is brought into direct contact with the atmosphere.

PROBLEMS POSED AND METHODS EMPLOYED

The investigation of dynamic phenomena in soils is difficult, because of their relatively slow rate. With conventional methods of investigation, the difficulties can be overcome only when longer time intervals between observations do not affect the results in an essential manner. However, in cases in which intensity as well as direction of the reaction are subject to frequent changes, single observations at extended time intervals give unsatisfactory results and may even lead to contradictory conclusions. This is true for the phenomena of structure formation under consideration. Fortunately, they occur in macroscopic dimensions and can be recorded photographically. For this, fixation by means of single pictures is not always sufficient. While it makes possible diagrammatic presentation of structural changes as a function of time, it suffers from the disadvantage that the dynamic features of the phenomena cannot be shown in their continuity as is possible with moving pictures. Moving pictures possess the advantage that they can be run off as often as desired and that by repeated viewing, details can be discovered which often remain hidden in still pictures, because they cannot betray themselves by motion. These advantages of motion pictures can be utilized by means of fast or slow action photography even for phenomena whose rate of change as in the present case lies outside of the detection range of the human eye. Numerous investigations have been reported concerning the effect on soil structure of changes in moisture content. They show that this effect is bound to swelling and shrinkage phenomena. Haines (8) made the important observation in his swelling and shrinkage studies that in re-wetting the soil increases its volume beyond that of the original moist soil. This shows that a loosening of the soil has taken place during the

experiment. Of special importance for the soil structure is, according to many authors (10, 15), the behavior of the soil air during the moistening process. Since water is more strongly absorbed by soil than air, the latter is pushed out during the moistening process. However, often air becomes occluded at elevated pressures in pores that have not yet been moistened and explodes the soil when its pressure exceeds the cohesion of the soil particles.

It is known that a clay soil develops cracks in shrinking, especially in vertical direction, which subdivide it often into relatively large clods. In addition to this rough fissuration, a considerable number of smaller aggregates is observed in places especially exposed to weather-

Figure 1. Layered edge structure of a soil clod after repeated wetting and drying.

ing action which must be attributed to the same causes as the formation of the coarse fragments (Fig. 1). Aggregate formation as a result of swelling and shrinking due to meteorological influences occurs, therefore, in several orders of magnitude; differentiation is impossible without a further analysis of the involved processes. In the investigations reported so far, little consideration has been given to the formation of aggregates by swelling and shrinkage phenomena. Also, little information is found concerning the shape of the resulting aggregates. In view of the importance ascribed to the aggregate shape with respect to the macro-morphology and the physical properties of soils, there exists a definite need for obtaining additional facts that bear on this important question. This is especially evident from the large number of attempts to make the aggregate shapes the starting point of visual methods for judging the physical condition of agricultural soils and to use them for following and checking the effects of certain methods of cultivation (12).

For the reasons given above, the usual methods for swelling and shrinkage investigations, such as determination of linear expansion on test specimens, were abandoned; in their place cinematographic methods with time compression were used. This method combines the advantages of moving pictures with the possibility of evaluation by measurement.

STUDY OF THE FORMATION OF AGGREGATES AS A RESULT OF ALTERNATE MOISTENING AND DRYING BY MEANS OF MOVING PICTURES[1]

After several preliminary experiments, a soil developed on Opalinus clay of the Brown Jura near Schwäbisch Gmünd (Württemberg) was chosen for this investigation. This soil covers a large area and offers many agricultural difficulties. Because of the large swelling capacity of this soil, a great influence of moisture changes on aggregate formation was expected. Mechanical analysis of the soil gave:

Coarse sand	(2 - 0.2 mm)	= 1.2 percent
Fine sand	(0.2 - 0.02 mm)	= 9.2 percent
Silt	(0.02 - 0.002 mm)	= 36.5 percent
Clay	(<0.002 mm)	= 53.1 percent

The soil was first stirred mechanically with water until its aggregates were destroyed. Subsequently, a brick of 30 cm length, 20 cm width and 4 - 5 cm thickness

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[1] The movie was made in cooperation with the "Institut für den wissenschaftlichen Film, Göttingen, (Director: Dr. Ing. G. Wolff, Specialist: Ober-Ing. H. Schladerbusch). It can be obtained from this Institute or from the "Institut für Bodenbearbeitung, Braunschweig-Völkenrode."

Figure 2. Formation of vertical fissures by alternating wetting and drying--after first drying.

Figure 3. Formation of vertical fissures by alternating wetting and drying--after second moistening.

Figure 4. Formation of vertical fissures by alternating wetting and drying--after third drying.

Figure 5. Formation of vertical fissures by alternating wetting and drying--after fourth moistening.

was molded from the tough slip. The alternating wetting and drying of the soil during the taking of the motion pictures was effected by spraying with fine water drops and subsequent drying at 30 to 40 C under a heating lamp. By these means, five wetting and drying sequences of increasing durations were made in the total time of 24 hours. At the first experiment, the movie camera was fixed in a way that it took a picture of 9 by 14 cm of the soil surface viewed at an angle from above. During the wetting period, four pictures were taken per second, during the drying period, one picture was taken per minute. During the first very short moistening, the previously smooth surface of the dry soil becomes rough and coarse-grained.

Figure 6. Formation of vertical fissures by alternating wetting and drying--after fifth drying.

The film shows that one of the causes for this phenomenon is the air replaced by the spray water. The emergence of the air from the soil surface is manifested by the formation and bursting of blisterlike excrescences. The first wetting phase takes only a short time since the soil is not yet able to take in a larger amount of water. In the

Figure 7. Angular view of the top surface and of a vertical surface. Depth penetration of vertical fissures and formation of fine horizontal fissures after the second drying.

Figure 8. Angular view of the top surface and of a vertical surface. Depth penetration of vertical fissures and formation of fine horizontal fissures after the fourth drying.

Figure 9. Angular view of the top surface and of a vertical surface. Depth penetration of vertical fissures and formation of fine horizontal fissures after the sixth drying.

subsequent drying phase, a network of fine fissures is formed soon after the start of the drying. These fissures grow in size for a while, but after a short time no further changes are observed. This short shrinking period shows that the water has penetrated the soil only to a very shallow depth during the first moistening phase.

The first moistening and drying sequence shows already the essence of the fundamental phenomena occurring in the later sequences. These phenomena, however, become more marked with increasing number of sequences. This shows the great importance which extended repetition of the wetting and drying sequence has for aggregate formation.

During the second moistening, the soil can take already considerably more water because of the originally open fissures and the rough surface. Already after short spraying, the fissures begin to close while the edges of the fissures swell strongly in contact with the vertically moving water and form scar-like excrescences. In addition to this phenomenon caused by swelling, the movie also shows that very fine micro-aggregates are detached from the surface and carried along by the water. During the next drying, only a portion of the fissures open at the old locations. The following moistening and drying phases become increasingly longer since each time deeper layers are affected by the water. However, the observed phenomena remain the same as previously described. The fissures open and close at the same places and the edges bulge like pock-marks. During the opening of the fissures, jerking movements are observed at some places in the soil. These movements show that, as a result of the increasing fissuration of the soil, the moistening and drying proceed in a non-uniform manner and cause an irregular distribution of capillary tensions. Figures 2 to 6 show the final condition of the soil surface after several wetting and drying sequences.

The moving pictures that have been described so far depict the course of the events in two dimensions only. Since swelling and shrinkage of a soil take place in three dimensions, the camera was placed so that the picture would show both the surface and a plane at a right angle to it. A heavy alluvial valley loam was chosen for this experi-

ment; it had the following grain size composition:

Coarse sand (2 - 0.2 mm) = 0.9 %
Fine sand (0.2 - 0.02 mm) = 27.5 %
Silt (0.02 - 0.002 mm) = 29.5 %
Clay (<0.002 mm) = 42.1 %

The moving pictures taken show very impressively the swelling of the soil in vertical direction in addition to the previously described phenomena. During the spraying, the water was added in separate dosages. Hence, the swelling was also discontinuous and gave the impression of seismic movements on the surface which were propagated downward in a wavelike fashion as the water penetrated deeper

Figure 10. Fracture, after termination of movie-taking, with horizontal layers inside the soil.

into the soil. During the succeeding drying phases, the depth progression of the surface fissures can be followed on the vertical face. These fissures run irregularly in a zigzag manner and form lateral branches in their advanced stages of development. In addition to this phenomenon, one observes at a certain time the formation of fine horizontal fissures, the number of which increases slowly with time. They lie closely below each other and form a zone of horizontal layer-structure. Figures 7 to 9 show the progressive formation of vertical and horizontal fissures; Figure 10 shows a fracture-surface at the end of the experiment, and Figure 11 shows crumbling into flake-like aggregates. To be sure, the zone of horizontal layer formation does not reach the full depth of the vertical fissures, but is restricted to a shallow layer. Thus, it seems to represent a form of aggregation typical for the soil surface. This process is of greatest consequence for soil structure, since it creates small aggregates that are important for most physical properties of a soil and which, therefore, must also be present in a soil in which the aggregates have been formed by mechanical breakdown with agricultural implements. In heavy soil in which these fine aggregates can be produced artificially only by means of a large amount of power, this natural process of aggregate formation by wetting and drying is of utmost importance for rational soil cultivation.

THE EFFECT OF FREEZING ON SOIL STRUCTURE

Moving Pictures Investigations

The essential features of the effect of frost on soil structure are known and the morphology of frost structure has been described in numerous publications (2, 3, 7, 9, 11, 13, 14). However, it appears that no observations are available on the course of soil freezing or on the start and development of ice crystal formation immediately at the freezing front. To be sure, the penetration of frost in soil can be recorded photographically by means of suitable experimental arrangement; however, by these means it cannot be reproduced as a rate reaction. It was, therefore, attempted to study and record the freezing of soil using the same cinematographic methods as employed in the case of wetting and drying phenomena.

During the cooling below 0 C of a water saturated soil and the resulting change of
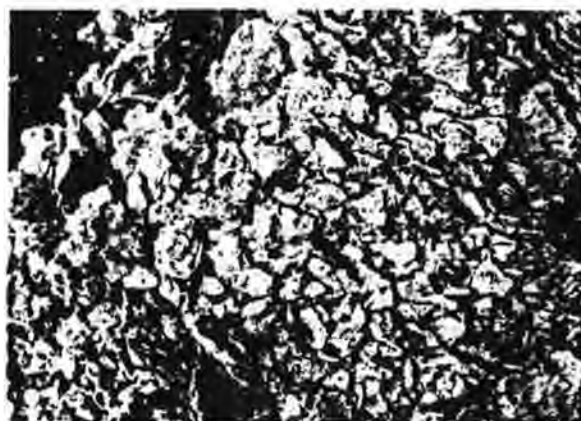
Figure 11. Break-up of horizontal layers shown in Figure 10 into flake-like aggregates.
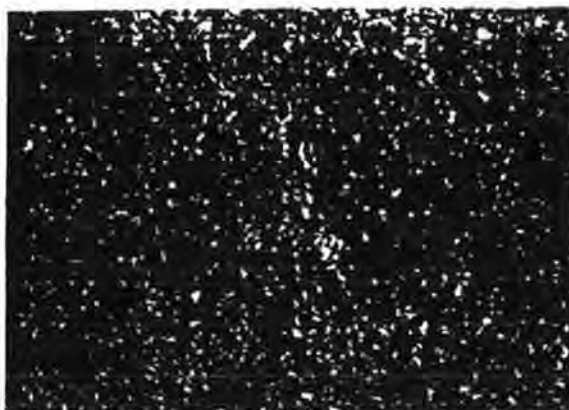
Figure 12. Homogeneous frost structure in sandy soil. Freezing front marked by line.

Figure 13. Formation of frost structure in a black earth on loess. Figures 13 to 16 were photographed at intervals of approximately seven hours.

water into ice, two phenomena take place which differ in intensity depending upon the type of soil and the freezing conditions, viz.:

1. Movement of the capillary water to the freezing front, and
2. Incorporation of this water as ice in intermittent layers in the soil.

If the frost penetrates into the soil then this ice segregation leads to frost structures which can be differentiated into "homogeneous" and "heterogeneous" structures. In the case of homogeneous frost structure, practically no change in appearance as compared with the unfrozen soil can be recognized macroscopically. The heterogeneous frost structure, however, may occur in markedly different forms depending on soil type, rate of freezing and water movement to the freezing zone. In soils containing fine sands and silts, the ice formation is predominantly in horizontal layers, while in clay soils polygonal structures are formed as a result of moisture loss and shrinkage of the clay which accompany the freezing process. Since every soil freezes homogeneously if its water content is below a certain limit determined by the soil type and the freezing temperature, a sufficient supply of water or the possibility of easy movement of water to the freezing zone is an important prerequisite for a strong formation of frost structures.

These relationships had to be taken into account in the experimental arrangement for the taking of the motion pictures in order to show the phenomena occurring in soil freezing as clearly and as true to nature as possible. Most suitable for this appeared to be the method employed in soil mechanics research in which the frost penetrates from one side and in which the soil is treated as an open system with respect to water

Figure 14. Formation of frost structure in a black earth on loess.

Figure 15. Formation of frost structure in a black earth on loess.

Figure 16. Formation of frost structure in a black earth on loess.

Figure 17. Thickening of ice layer at the freezing front at low penetration rate of the front.

supply; this means that during freezing, the soil is supplies with an artificial ground water level.

In order to fulfill these conditions, the soil samples were placed in a modified kitchen refrigerator in a way that the frost could penetrate only from the top, and the bottom was connected with a ground water level by means of a ceramic filter plate. To permit the photographing of the frost structure, a vertical area was cut out on the front side of each specimen. As a rule, one picture was taken per minute. The refrigerator was so regulated that the temperature on the surface of the soil specimen was between -1 and -1.5 C. Movies were made with different soils and yielded the following results:

Sandy Soil. Grain size composition: Coarse sand : 37.7 percent
Fine sand : 50.3 percent
Silt : 8.5 percent
Clay : 3.5 percent

The penetration of the frost into the soil can be recognized only by the slow movement of a shadow in the picture. This shadow is caused by an ice film formed by the water which, because of volume increase in freezing, is forced out of the soil pores. No macroscopic change can be observed in the structure of the specimen surface; this means that the soil freezes homogeneously. Figure 12 shows a photograph in which the extent of frost penetration is marked by a line.

Soil from the A-Horizon of a Black Earth on Loess. Grain size composition:

Coarse sand : 5.2 percent
Fine sand : 40.1 percent
Silt : 35.7 percent
Clay : 19.0 percent

Humus content : 2.3 percent

Figure 18. Thickening of ice layer at the freezing front at low penetration rate of the front.

Frost penetration from the top surface results in this soil in the formation of horizontally oriented ice lenses placed in intermittent layers below each other. Many of the ice lenses are touched by the upwards bent ends of the ice layers underneath in a manner that during the freezing process a characteristic and in many places almost net-like frost structure is formed. The originally thin ice lenses form much faster in the beginning than toward the end of the experiment where

the freezing rate decreases more and more while the ice lenses increase in thickness. The increase in thickness of different ice lenses continues even after the freezing front has passed the specific ice lens and has already formed a new one below. At the end of the experiment, the soil shows the horizontal frost structure which is characteristic for loess soil; however, in the vicinity of the water source, some polygonal structures are also found. Figures 13 to 16 give an insight into the course of the freezing process in this soil.

Figure 19. Thickening of ice layer at the freezing front at low penetration rate of the front.

A₃-Horizon of a Para-Brown Earth on Loess. Grain size composition:

Coarse sand : 1.7 percent
Fine sand : 55.5 percent
Silt : 29.9 percent
Clay : 12.9 percent

The freezing process shows initially the same course as in the case of the Brown Earth (2) and results also in a horizontally layered frost structure which, however, possesses more strongly broken contours. During the experiment, the freezing process was arrested for a while by decreasing the refrigeration. During this time, the amount of refrigeration surpassed the heat gain from the change of water to ice only to such an extent that it just sufficed to form a thick ice lens at the freezing front. This approximate equilibrium condition was terminated by returning to the original refrigeration and the experiment was concluded. Figures 17 to 19 show very clearly the growth in thickness of the ice lenses at the freezing front. The frost structure below the ice lens is coarser than above, probably because the soil had become enriched in water while the advance of the freezing front was arrested.

Chalk Clay. Grain size composition:

Coarse sand : 7.7 percent
Fine sand : 29.2 percent
Silt : 37.4 percent
Clay : 25.7 percent

Because of the low water conductivity of this clay soil, it was not possible to feed the formation of ice from an artificial ground water reservoir. Therefore, the soil specimen was made up with sufficient water that ice layers could be formed from its

Figure 20. Course of the freezing process in clay soil.

Figure 21. Course of the freezing process in clay soil.

Figure 22. Vertical section through frozen Ca-montmorillonite.

Figure 23. Advance of the vertical ice layers at the freezing front into the unfrozen zone (montmorillonite).

own supply in the immediate vicinity of the freezing front. This, however, leads to soil shrinkage in the immediate vicinity of the freezing front and cracks are formed which become filled with ice already during their formation. This companion phenomenon of soil freezing results in frost structures that differ essentially from those in loess soil. As against the horizontal layer orientation of the ice lenses in the loess, parallel needle-pointed almost vertical ice layers are at first formed from the surface down into the clay soil. These needles increase in thickness during the freezing process to well developed ice bands and only later are joined to relatively coarse polygonal frost structures by means of horizontal ice lenses (Figs. 20 and 21).

Form of the Frost Aggregates in Clay

In the case of the freezing experiments—in contrast to that of the wetting and drying experiments—the freezing process could be photographed only in the vertical plane. Hence, the moving pictures alone do not give a complete presentation of the form of the aggregate structures. They were, therefore, complemented by experiments in which a large number of soil specimens were frozen in the described manner and then cut into vertical and horizontal slices. This way, very informative pictures were obtained concerning the geometric features of frost structures in clay-rich agricultural soils and also in montmorillonite clay.

In montmorillonite, especially regular frost structures were found because of its large and uniform shrinkage. Figure 22 shows a vertical section through a frozen Ca-
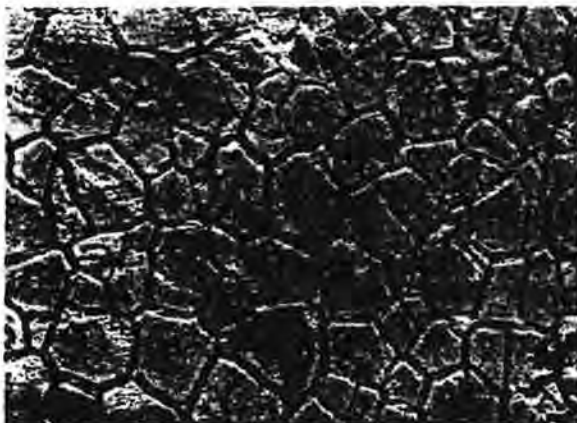
Figure 24. Horizontal section through frozen Ca-montmorillonite showing polygonal bases of the frost aggregates.

Figure 25. Frost structure of the Ca-modification of a sandy-clayey loam, vertical section.

Figure 26. Frost structure of the Ca-modification of a sandy-clayey loam, horizontal section.

Figure 27. Frost structure of the Na-modification of a sandy-clayey loam (see Fig. 24), vertical section.

montmorillonite: the vertical ice layers are especially marked since they run through the picture in a straight course. The horizontal ice layers, however, are relatively thin and seldom extend over two vertical layers. Since both ice formations are almost normal to each other, rectangular aggregate edges are obtained. The stronger formation of the vertical ice layers is explained, as shown in Figure 23, from their advance ahead of the freezing front into the shrinkage fissures of the unfrozen soil. These fissures provide a stress-free space into which the easily moving water can crystallize. The later occurring horizontal ice formation produces only relatively thin ice lenses since the water must be pulled against an ever increasing suction tension.

The frost structure of a horizontal section, taken parallel to the freezing front, is shown in Figure 24. This structure does not show the rectangular features of the vertical section, but hexagons and pentagons in cell-like arrangement. Formations of this kind are widely found in nature, for example, in basalt, whose polygonal forms are also the result of shrinkage phenomena.

Since swelling capacity and intensity of water binding of a clay is influenced by its exchangeable cations, an influence of the adsorbed cations on the frost structure can be expected. While Na-montmorillonite under the same experimental conditions showed the same aggregate forms as Ca-montmorillonite, the aggregates were smaller and more irregular than those of the latter. Additional experiments with a sandy-clayey loam showed, under the same experimental conditions and at the same plasticity as the comparison samples, that the soil with Ca-exchange ions formed the soil struc-

Figure 28. Frost structure of the Na-modification of a sandy-clayey loam (see Fig. 24), horizontal section.

Figure 29. Streaked course of shrinkage fissures in the Na-modification of a clay soil.

ture characteristic for this soil modification (Figs. 25 and 26). The Na-ion modification, however, showed in the vertical section an irregular and streaked frost structure (Fig. 27) and in the horizontal section an arrangement of ice lenses looking like a set of fine parallel lines (Fig. 28).

Aggregate formation in clayey soils as a result of frost action or of wetting and drying are related processes, since both are connected with swelling and shrinkage phenomena in the soil. This is why the resulting aggregate forms show great similarities and why, when both factors have acted on a soil, the specific cause can hardly be recognized. An example of this is the pattern of shrinkage fissures in a Na-soil modification (Fig. 29) which is similar to the frost structure in Figure 27. Although both patterns may be influenced in part by unavoidable flow structures, formed during preparation of the soil specimens, they prove the similarity of the effect of the factors involved. The same can be said for the layered structures and aggregates whose formation, according to the motion picture evidence, may be due either to wetting and drying or to freezing action.

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Effect of Water Movement on Soil

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Introductory Remarks by the Chairman

Much has been said in this symposium about the effect of the geometry and the physico-chemical character of the surfaces of the solid soil constituents on the movement of water through a soil system. It is well to supplement this by taking a different perspective, namely, to consider the effect of water movement on the soil. This Mr. Barber has done in his present paper which deals not only with microscopic, but also with macroscopic effects and their consequences as regards engineering structures. We are grateful to Mr. Barber for condensing into precise and lucid statements so much of his large research and practical engineering experience.

● MOST OF the problems of soil engineering are concerned with soil and water, rather than with dry soil.

Surface reactions are often important, especially if they have an opportunity to affect the dispersion or aggregation of the soil particles before compaction or consolidation. However, many effects of water movement are explained by mechanical reactions on a scale much larger than colloidal sizes.

WEATHERING AND EROSION

Water seepage often causes weathering at depths beyond the reach of surface temperatures and organisms. Figure 1 indicates how rainwater charged with carbon dioxide infiltrated to the water table whence it went horizontally and leached lime from a clayey shell layer resulting in very soft material along its path of flow to springs. A soft arkosic silt near Alexandria, Virginia, was found below 10 ft of firm gravel. While it had once been loaded by over 100 ft of gravel, it had apparently been weathered after most of the load was removed by erosion.

Water erosion begins with the impact of raindrops followed by sheet erosion and gullying where water concentrates. Cohesion retards the beginning of erosion but fine soil is easily carried away once it is displaced. Weakly cemented soils, such as loess and volcanic ash, may

Figure 1. Softening of calcareous soil by solution—Yorktown.

TABLE 1
MAXIMUM SWELL FOR DIFFERENT SOILS[1] UNDER VARIOUS LOADS[2]

Soil	Thickness Increase, percent							
	8 kips per sq ft	4 kips[3] per sq ft	2 kips[3] per sq ft	1 kip[3] per sq ft	0.5 kip[3] per sq ft	0.2 kip[3] per sq ft	0.02 kip[3] per sq ft	0.02 kip per sq ft
A-1	-0.4	-0.3	-0.1	0.0	0.1	0.5	2.1	11.8
A-2	0.0	0.6	1.0	1.4	2.0	2.7	6.6	13.1
A-3	0.0	0.0	0.2	0.2	0.3	0.3	0.6	0.4
A-4	0.8	1.9	3.2	4.3	5.7	7.4	12.9	22.5
A-5	0.5	2.1	2.9	4.6	6.2	7.8	15.1	17.1
A-6	12.2	13.9	16.0	18.2	23.1	-	38.4	70.7
A-7	1.4	4.7	5.5	6.6	7.6	9.0	13.2	21.4
A-8	10.1	12.9	15.6	16.4	17.4	19.1	63.5	98.7

[1] Air-dry soil compacted under 500 kips per sq ft.
[2] In kips per square foot.
[3] After swelling under previous load.

Figure 2. Effect of subsurface erosion in Guatemala.

stand undisturbed on very steep slopes, but are extremely erodible when placed in a fill after the cohesion is destroyed by manipulation.

Internal erosion may also occur. Where surface drainage is lacking, infiltrating water may flow laterally through pervious strata and cause backward
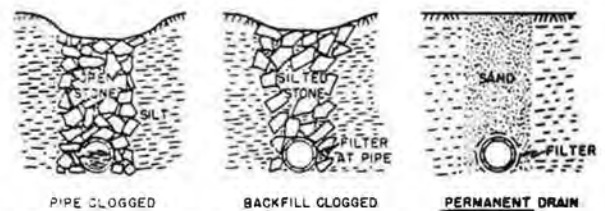
Figure 3. Intrusion of silt into drains.

Figure 4. Soil pumping.

Figure 5. Hysteresis in consolidation of Tuxedo clay from liquid limit.
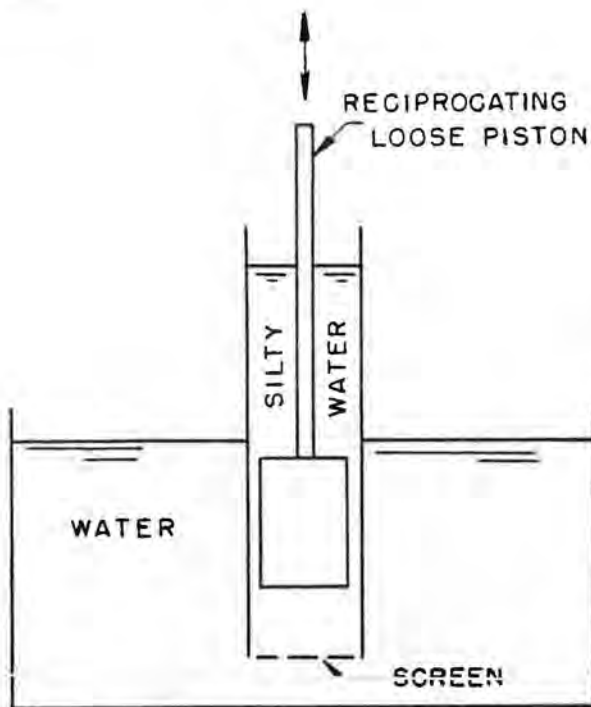
erosion or piping from an outcrop in a depression. Figure 2 shows the result when the roof of a piping tunnel collapsed. The tunnel is seen in the middle of the bottom picture showing a hole where a house had been.

Similar internal erosion causes failure of subdrains as shown in Figure 3, unless sand is placed between the pipe and the soil. Unless porous or perforated pipe is used to prevent open joints, a supplementary filler is required around the joints.

The displacement of soil and water from beneath concrete slabs deflected by heavy loads is a type of erosion. In addition to the splashing effect, the reciprocating vertical movement can actually pump water upward as demonstrated by the device
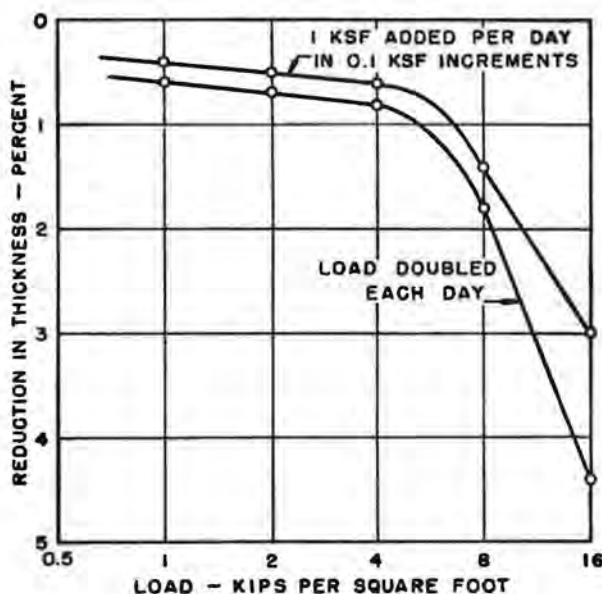
Figure 6. Effect of slow loading on consolidation.

Figure 7. Soil structure.

Figure 8. Slaking due to sudden wetting.
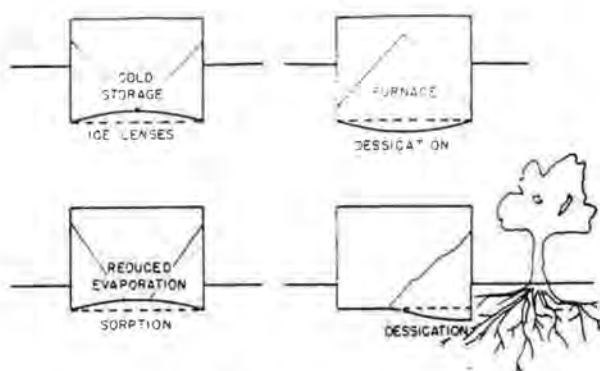
Figure 9. Volume change of clay under buildings.

shown in Figure 4. The soil particles in the water act as valves on the screen which represents the subgrade.

CONSOLIDATION AND SWELL

When a load is applied to a confined clay soil, the volume decreases due to slipping and bending of the plate and needle-like particles. When the load is removed, unbending causes an increase in volume but the slipping is inelastic so the soil is only partly elastice. If the same load is reapplied, friction between particles causes a hysteresis loop as shown in Figure 5. Similar effects are obtained with drying and wetting where the mechanical load is replaced by stresses balancing the surface tension of the water.

Slow application of loads may cause less consolidation as shown in Figure 6, possibly due to less slipping of particles.

The rate of consolidation under a given load is controlled by the escape of air and
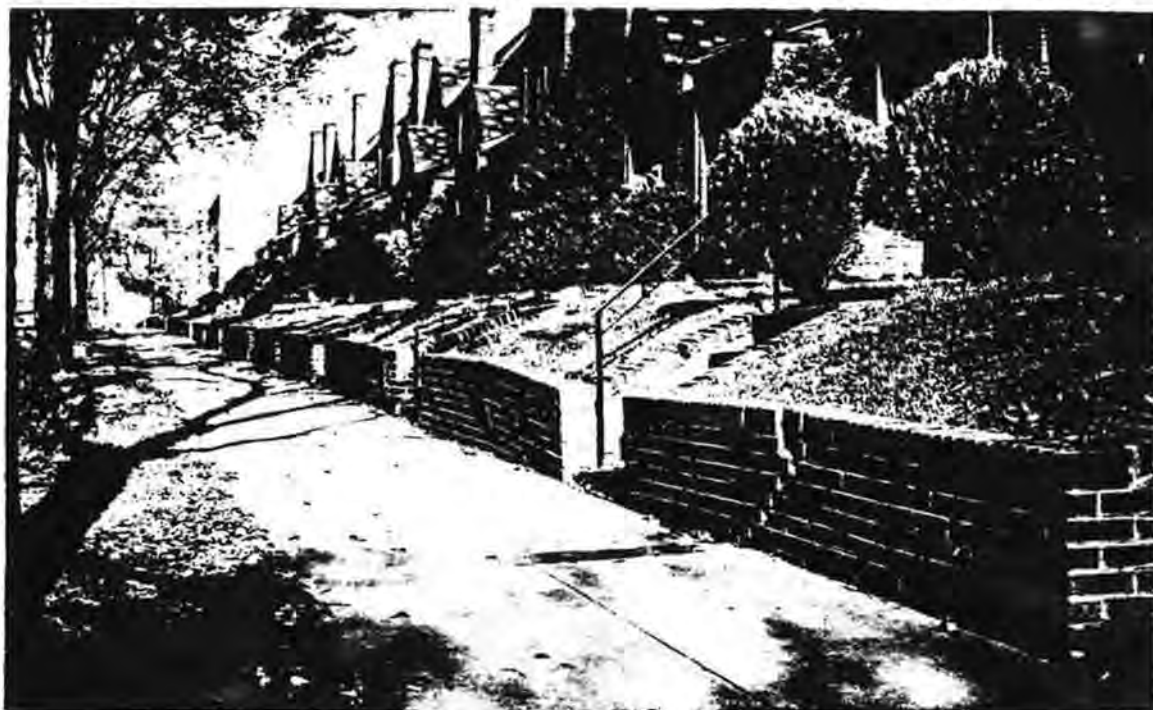
Figure 10. Evidence of bowl-shaped depression by trees.

water and thus depends upon the amount of fluid escaping and the permeability or fluid conductivity of the soil. An additional delay or secondary consolidation evident in cellular material such as peat may be caused by forcing hygroscopic water from the cells.

Both the amount and rate of consolidation depend upon the arrangement of the soil particles or structure. This is the reason for undisturbed sampling of foundation soils but also applies to compacted
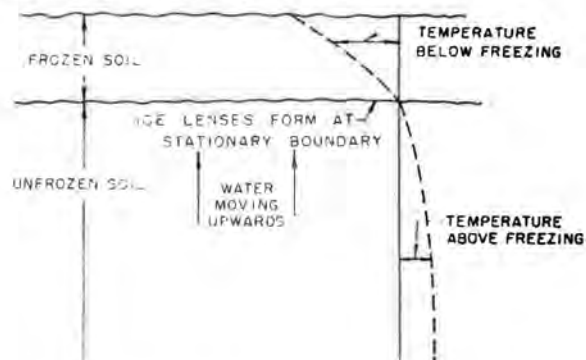
Figure 11. Mechanics of frost heave.

soils. Figure 7 compares the uniform structure of dispersed soils to the non-uniform structure of aggregated soils.

Sensitivity to disturbance increases with non-uniformity of structure. Marine clays may become extremely sensitive or quick if the salt which caused aggregation is leached out.

Compaction with a limited amount of water causes a non-uniform structure since the aggregations due to drying are not dispersed. Table 1 shows the swell or rebound of several soils. Comparison of the last two columns indicates that when swell is retarded, some of the elasticity is lost by dissipation laterally into the less dense parts of the non-uniform structure. This reduction was not found in highly dispersed samples.

It is noted that the A-6 soil swelled 12 percent against 8 kips per sq ft. With no movement, a pressure of 38 kips per sq ft was noted. The sudden release of this energy is the cause of slaking. If dry clay is immersed in water, air trapped in the interior may be compressed and help to disrupt the sample when it escapes. However, slaking will occur if the lump of clay just touches the water as shown in Figure 8 and the air is free to escape upward. If dry clay is permitted to take up water very slowly, it is weakened much less.

Figure 9 indicates some effects of soil volume change on structures. An apartment
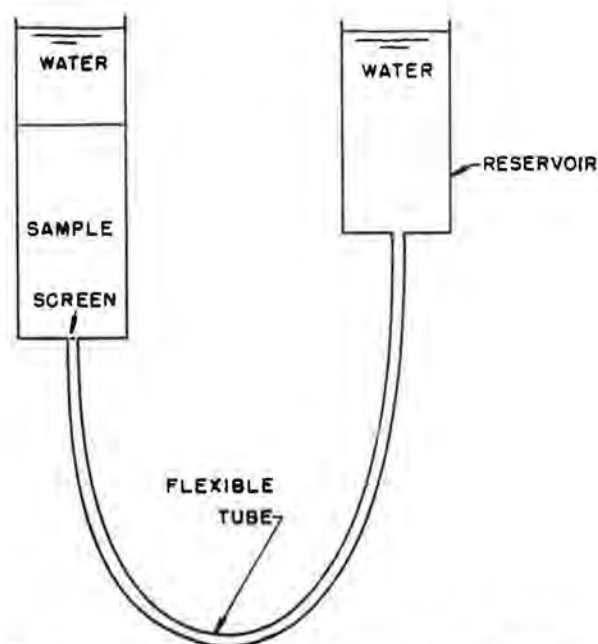
Figure 12. Device for applying vertical seepage force.
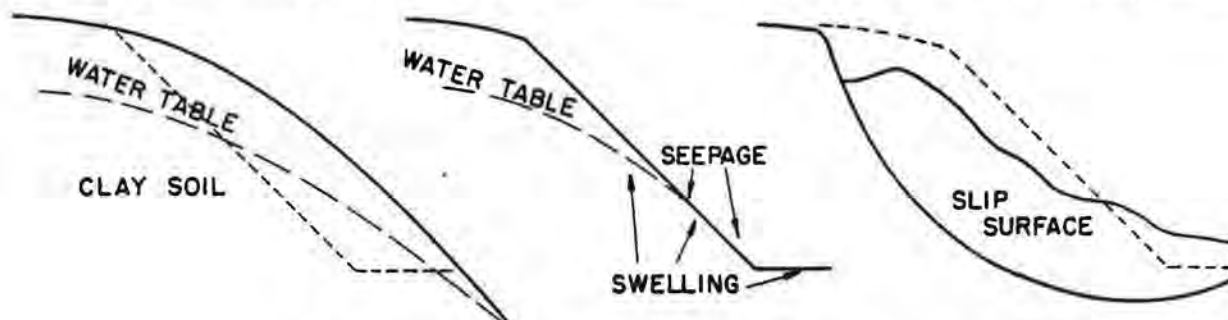
Figure 13. Development of slip in cut in clay.

OPEN CUT   BULKHEAD   CONSOLIDATION
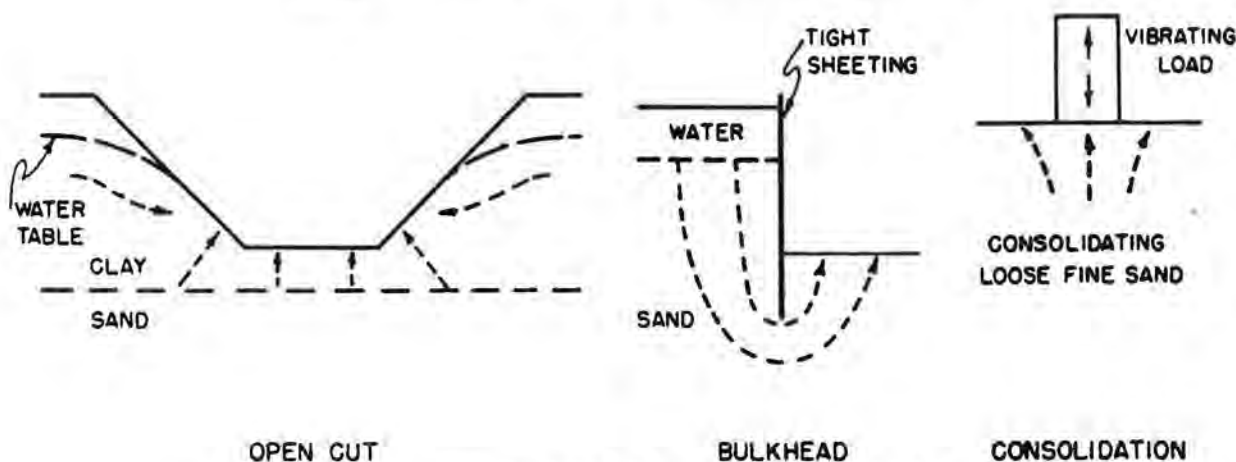
Figure 14. Illustrations of upward flow of water.

SHEARING DIRECTION

FLUID ESCAPES

Direction Of Slip

SHEARING DIRECTION

FLUID ENTERS

Direction Of Slip
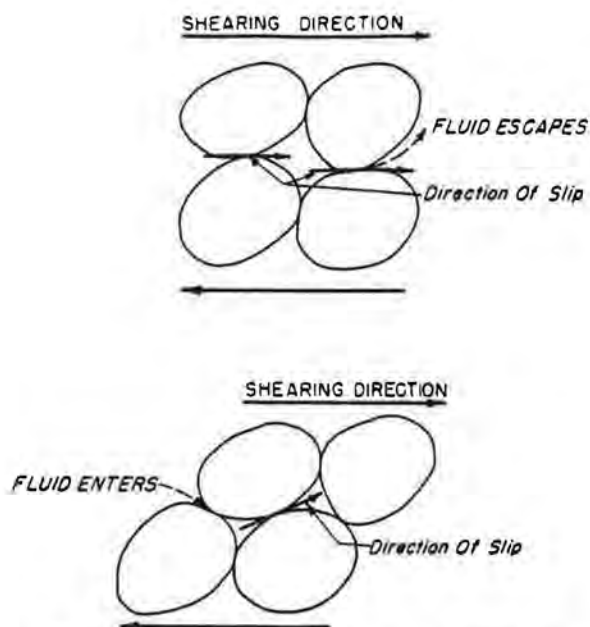
Figure 15. Volume change with shearing.

DRY

DAMP

DAMP AND MIXED

SATURATED
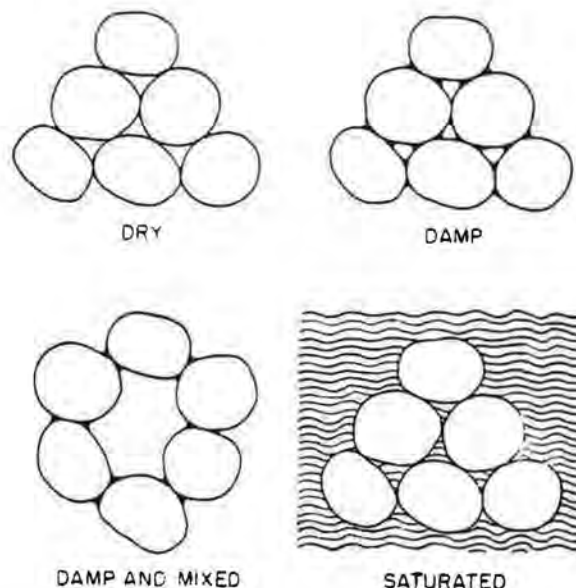
Figure 16. Bulking of sand.

house in Washington, D.C., was disrupted when surface water reached the dry clay supporting a central stairwell. The movement of the wall in Figure 10 indicates the bowl-shaped depression caused by a tree growing in clay. Frost heave under cold storage plants may be prevented by placing heaters below an insulated floor on soil. Figure 11 indicates that ice lenses are formed when the rise of water causes the freezing depth to remain static.

SEEPAGE FORCES

Soil below a static water table is bouyed up in proportion to the water it displaces. If the water table is lowered, the bouyancy is reduced and settlement occurs. This may be demonstrated by the device shown in Figure 12, using powdered mica as the sample and lowering the reservoir to create a downward seepage force. A similar device was used to apply consolidation loads to fluid samples of sediment from Lake Mead behind Hoover Dam. Large settlements in Mexico City have been caused by pumping water from sand below a very compressible clay.

Lateral flow is an important factor in many landslides. The force is not necessarily reflected in the amount of seepage and may be critical only occasionally. In cut slopes in clay, the weakening of seepage is augmented by the gradual swelling of clay which may cause sliding (as shown in Figure 13) sometimes several years after making the cut.

Upward flow of water may cause various difficulties as illustrated in Figure 14. Blowups may be caused by too rapid excavation in clay over sand. The lateral support of sheeting for bulkheads may be

Figure 17. Water menisci between sand grains.
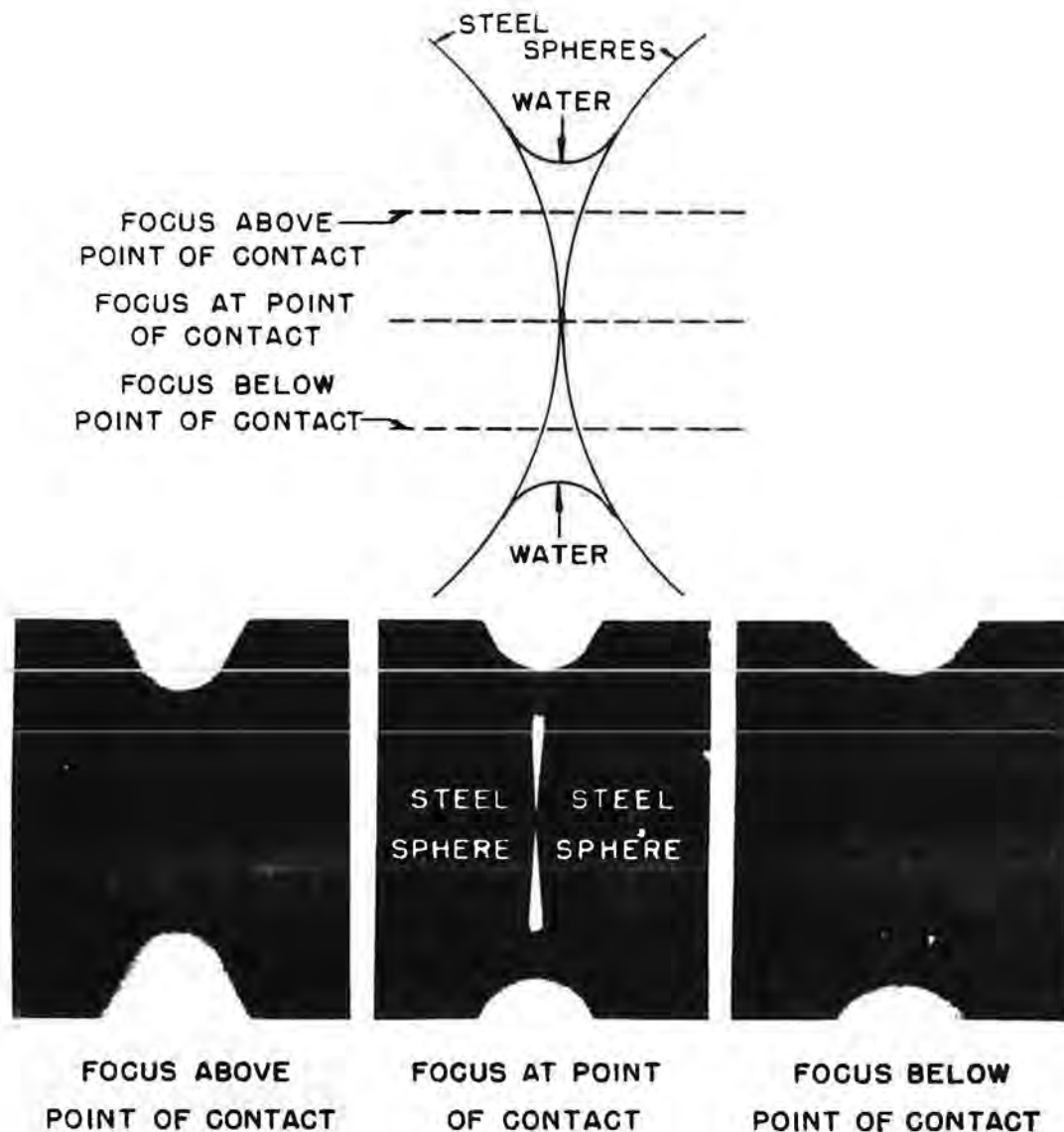
Figure 18. Water menisci around points of contact of steel spheres.

lost if too high an upward gradient causes quicksand. The tendency for a vibratory load to densify a loose saturated sand may cause a temporary quick condition as water is forced upward.

Figure 15 shows the volume changes that accompany shear. A saturated loose material loses strength as load is applied to the pore water; whereas above the critical density, the tendency to increase in volume causes a reduced pore water pressure which gives a temporary increase in strength. The coefficient of interval friction is increased by densification since the direction of slip is in effect uphill. This interlocking effect is added to the friction of loose material.

The bulking of sand when damp and mixed is caused by the surface tension of
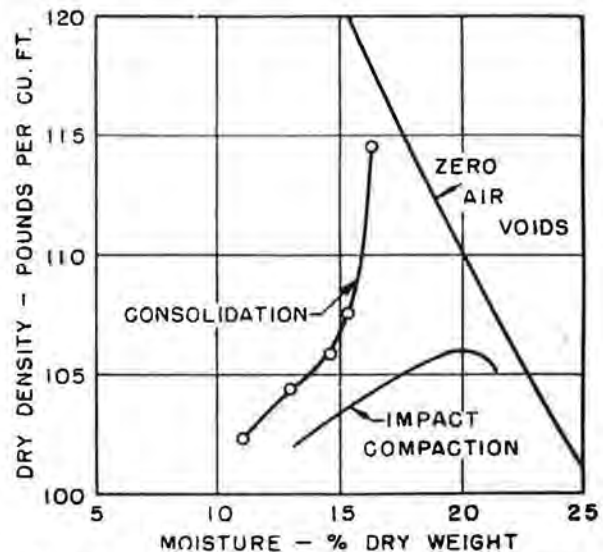
Figure 19. Consolidation versus impact compaction.
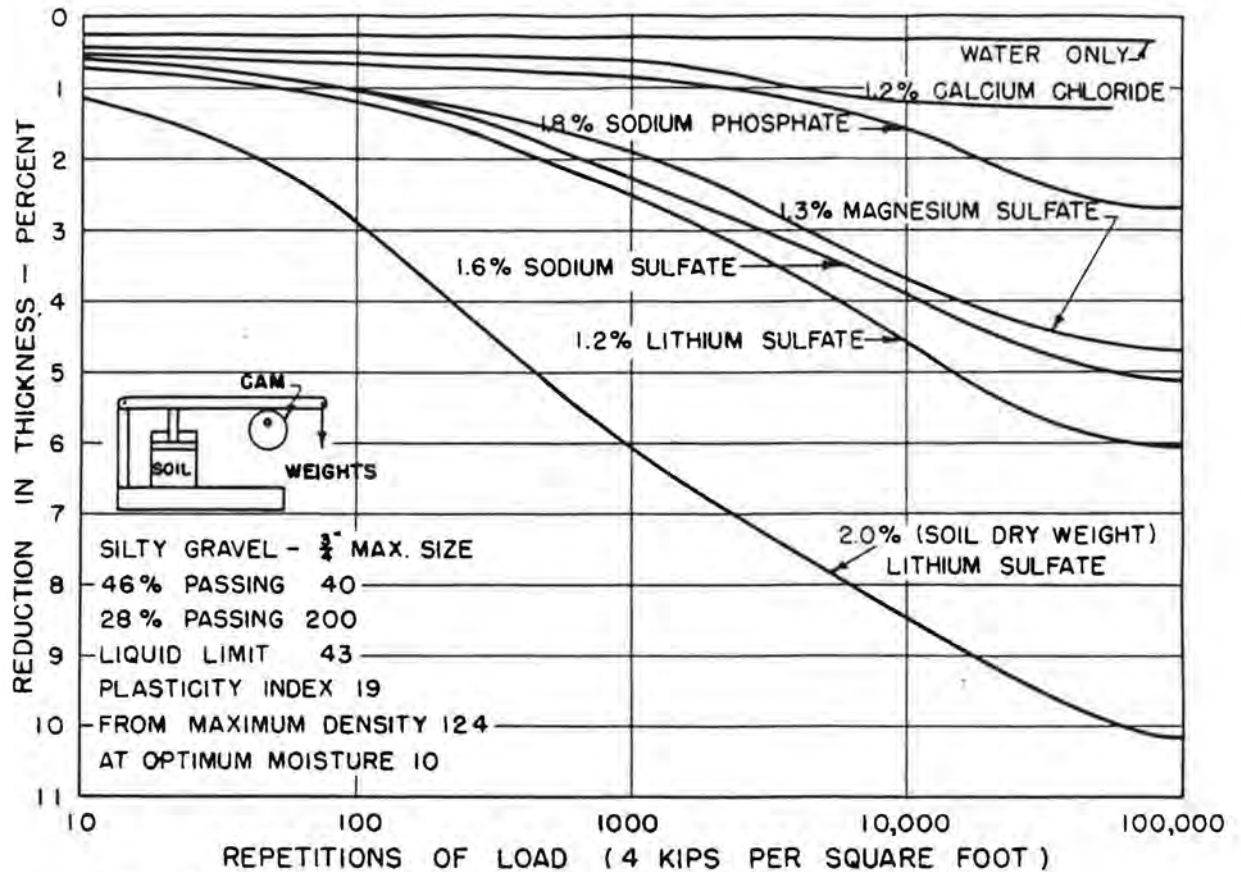
Figure 20. Effect of chemicals on densification under repetitive loading.
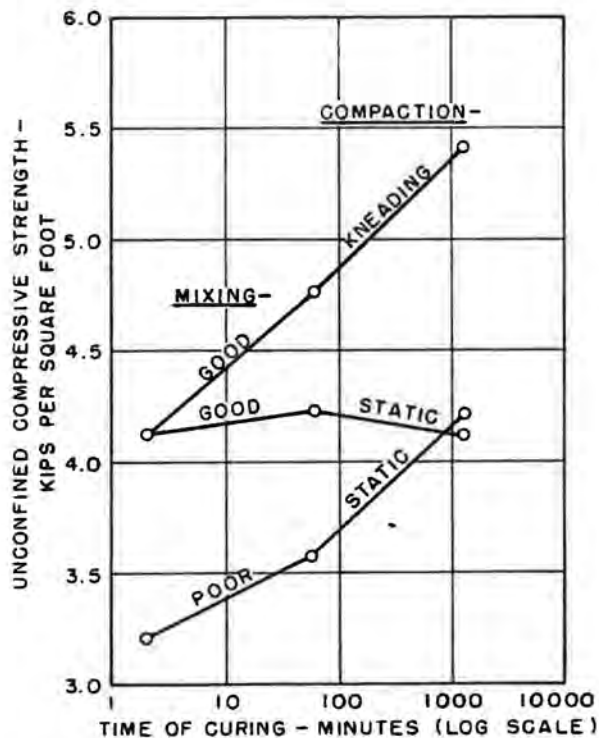
Figure 21. Thixotropy in clay near optimum (17) and maximum density (109).
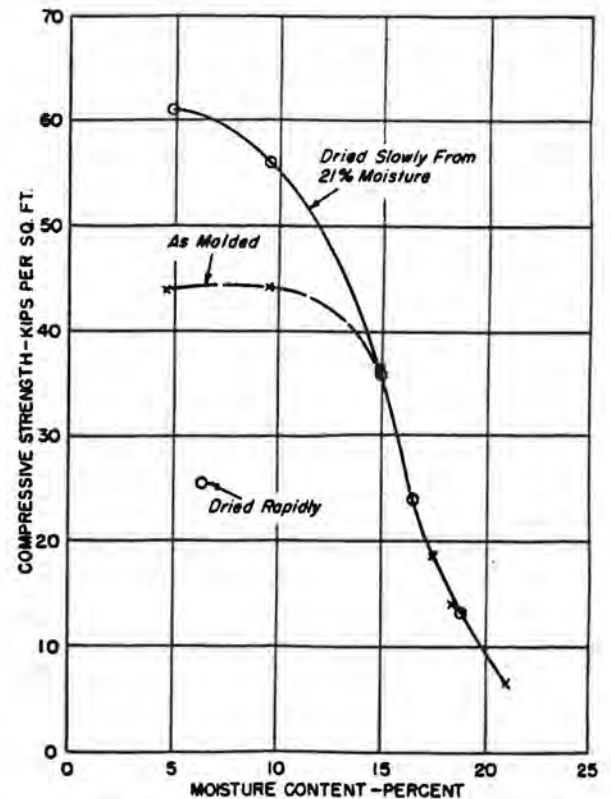
Figure 22. Effect of structure on strength of Tuxedo clay.
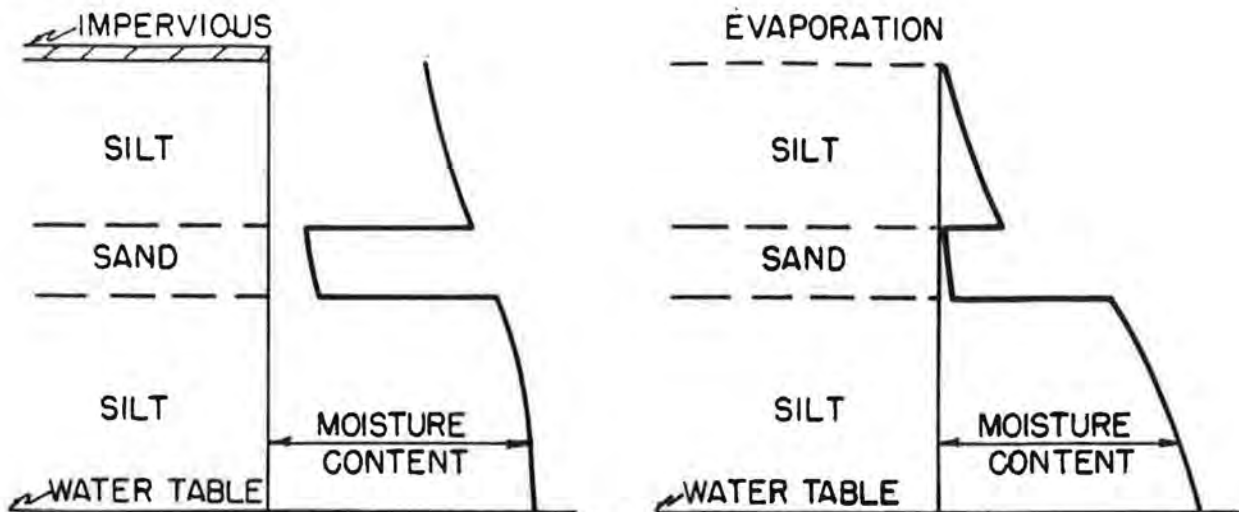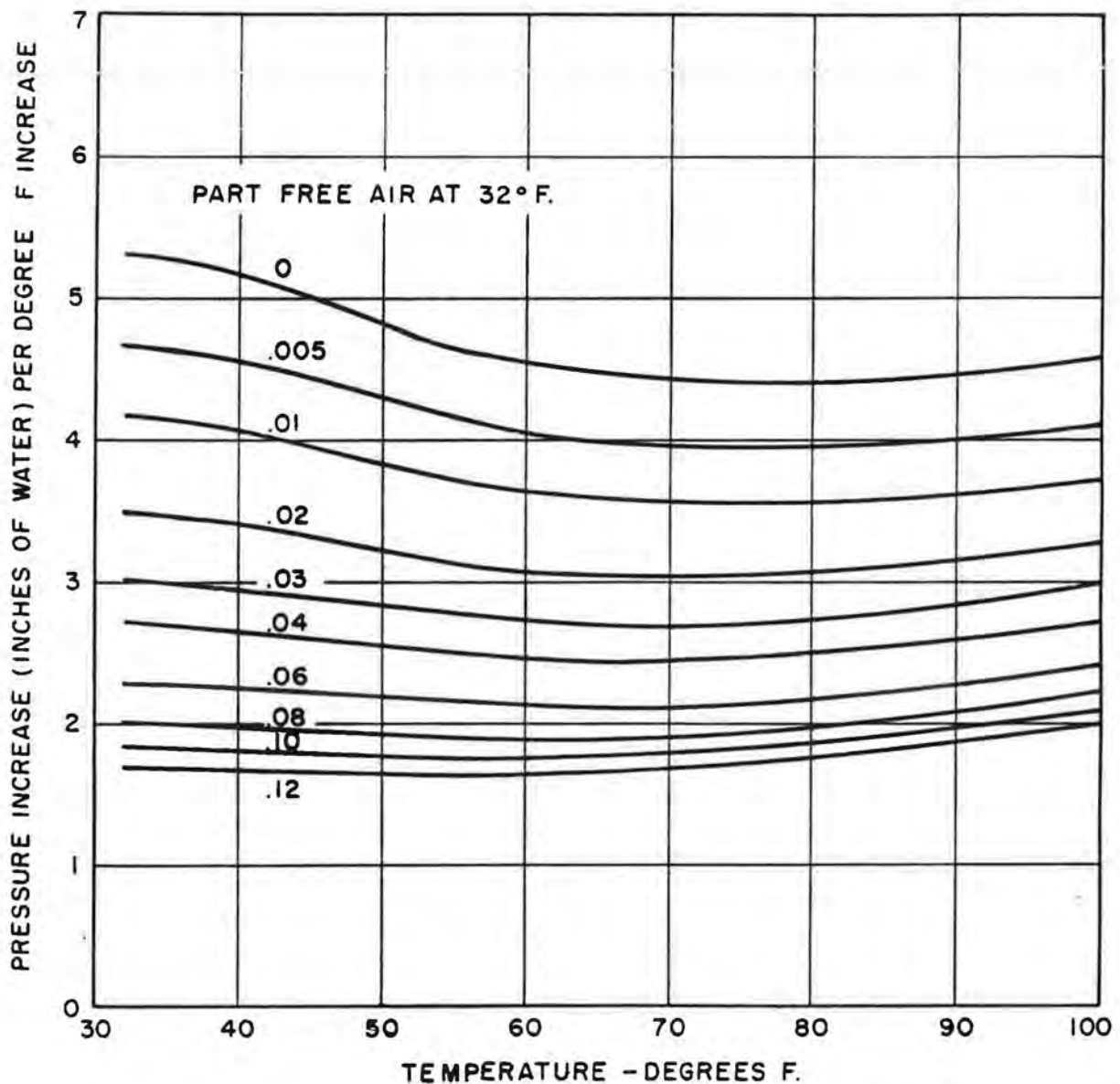
Figure 23. Capillary rise of water.

Figure 24. Pressure increase with temperature at constant volume for various air-water mixtures.

water holding the particles together as shown in Figure 16.

Bulking of sand was once wrongly attributed to water holding particles apart. This idea was supported by photographs of damp sand under a microscope as shown in Figure 17. The particles appear to be separated by water because an average focus cannot be at the level of most of the points of contact between particles. This fallacy is illustrated in Figure 18 which shows three photographs of two steel spheres with water around their point of contact. The middle photographs shows the point of contact;
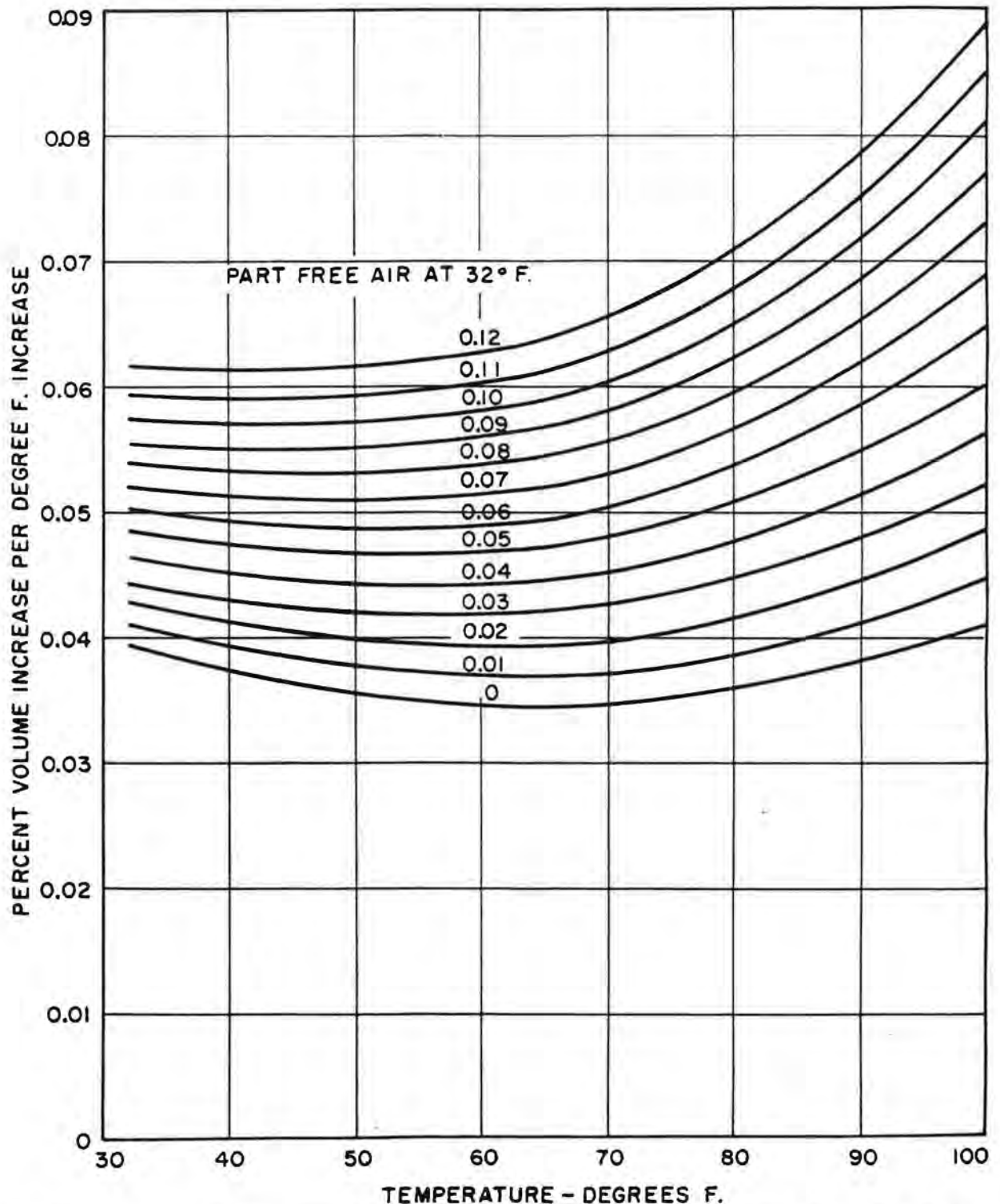
Figure 25. Volume increase with temperature at zero gage pressure for various air-water mixtures.

while in the other photographs the spheres appear to be separated because the focus is above or below the point of contact. (This apparent contact does not preclude separation by a molecular layer.)
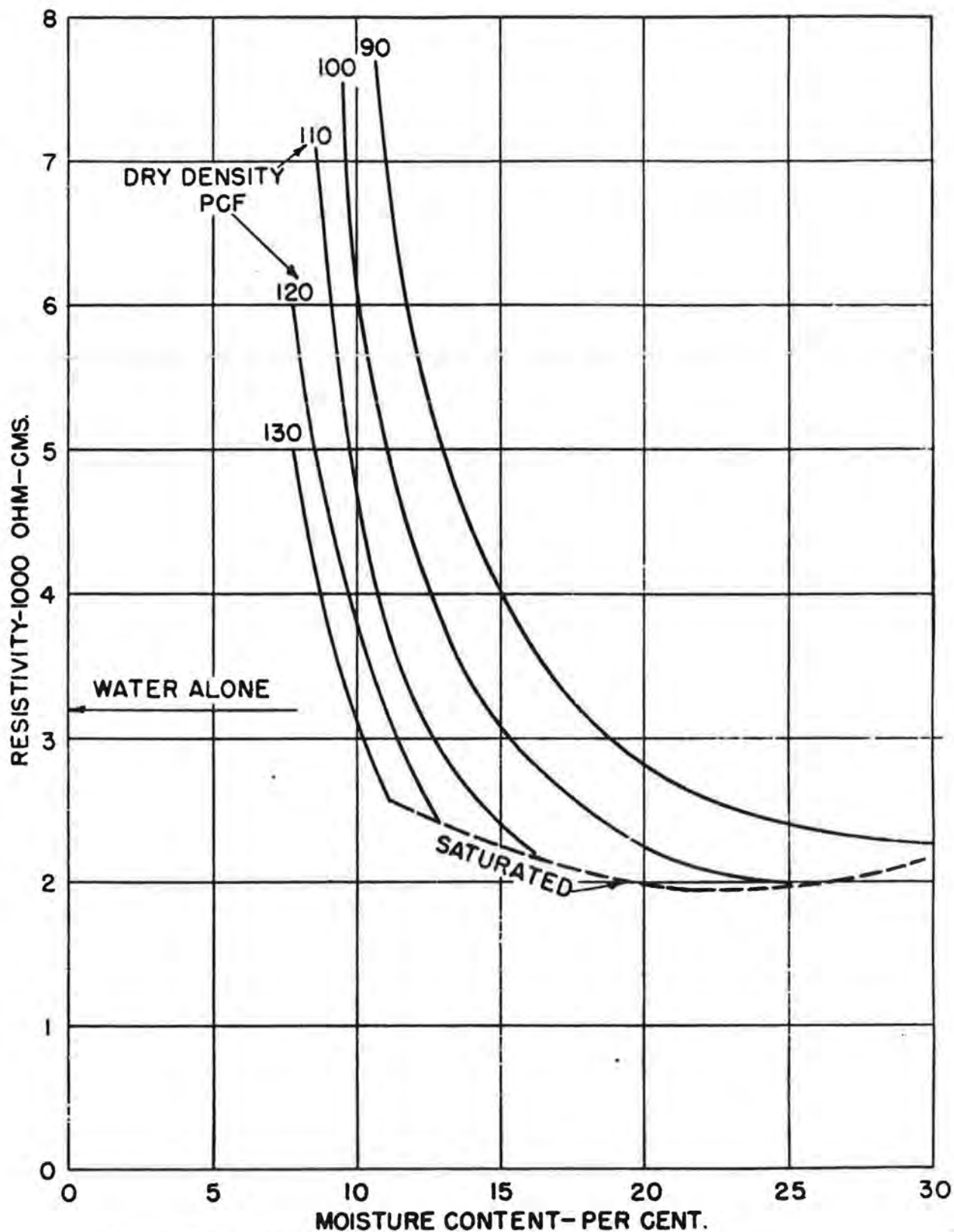

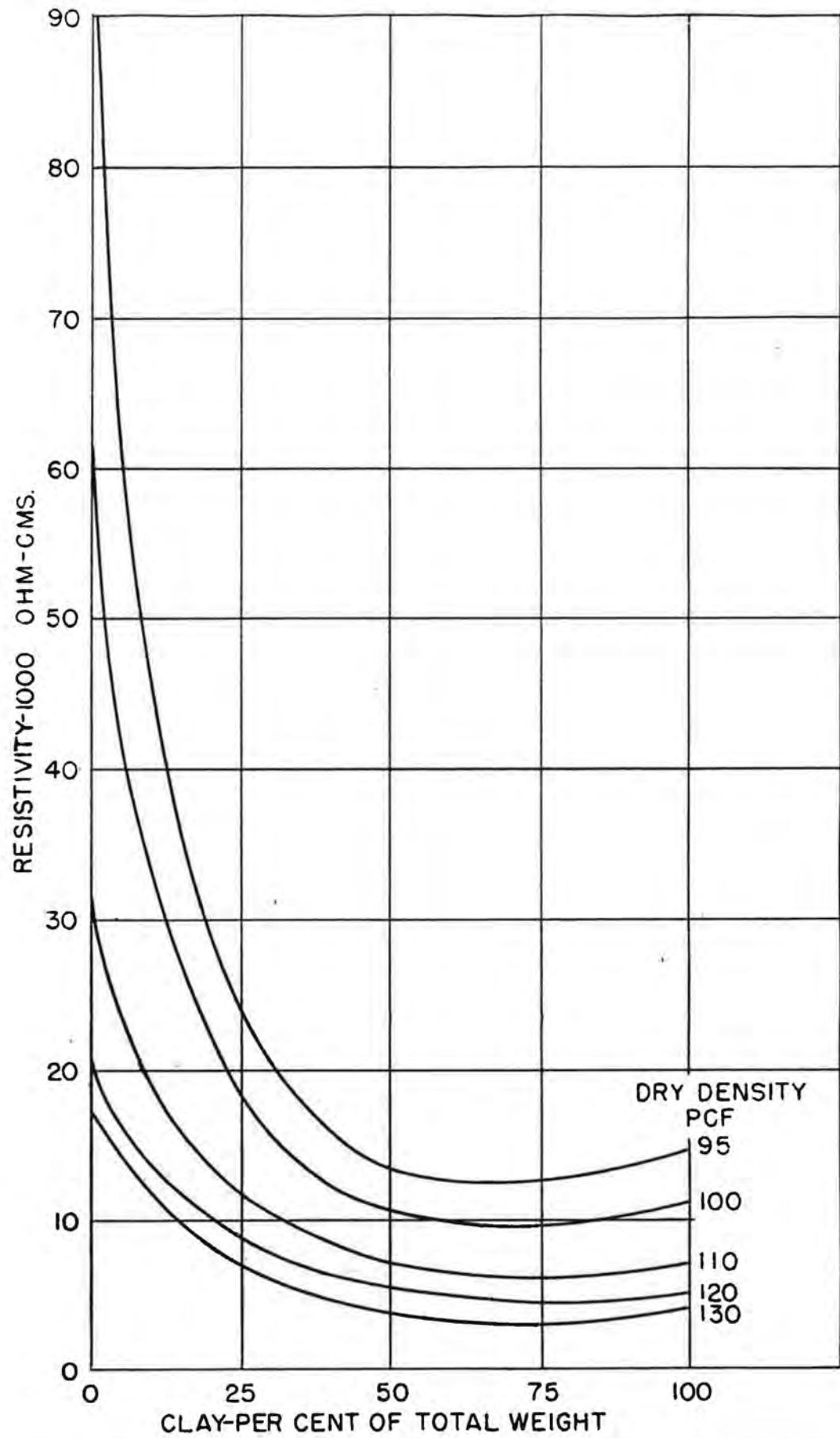Figure 26. Resistivity of clay at different moistures and densities.

Figure 27. Resistivity of sand and clay mixtures with 10 percent moisture.

COMPACTION

When a given compactive effort is applied to a series of samples (not extremely dry) with increasing moisture content, increased moisture reduces the surface tension permitting rearrangement into a denser structure. If any excess water can escape, there is no optimum moisture. This is true for very permeable materials or for fine soils if the load is left on as shown by the curve marked "consolidation" in Figure 19. For quickly applied loads on fine soils, the density decreases with increased moisture at about 85 percent saturation where the air permeability becomes very small and requires the exudation of water for further densification. Continued impact compaction beyond the optimum causes weakening due to formation of shear surfaces.

Density is increased by repetitions of even moderate loads if there is opportunity for rearrangement of particles—lack of cohesion in sands, water or dispersing agents in clay. Figure 20 shows the effect of several chemicals on densification under repetitive loading.

The distribution of moisture is important to the strength of fine soils. Figure 21 shows the increase of strength with time as the moisture distribution is equalized. Non-uniform moisture distribution may be caused by poor mixing or by expansion on shear planes from kneading compaction. The strength was constant for good mixing with static compaction which formed no shear planes. The thixotropy of undisturbed soils after disturbance also depends upon the redistribution of moisture after shearing.

Figure 22 shows less strength for samples molded with limited moisture than for samples dried from a wet state to the same moisture and density. This is due to the less effective distribution of moisture in the "as molded" samples.

CAPILLARY FLOW

Each soil has a characteristic moisture distribution above the water table for no-flow as shown in the left of Figure 23. If evaporation occurs at the surface, the moisture is reduced, especially if there are sand layers which, at some distance above the water table, have less permeability than fine soils. For downward flow, such a sand layer may actually retard drainage. Many earth roads, with an average condition as shown in the right of Figure 23, failed when surfaced because the moisture increased toward the no-flow condition. Buried bituminous layers have been used to prevent this upward flow. In a few cases parts of fills have been encased in bituminous mastic or sheet plastic.

The upward flow of capillary water has required impervious covers over soil to prevent condensation in unventilated spaces under buildings. Any salts in the soil will be brought to the surface, often causing pavement failures in irrigated arid lands and generally requiring drainage as an adjunct to irrigation. This also causes soluble stabilizers to migrate to the surface to be washed away. Migrating of cementing agents to evaporation surfaces sometimes causes "case-hardening" of cut or natural surfaces.

TEMPERATURE

If a mixture of air and water is heated with no volume change, pressures are developed as shown in Figure 24. For a given temperature change, the maximum pressure is for no air at the freezing point. This may be a factor in spring break-up. The maximum volume change at constant pressure (see Fig. 25) is at high temperatures with a maximum of air as long as the air cannot escape.

These temperature effects have caused water to come up through pavements, reduced the strength of base courses, caused higher soil permeability at lower temperatures, prevented base drainage after a cold rain and caused drainage in fair weather with rising temperatures.

ELECTRICAL

The movement of water through soil by direct current has been used for drainage stabilization, increasing friction of piles, reducing friction of plows and replacing chemicals in soil. When soil settles through water in the hydrometer test, a small

voltage may be measured. This streaming potential produces several millivolts in a permeability test (using a lucite cylinder). Such a potential may be used to indicate subsurface flows, perhaps even by water diviners.

Variation in electrical resistivity is used in geophysical prospecting, detection of soluble salts and indication of moisture content where density is controlled. Figure 26 shows the variation of resistivity with moisture and density. Figure 27 shows a minimum resistivity for sand clay mixtures where the limited amount of water is balanced against the conductivity of clay.

CONCLUSION

Without water, the mechanics of soil would be quite simple. Pressure or tension on water in the pores of the soil often controls its strength and volume change. Movement of water may change these pressures as well as cause movement of particles and change the chemical composition. The distribution of water and the arrangement of the particles, that is, the structural arrangement, are as important as the over-all composition and total moisture and density.

Movement and Distribution of Water in Soil in Relation to Highway Design and Performance

D. CRONEY, J. D. COLEMAN, and W. P. M. BLACK, Road Research Laboratory, Department of Scientific and Industrial Research, United Kingdom

Introductory Remarks by the Chairman

In 1907, Buckingham published his pioneering work on the capillary potential. Ever since, agronomists and engineers have tried to develop this concept into a practically useful methodology. With respect to highway engineering, Mr. Croney and his associates at the Road Research Laboratory have made the most outstanding contribution in this development. The present paper is a lucid exposition of this concept and what they have done with it.

The essence of science is abstraction and generalization; the essence of engineering is to use abstractions and generalizations as guides to treatment of actual systems possessing specific geometrical and material properties. This means that before becoming useful engineering tools, abstract concepts must be reinvested with real properties and must be modified according to the actually obtaining conditions, if the latter differ from those that had to be assumed in the formulation of the theoretical concept. Some of the basic assumptions on which the capillary potential concept is based, such as equilibrium conditions and reversibility, are seldom fulfilled in actual road soil structures. There exists an urgent need for more information concerning the extent to which such actual deviations from the theoretical assumptions determine the behavior of real systems. The work reported by Deryaguin and Melnikova and by Hallaire in this symposium touches on a number of problems that must be solved before we can be sure that we know the real limits within which we can safely employ this valuable and attractive concept of the capillary potential. This acknowledged need does not diminish, however, our great respect for the fine work and achievement of Mr. Croney and his associates.

● THE ENGINEER responsible for the design of pavement foundations is primarily concerned with the soil above the water table in which the pore pressures are negative. In this respect he may be regarded as having more in common with the agriculturalist than with his colleagues dealing with the soil mechanics of deeper foundations. At the Road Research Laboratory in Great Britain the importance of the energy concept of soil moisture, developed by agricultural research workers, has for long been recognised and over the past 12 years its application to subgrade moisture problems has been systematically developed.

In the saturated zone beneath the water table the fundamental importance of the soil moisture suction or tension in determining moisture flow is not immediately apparent. It is only in the last few years that the growing interest in the strength characteristics of unsaturated soils has focused general attention on the influence of soil suction both in relation to soil moisture migration and shear strength. It is felt therefore that this may be an appropriate time to summarise some of the work in this field carried out by the Road Research Laboratory since the World War II.

THE THERMODYNAMIC APPROACH TO SOIL MOISTURE MOVEMENT

Moisture content on a weight basis provides the simplest method of evaluating the water in soil. At the same time the inadequacy of moisture content as a criterion when the mechanical and physical properties of the soil/moisture system are being considered, has become apparent. To establish moisture equilibrium, water may

flow from a granular soil of low moisture content into an adjacent clay soil of initially much higher moisture content.

Even in a mass of uniform soil, moisture migration may take place from areas of low moisture content to areas of higher moisture content, depending on the previous moisture history of the soil. Moisture content does not therefore provide the gradient responsible for liquid flow. Similarly the work necessary to extract or displace moisture in soil is not fundamentally related to the moisture content on a weight basis. It seems reasonable to suppose that the stresses required to shear or compact the soil are more likely to be related to the stress condition of the water than to the weight of the water.

It was considerations of this type that led agricultural research workers, commencing with Buckingham (1) as long ago as 1907 and followed by Thomas (2) and Schofield (3), to develop the energy approach to soil moisture problems. This early work has led to a general thermodynamic approach which enables equilibria following all reversible changes of pressure, volume and temperature in the soil/water/air system to be expressed mathematically (4). Although not quantitatively applicable to irreversible processes such as compaction and shear, energy concepts, as is shown later in this paper, provide a powerful adjunct to the standard soil mechanics approach to such processes.

Figure 1. Variation of soil vapour pressure with temperature.

In a soil mass, the potential gradient causing water to flow from one point to another may be one of hydrostatic pressure, of vapour pressure or of both in combination. Under uniform temperature conditions, the variation of vapour pressure with moisture content is small for soils at the moisture contents likely to be found in practice, as is
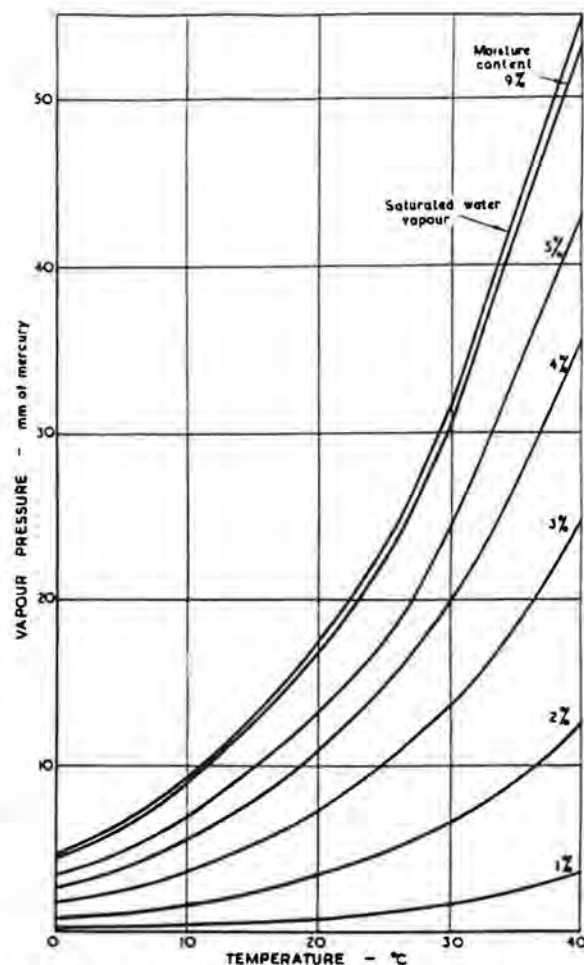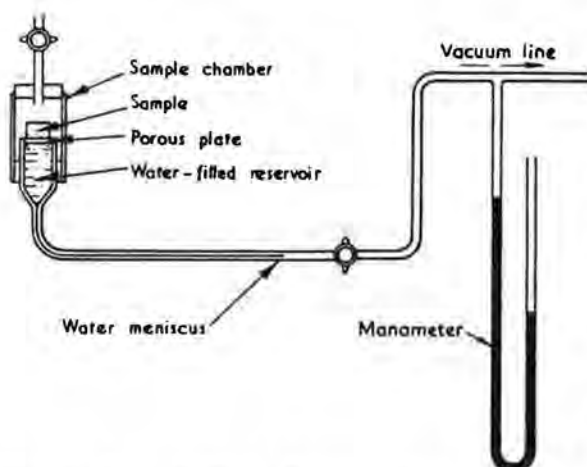

Figure 2. Method of measuring soil suction.

shown in Figure 1. It is only in very dry soil that vapour-pressure gradients are likely to be appreciable, assuming uniform temperature conditions. On the other hand the large variation of vapour pressure with temperature does give rise to considerable gradients of vapour pressure when temperature differences exist. In considering uniform temperature conditions, however, the contribution of vapour flow to soil moisture migration can be neglected.

The surface forces by which water is retained in the soil structure are responsible for the pressure reduction (below atmospheric pressure) known as the soil suction or tension. In Great Britain this term has been reserved for the pressure reduction in a small sample of the soil measured when the sample is entirely free

from externally applied stresses. Figure 2 shows a simple apparatus used for the detection and measurement of soil suction, in which the suction of the soil moisture is balanced by a suction applied to the system. On the pF scale of measuring soil suction, the pF value of the soil moisture is equivalent to the common logarithm of the suction expressed in centimeters of water. The letter F represents the free energy of the soil when not subjected to external stress (3).

In the ground, each small element of soil is subjected to stress by the surrounding soil and hence indirectly by externally applied loads. Since this stress may be effective in changing the stress-free suction of the moisture in the element, the pressure of the water in the soil pores, generally known as the pore water pressure, can be regarded as the algebraic sum of two components, viz., the suction and the effect on the suction of applied stress. The effect of external

Figure 3. Determination of compressibility factor for soil by measuring the change in pore water pressure caused by an applied load.

stress on pore water pressure can be measured by the apparatus shown in Figure 3. The suction of a small unloaded sample is first measured by an apparatus inverted but otherwise exactly similar to that shown in Figure 2. The sample, enclosed in a thin rubber membrane, is then subjected to increments of all-round pressure by introducing mercury into the concentric external tube. The effect of each increment of external pressure is measured by adjusting the suction applied to the system to give a static condition of the meniscus in the flow-tube.

If u is the pressure of the pore water when the sample is loaded (the pore-water pressure), s is the suction in the sample when the soil is free from external loading and P is the applied pressure, the relationship between these quantities can be expressed by the equation

$$u = s + a P \qquad (1)$$

where a is the fraction of the applied pressure P which is effective in changing the pressure of the soil water. The limits of a are therefore 0 and 1.

If the change of pore-water pressure with applied pressure, determined by the apparatus shown in Figure 3, is plotted in the manner shown inset on that figure, the intercept on the vertical axis corresponds to the suction s and the slope of the pore-water pressure/applied pressure relationship gives the value of a, to which the term "compressibility factor" has been applied. For moderate applied pressures the relationship between pore pressure and applied pressure is found to be approximately linear except when the suction is numerically small in relation to the applied pressure, which is likely to be the case when the soil is close to saturation. Figure 4 shows measurements of the compressibility factor carried out on a sand, a heavy clay and an intermediate soil. For the unsaturated sand the value is close to zero, although a value approaching unity would be obtained for the same soil in the saturated condition. For the heavy clay the value is substantially 1 and for the silty clay 0.3.

Since the value of suction for a soil increases as the soil becomes drier any local change in moisture content will cause a redistribution of water in the soil. Similarly the application of a local pressure to a soil mass may set up hydrostatic pressure gradients tending to cause a redistribution of moisture. In either case, Eq. 1 can be used to calculate the magnitude of the redistribution, as is shown later in this paper. In making such calculations the possibility of irreversible changes in the suction of the soil due to changes in the soil structure, that is, the particle arrangement, must be taken into account.
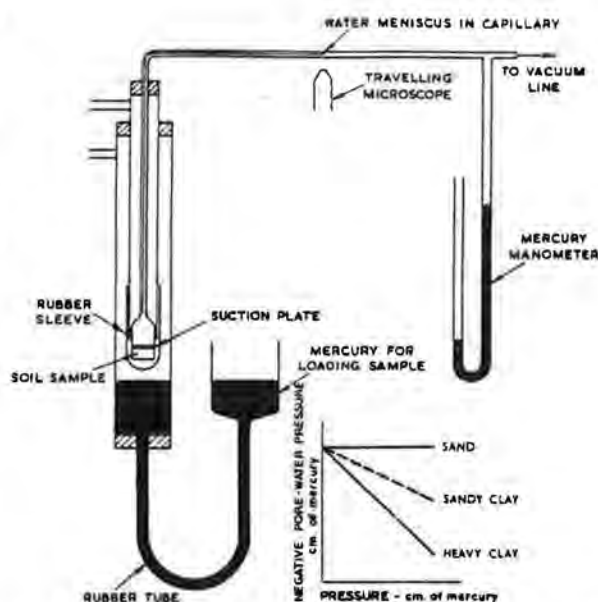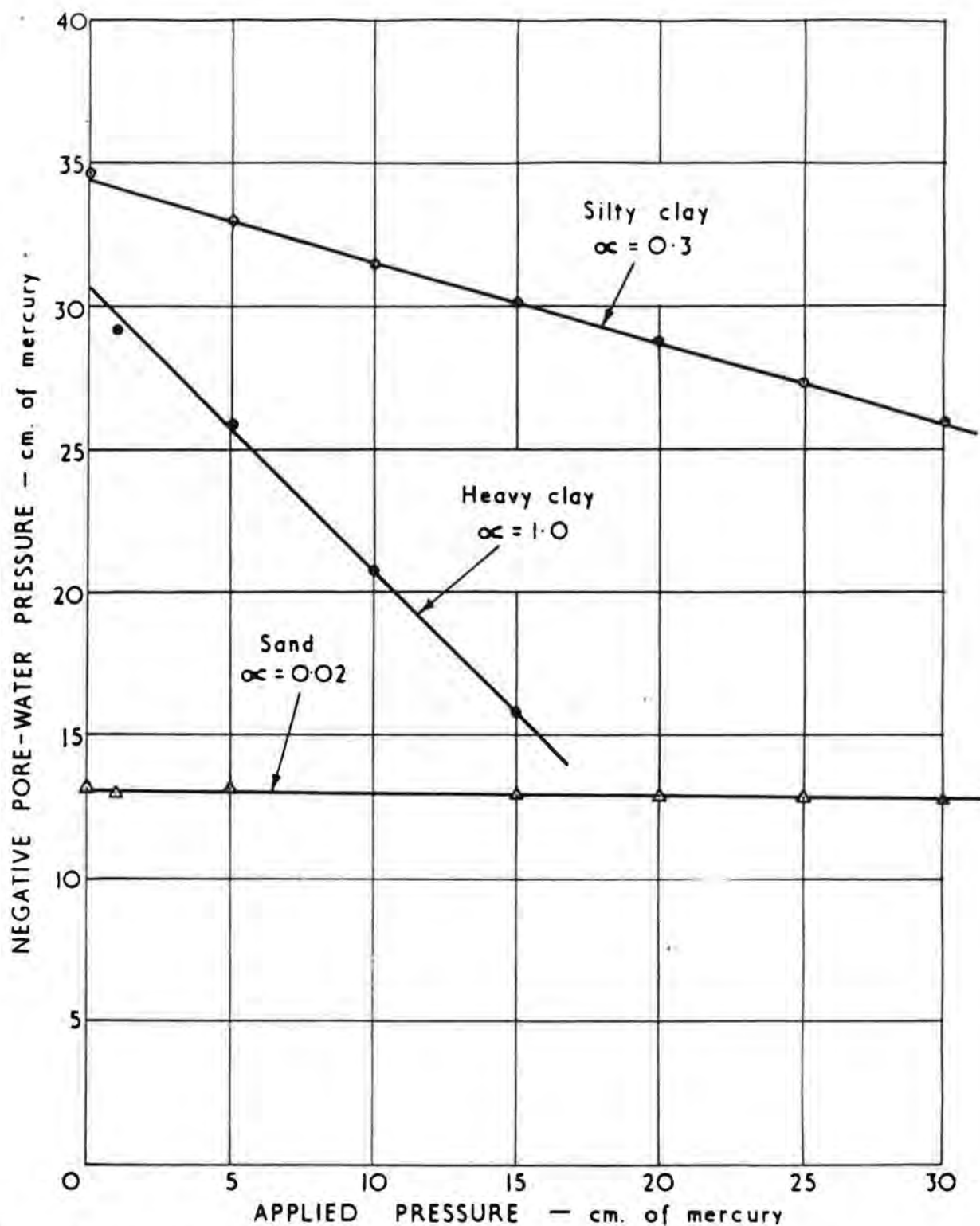
Figure 4. Relationship between pore-water pressure and applied pressure for various soils.

The migration of water in soil is accompanied by some change of volume. This may be reversible or irreversible again depending on whether any permanent structural modification has occurred due to the moisture movement. The subsoil within a few feet of the earth's surface will by virtue of its relatively exposed condition tend to behave reversibly for any normal seasonal climatic fluctuations.

Volume changes resulting from applied pressure can be measured unidirectionally
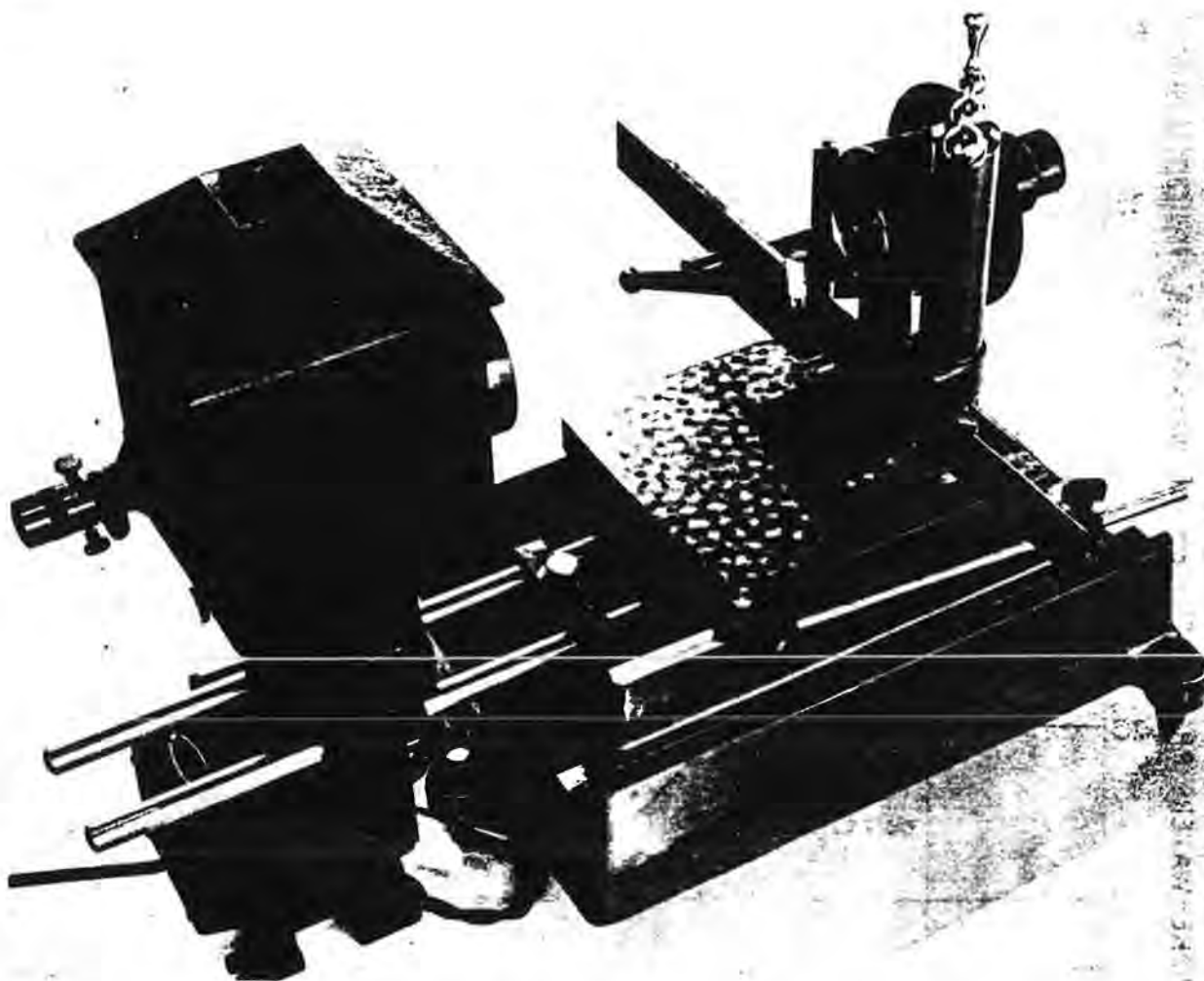
Figure 5. Optical projector used to measure the shrinkage of soil.

by the oedometer apparatus or three-dimensionally by a triaxial cell. The mercury displacement method has been used for studying the shrinkage and swelling of soils with change in moisture content. In recent years, however, an optical projection method developed at the Road Research Laboratory has been found to be more convenient and capable of greater accuracy. An engineering profile projector (as used for screw threads) is used. A cylindrical sample of the soil up to 2 cm in height and in diameter is placed in the focal plane of the projector, Figure 5, and an image is obtained at a magnification of about 50 times. Diameter and height measurements are made in three planes and the volume of the sample is computed. To overcome the difficulty of focusing the flat ends of the sample, the latter is placed in a rotating stage between upper and lower sets of knife-edges, each set consisting of three knife-edges mutually at 120 deg. The height measurements are made between the projected images of the knife-edges. In studying soil shrinkage, the sample after the initial measurement of weight and volume is allowed to dry in air for a few minutes, after which it is sealed in an enclosure to allow the moisture to equilibrate within the soil, before the next set of measurements is made. This process is repeated, the final stages of drying being carried out in the oven. Using this method the shrinkage curve can be studied in detail, particularly the critical region for heavy clays where the shrinkage curve begins to deviate from the saturation line. Typical curves obtained by this method are shown in Figure 6.

Temperature gradients in soil give rise to vapour pressure differences, the magnitude of which can be deduced from curves of the type shown in Figure 1. In soils with continuous air voids a rapid transfer of moisture by a process of evaporation and con-

densation would be possible. Any equilibrium set up by a steady temperature gradient would be a dynamic one. The moisture transferred in one direction in the vapour phase would equal the liquid transfer in the other direction arising from the hydrostatic gradient created by vapour flow. The transfer of moisture by temperature gradients has been studied fairly extensively (5, 6, 7). Some results obtained many years ago at the Road Research Laboratory (6) are shown in Figure 7. The tests were conducted on sealed cylinders of soil 11 cm long compacted at various initial moisture contents, to the same dry density, that is, to various air contents. The ends of the samples were maintained at temperatures of 22 and 42 C and the moisture distributions were obtained by slicing the specimens after preliminary tests had shown that moisture equilibrium had been attained.

Although these results confirm that the movements of moisture are greatest in the least saturated soils, that is, those in which transfer in the vapour phase is likely to be greatest and transfer in the liquid phase least, the fact that some transfer occurred
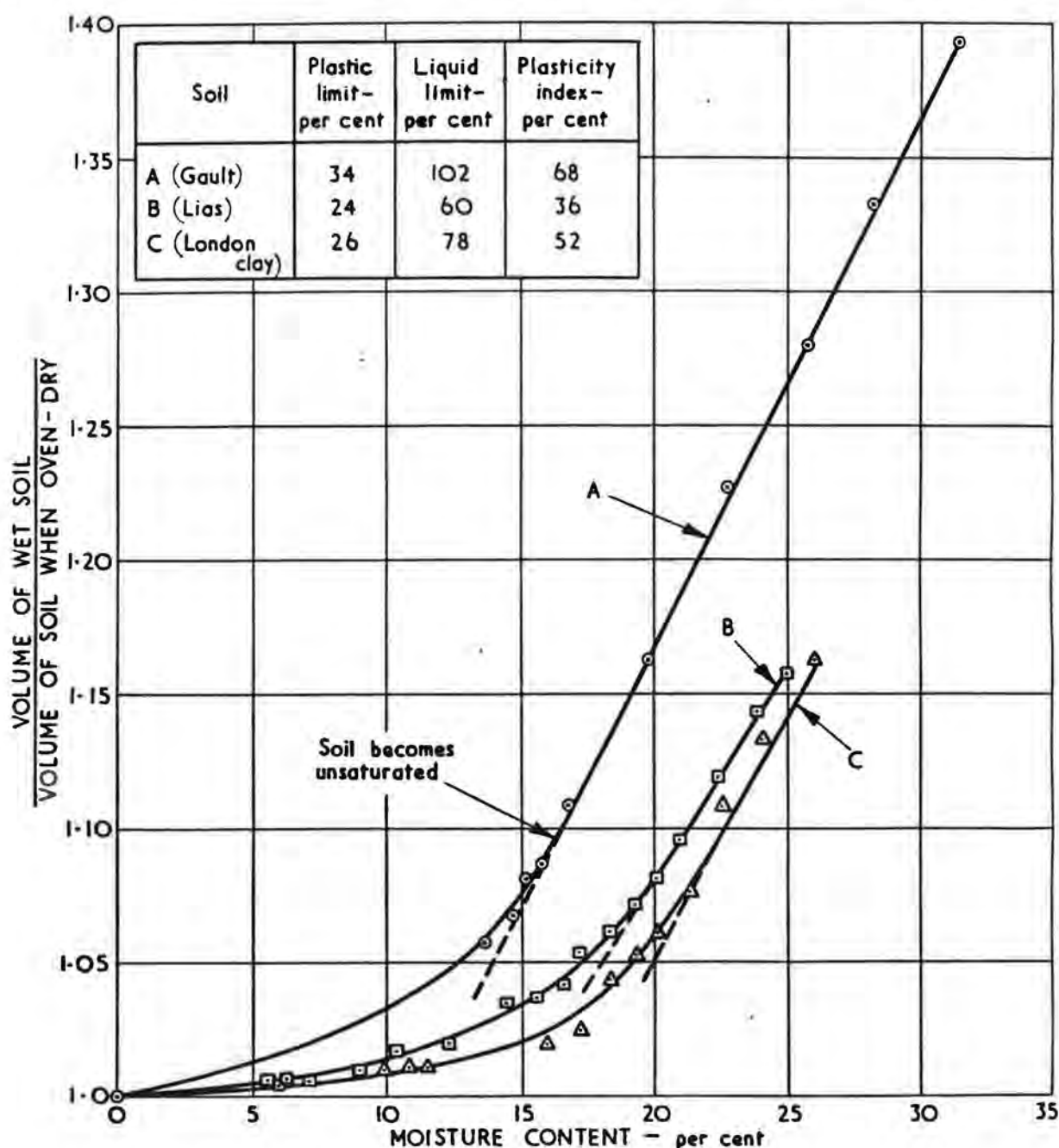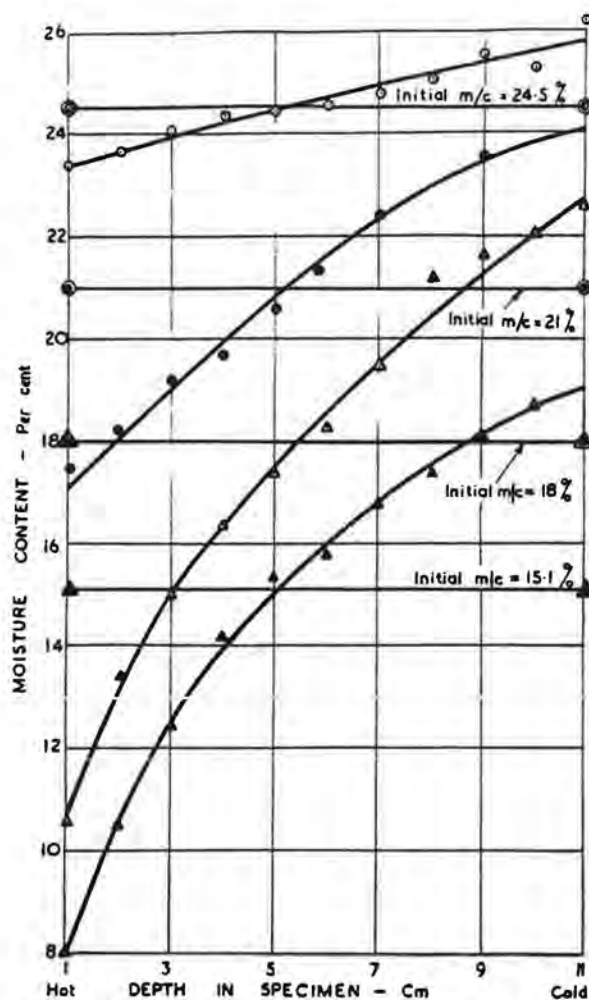

Figure 6. Shrinkage curves for three heavy clay soils.

Figure 7. Effect of moisture content on equilibrium moisture gradient in clay specimens at a dry density of 97 pcf.

Figure 8. Correction to be applied to pF of soil at 20 C to obtain pF at other temperatures.

in the soil when the air content was less than 5 percent of the total volume, suggests that some other mechanism may be present. Theoretically the effect of temperature on soil suction can be shown to be small (8). Figure 8 shows that raising the temperature of a soil from 20 to 40 C would reduce the suction by about 0.015 units on the pF scale. Thus, although a small hydrostatic gradient would be created tending to move water from the hot end of the samples, referred to in Figure 7, to the cold end, the gradient would hardly be sufficient to cause any appreciable change in moisture content. Work recently reported from France may throw more light on the mechanism of moisture transfer resulting from temperature differences (9).

It has been established in some actual subgrades that wetting has occurred subsequent to construction, even in quite arid
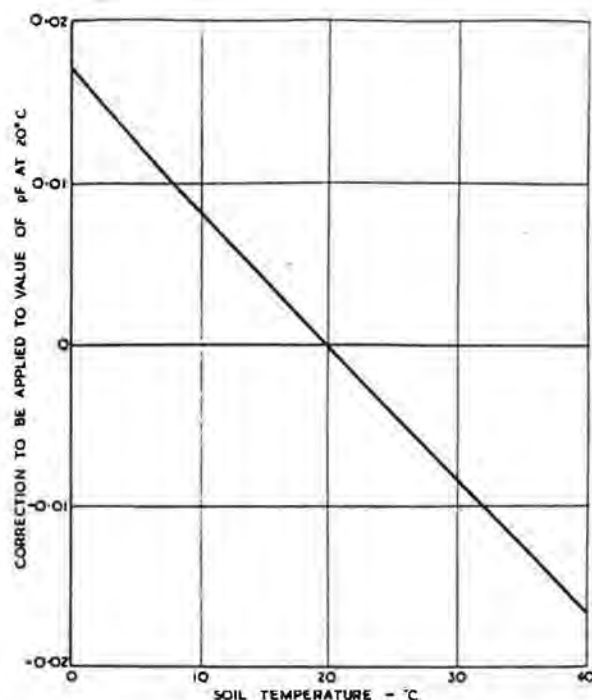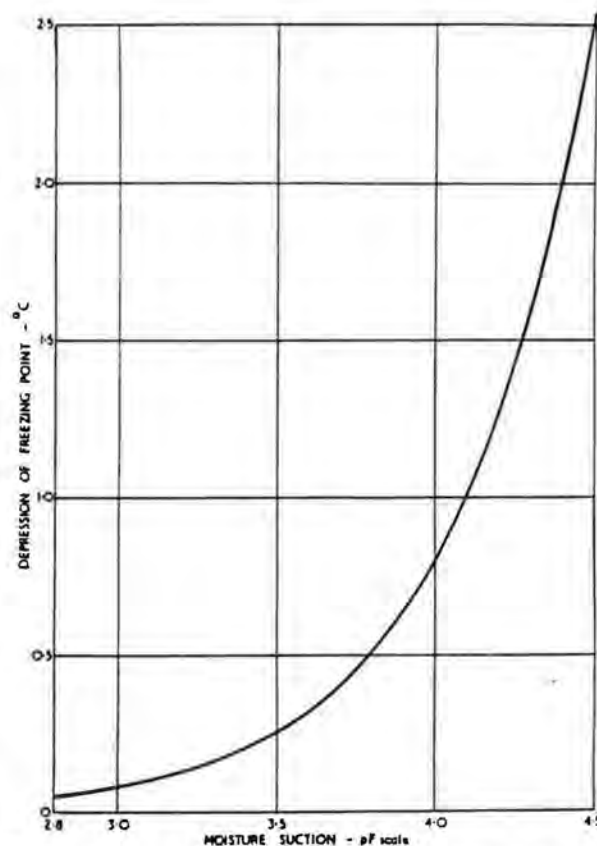

Figure 9. The relationship between suction and freezing point depression of moisture in porous materials.

climates. This moisture transfer could be due to liquid movements, or vapour movements. Theoretical studies (10), in which the transfer of heat and moisture in the soil are regarded as a coupled system, have suggested that for temperate climates there is unlikely to be any net upward movement of water caused by vapour transfer, the moisture merely rising and falling with season. (Any linear analysis describing the subgrade moisture movements caused by a moderate annual variation of pavement temperature is likely to lead to the same result.) For more extreme climates, however, the analysis describing the coupled heat and

Method	pF Range
Suction plate or pressure plate	0 - 3
Pressure membrane	0 - 6.2
Centrifuge	3 - 4.5
Freezing point	3 - 4
Vacuum desiccator and sorption balance	5 - 7
Calibrated electrical absorption gauges	3 - 7

moisture flow becomes non-linear, and a net upward flow of moisture is predicted. Studies of an airfield pavement abroad (11) have shown quite large subgrade moisture changes with season, which may be associated with vapour movement.

The forces by which water is retained in soil lower the freezing point. The thermodynamic relationship between soil temperatures below the freezing point of free water and the suction of the unfrozen soil moisture was first deduced by Schofield (3). This relationship, Figure 9, enables the suction distribution associated with any given temperature distribution within the frozen zone to be calculated. The suction curve then permits the amount of water frozen initially by this temperature distribution to be found. The extent to which water will move into the frozen zone to cause the phenomenon known as frost-heave, depends on the suction of the surrounding unfrozen soil, as
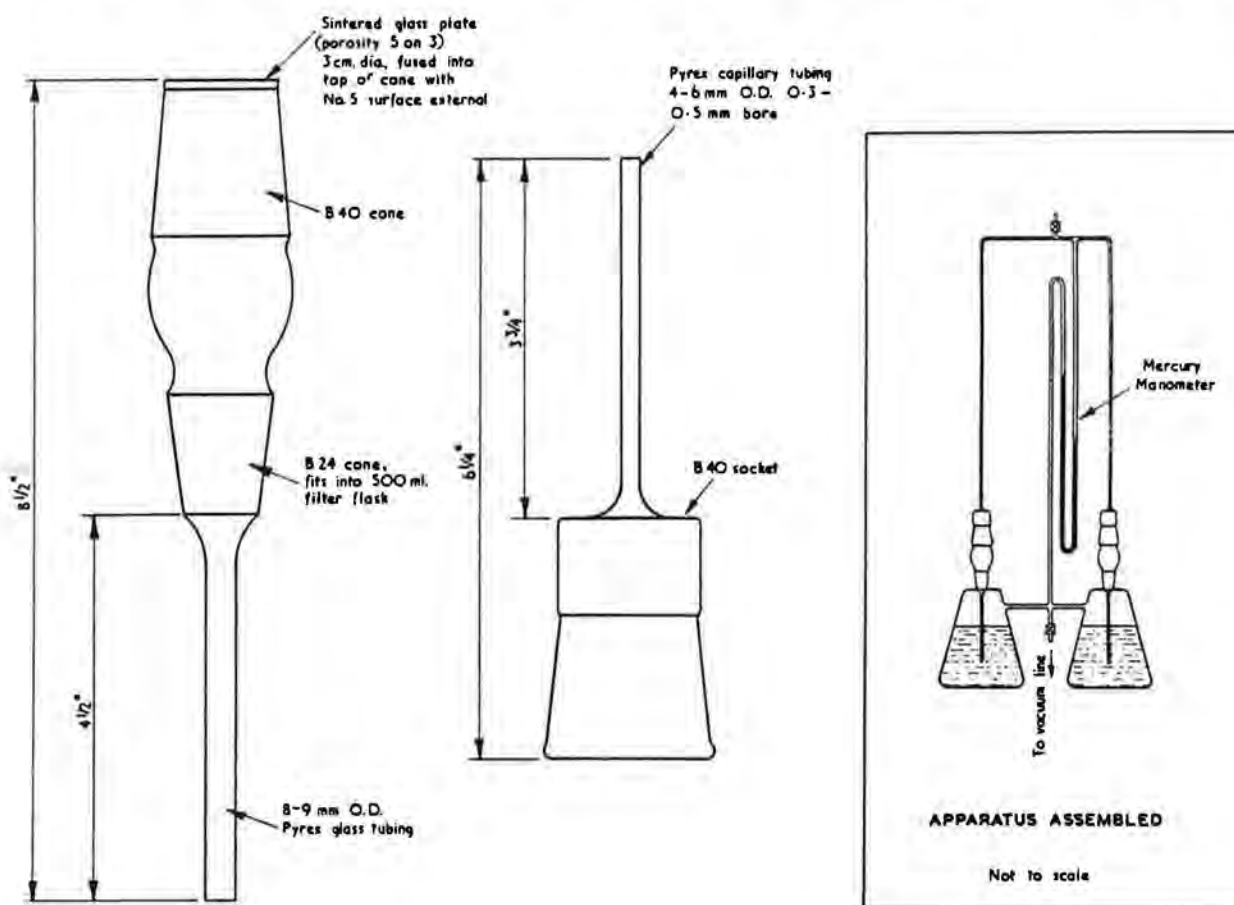

Figure 10. Suction plate apparatus.

well as on that of the frozen soil, and on the permeability to liquid flow of the soil at the high suctions present during freezing. The problem again is one of coupled heat and moisture transfer. The comparative rarity of severe frosts in Great Britain has not encouraged further research on the relation of soil suction and frost heave, but work is in progress in the United States (12).

THE RELATIONSHIP BETWEEN SOIL SUCTION AND MOISTURE CONTENT

Measurement of Soil Suction/Moisture Content Relationship

The thermodynamic approach to soil moisture movement can be used to evaluate moisture migration in terms of moisture content on a weight basis if the appropriate relationships between suction and moisture content are known.

There are a number of ways of determining these relationships. These are listed in Table 1 together with the range of suctions which each covers. Most of the methods can also be used in research for bringing soil samples to a predetermined suction condition.

Since the methods have been described fully elsewhere (13) it is not intended to discuss them in detail here. Mention may be made, however, of very recent developments in connection with the suction plate, pressure membrane and sorption balance techniques.

The form of suction plate equipment in use at the Road Research Laboratory is shown in Figure 10. De-mountable chemical glassware is used, the No. 5 sintered-glass porous-plate being fuzed into the narrow end of a No. B. 40 cone. This is fuzed at its other end into the wider end of a No. B. 24 cone to the narrow end of which is also fuzed a glass tube of about 5 mm internal diameter. The No. B. 24 cone fits into a female joint at the mouth of a standard filter flask, the length of the glass tube on the filter unit being adjusted so that it reaches almost to the bottom of the flask when the apparatus is set up. The filter unit is filled with air-free water and the flask itself contains air-free water above the level of the tube connected to the filter unit. A reduced pressure of between a few centimetres and one atmosphere can be applied to the sintered plate by evacuating the space in the filter flask, the minimum being determined by the difference in level between the plate and the water in the flask. A glass cap is fitted over the No. B. 40 joint carrying the sintered plate, and this is connected by a tube to what would otherwise be the open end of the manometer recording the pressure in the filter flask. This minimises fluctuations of pressure in the apparatus due to variations of atmospheric pressure and temperature. The suction/moisture content relationship is explored by allowing samples to reach moisture equilibrium successively with plates operating at a range of suctions. The equilibrium wet weight for each suction is measured and the moisture contents on a dry-weight basis are calculated from the dry weight determined at the conclusion of the tests.

In the pressure membrane apparatus, originally devised by Richards (14) and Woodruff (15), the sample is placed in contact with a cellulose membrane, which is itself in contact with water at atmospheric pressure. The air pressure surrounding the sample is increased to produce a pressure differential between the water in the soil and the water in the membrane. Moisture leaves the sample until the suction of the soil is numerically equal to the applied pressure. The suction/moisture content relationship can then be examined by carrying out tests at increasing suctions. For research purposes, the range of this method, previously regarded as pF 0 - pF 5.0, (16) has been extended at the Road Research Laboratory to suctions as high as pF 6.2, the latter value involving air pressures of 1500 atmospheres. The apparatus is shown photographically in Figure 11 and the constructional details can be seen from Figure 12. In carrying out a test, the sample is placed symmetrically on the membrane which is supported, in the manner shown, on a smooth sintered alloy-steel plate, which is itself in contact with water at atmospheric pressure. The cylinder is then bolted in position and the apparatus is mounted in the hydraulic loading press with the piston so arranged that the Bridgman seal is above the side inlet port. Compressed air at a pressure of about 1500 psi is then introduced into the cylinder through the port. When the piston is pushed down by the hydraulic press, the compressed air supply is auto-

matically isolated from the pressure cylinder as the piston passes the port. There-after any further downward movement of the piston intensifies the working pressure of the machine. No difficulty has been experienced in obtaining and maintaining pressures of the order 1500 to 2000 atmospheres. The actual operating pressure is deduced from the pressure gauge of the hydraulic press and the measured piston friction.

A new sorption balance, which has been developed at the Road Research Laboratory for studying the suction/moisture content relationships for comparatively dry soils, is shown in Figure 13. The sample of soil is allowed to reach moisture equilibrium with a known humidity and the equivalent suction is computed from the thermodynamic relationship between suction and humidity (4). The Joly spring balance enables continuous weighing to be made during the progress of equilibriation and a series of tests at different humidities can be conducted without the need to remove the soil from the apparatus. The detailed shape of the suction/moisture content relationship at low humidities gives a valuable indication of the mechanism of adsorption in soils containing different clay minerals, for example, where montmorillonite is present the suction curve oscillates slightly with moisture content. From such tests, surface areas per unit mass of clay fraction have been deduced for natural clay soils using
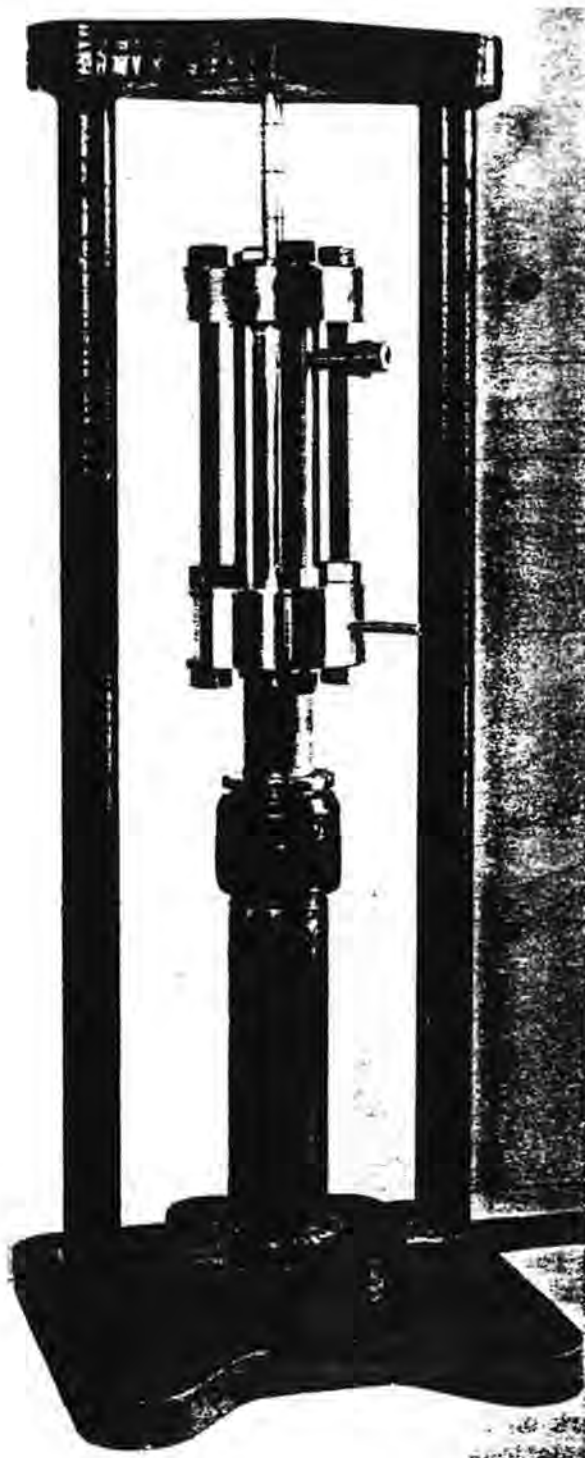

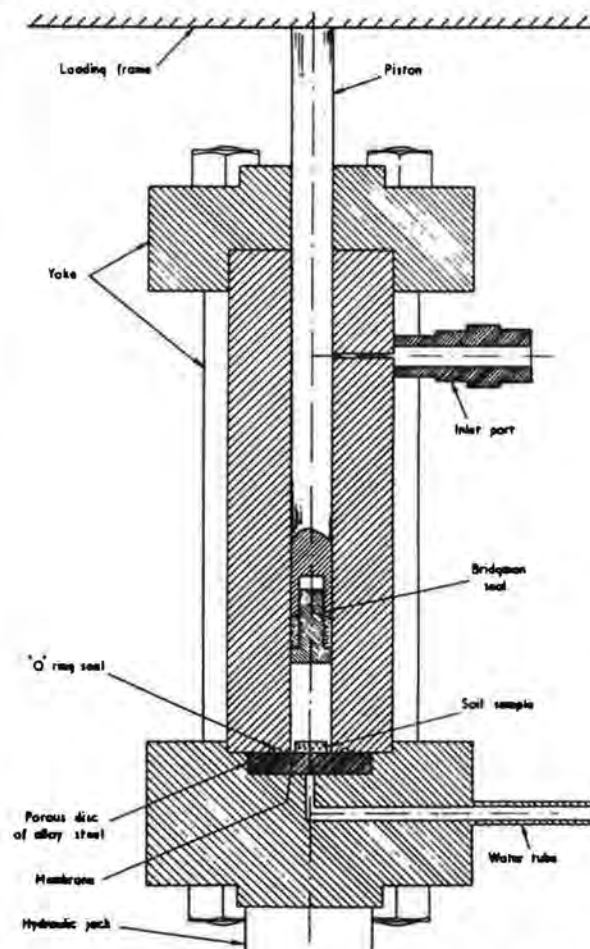Figure 11. Pressure membrane apparatus for use up to pF 6.2 (1500 atmospheres).

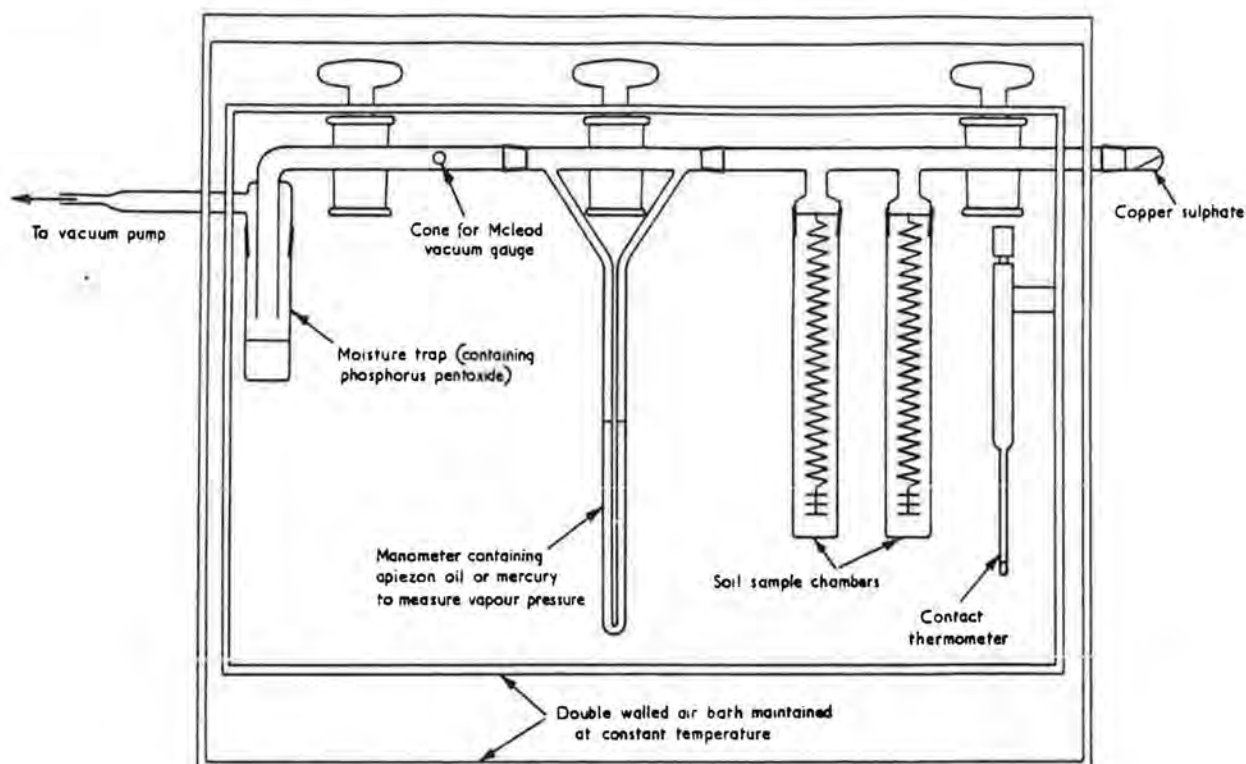Figure 12. Membrane apparatus for high pressure.

Figure 13.   Diagram of sorption balance.
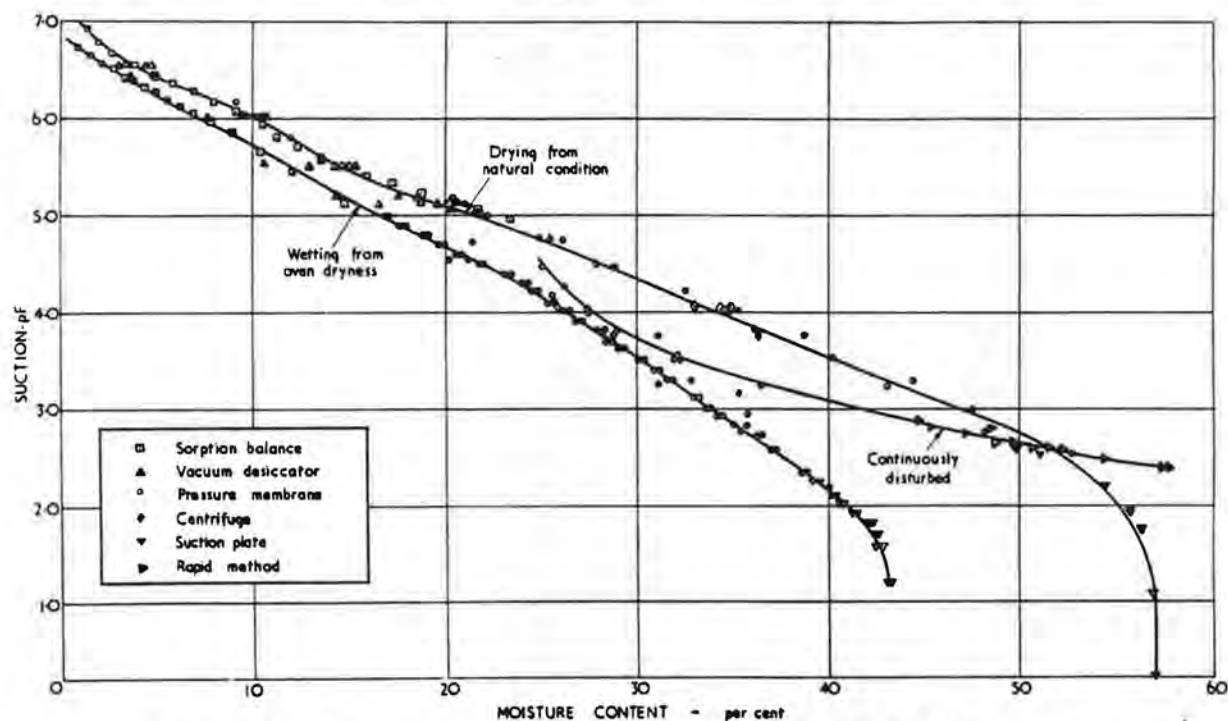
Figure 14.   Suction/moisture content relationships for Gault clay.

plots of the B. E. T. type, and the surface areas compared with published data for pure clays.   The results of X-ray analyses and nitrogen adsorption experiments at 195 C confirm that this may provide a useful approximate method for assessing the clay mineral constituents of natural soils.   Further work on these lines is in progress.

Figure 14 shows suction/moisture content relationships determined on a heavy clay soil in the undisturbed condition (a) drying from zero initial suction and (b) wetting from oven-dryness.   Use was made of all the methods listed in Table 1 (other than the

freezing point and electrical methods, which are not readily applicable to undisturbed soils) and the figure shows the substantial equivalence of the various methods where their ranges overlap.

Relationship Between Suction and Moisture Content. The nature of this relationship depends on the characteristics of the soil. It is convenient to consider three categories (a) incompressible soils and materials of rigid structure, (b) compressible soils which may remain saturated at high suctions, any change of moisture content being accompanied by a change in volume, for example, heavy clays, and (c) intermediate soils such as sandy clays.

Characteristic suction curves for two incompressible materials, in this case two grades of chalk (soft limestone), are shown in Figure 15. There is considerable hysteresis between the wetting and drying curves; this arising from the fact that pores may empty at a suction different from that at which they fill. The vertical part of the drying curves indicates that considerable suctions can be applied to the pore water without change of moisture content, the effect being only a change in the radii of the water menisci in the surface pores. When the air-entry suction of those pores is reached drainage
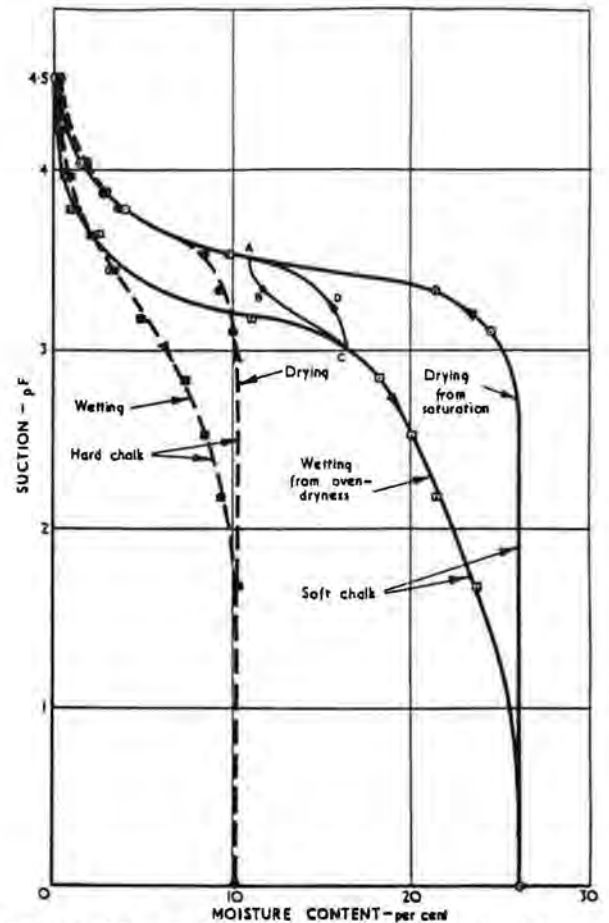
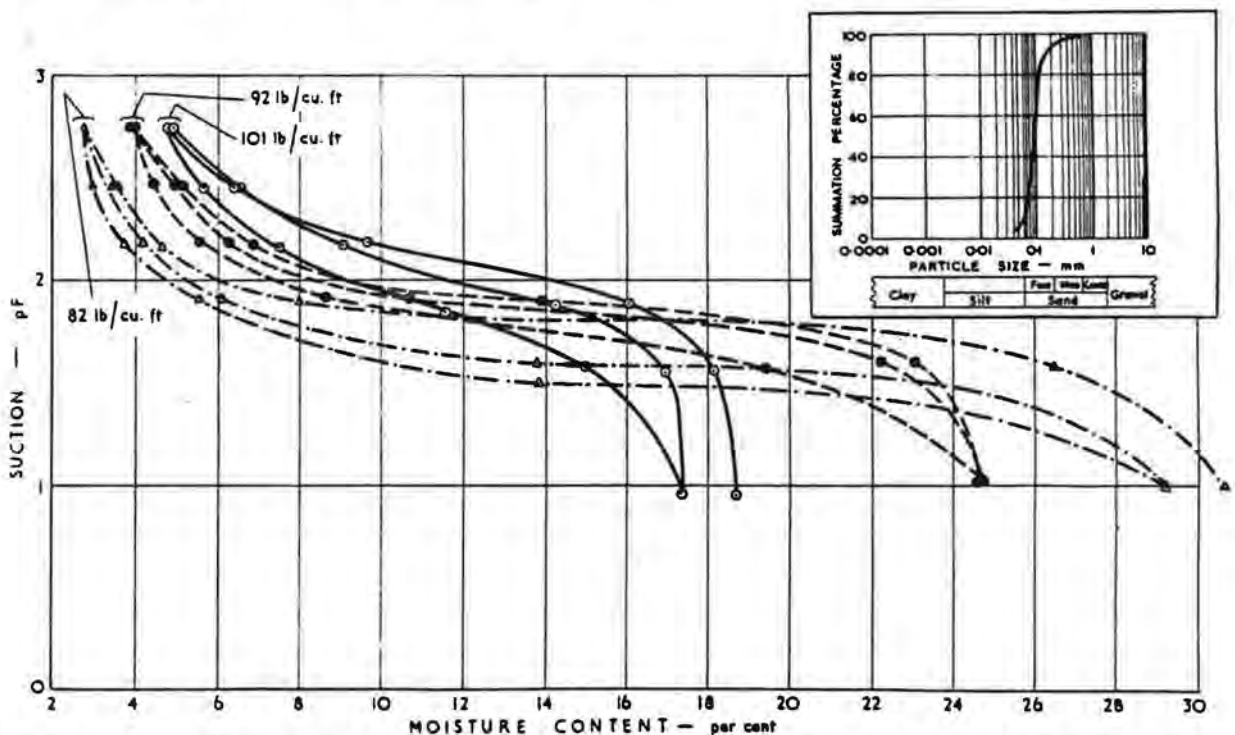Figure 15. Relationships between suction and moisture content for samples of hard and soft chalk.

Figure 16. Relationship between suction and moisture content at various dry densities for a fine sand.
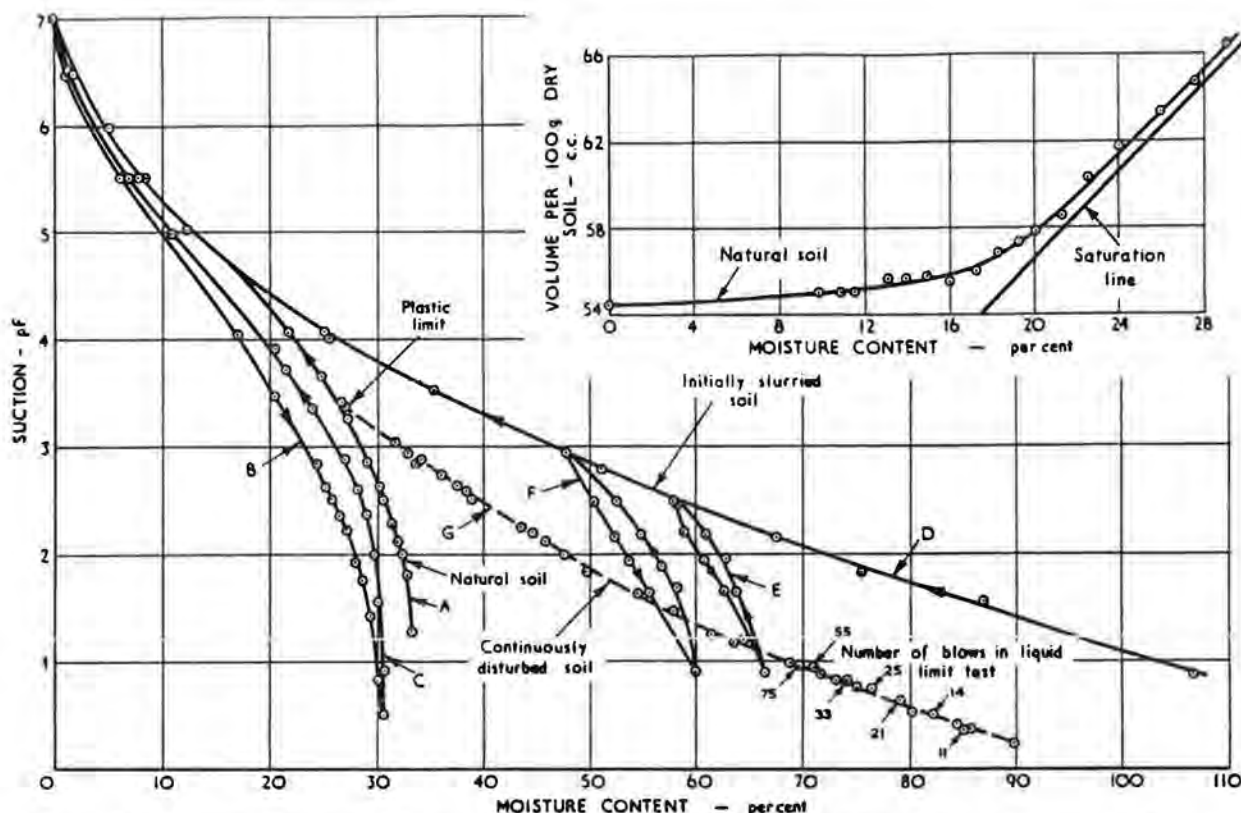
Figure 17. Suction/moisture content and shrinkage relationships for a heavy clay soil.

commences and is indicated by the change of slope of the suction curve. At high suctions the water may be discontinuous and concentrated at the points of intergranular contact. The difference between the two sets of curves in Figure 15 indicates different densities and hence different saturation moisture contents in the two materials. Much can be learned about the pore structure of rigid materials from the detailed analysis of tests of this type, and such tests may have further application, for example, to the pore size of acoustic absorbing materials.

When the material is incompressible (in that fluctuations of moisture content are not accompanied by density changes) but when it can nevertheless be compacted to various degrees, as with sands and gravels, the relationship between suction and moisture content can be expressed by a family of curves of the type shown in Figure 16. These curves cross because at low suctions the pore space available determines the moisture content, whereas at higher suctions the smaller pores associated with the higher densities remain full when the larger pores associated with low densities have drained.

The nature of the relationship for compressible heavy clay soils is shown in Figure 17. Curve A represents the drying condition for an undisturbed sample taken from the ground and initially wetted to a very low suction. Curve B refers to the same soil wetting from oven-dryness, and curve C is the second drying curve. The shrinkage curve corresponding to the initial drying condition (curve A) is shown inset and indicates that air does not enter the soil structure until the suction is in excess of pF 4. Curve D refers to the same soil drying from an initially slurried condition. The curve is identical with the drying curve of the natural soil (curve A) at suctions above pF 4.5, suggesting that the development of such high suctions produces a structural condition similar to that present in the natural ground. The intermediate suction loops E and F show the effect on the suction relationship of slurrying at lower moisture contents than that used in preparing the soil for the tests used to obtain curve D.

A most important and surprising fact which has emerged from tests such as these is that if the soil is sheared at constant moisture content (through an angle of about 60 deg) the suction changes to the value given by the dotted curve G, which is unique for

any particular soil. Thus, irrespective of whether the suction/moisture content value was initially represented by a point on curve A, B, C, D, E or F, on shearing the value would be found to be that given by curve G at the moisture content at which shear occurred. It follows from Figure 17 that for most natural conditions over-consolidated clays would increase in suction on shearing and normally consolidated clays would tend to decrease in suction on shearing. During shear tests such as are normally carried out in the triaxial apparatus, the suction component of the pore pressure will change in the shear plane or planes in this manner and the average pore pressure in the sample as a whole must also change to some extent in the same way. This may be either in the positive or negative direction depending on the initial condition of the soil. This could account for such changes of pore pressure reported during triaxial testing (17).

Curve G is not a suction curve in the same sense as the other curves shown on Figure 17. If a change of moisture content occurred in the soil after shearing the corresponding suction relationship would not follow curve G, but would rise above or fall below it depending on whether the soil was drying or wetting, and only by a repetition of the shearing process could the suction condition be brought back to curve G. The suction/moisture content condition of the soil during all tests involving shearing will be represented by a point on a curve of type G; thus all points obtained during a liquid limit test have been found to fall on that line as also does the plastic limit point, Figure 17. Tests on several heavy clays have indicated a value of about pF 3.4 for the plastic limit. One worker has attampted to obtain suction values for the liquid limit from drying curves carried out on slurried soils (18). Such a technique would give erroneously high values of suction.

Figure 18 shows the suction curves for samples taken from the principal clay deposits of the South of England. These curves were obtained on "undisturbed" samples and for the sake of clarity the drying condition only is considered. The heaviest clays shown, which are from the Gault stratum, contain a considerable amount of montmorillonite and in this respect have much in common with some of the black cotton soils of Africa and India. For comparison, tests on a sample of cotton soil from Nigeria are included in Figure 18 and the close similarity between the suction properties of this sample and those of the Gault clay samples is apparent. Although the Gault pre-
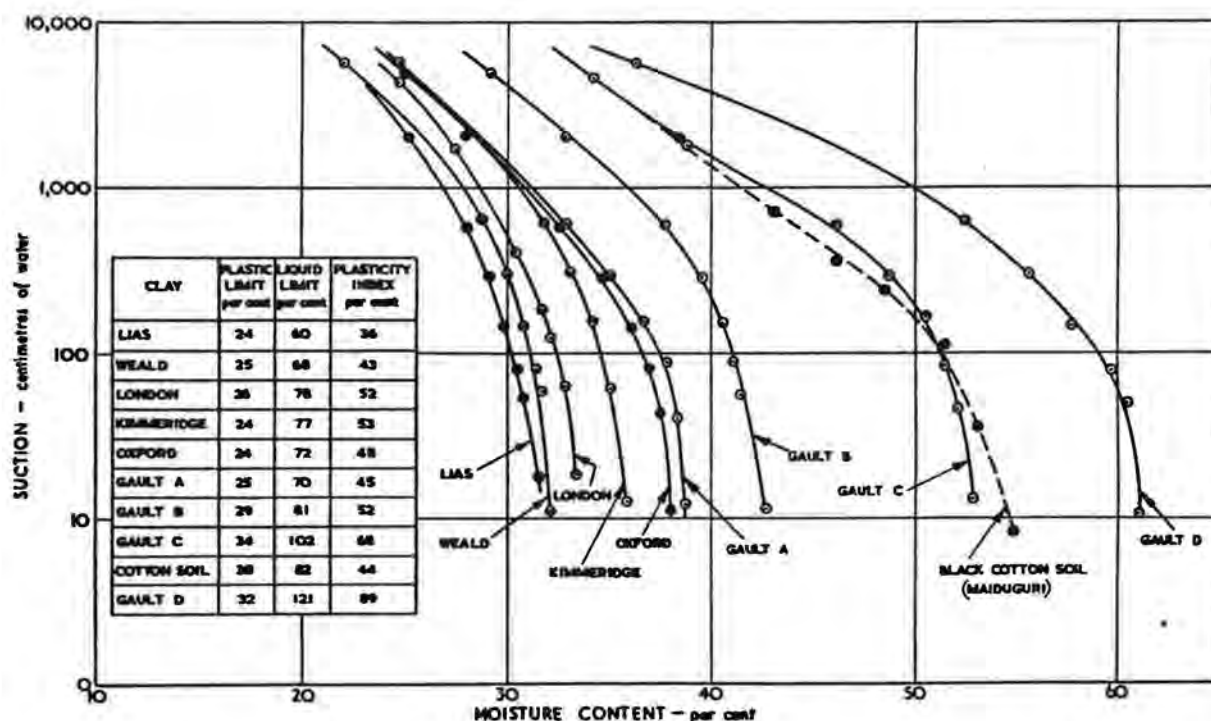

Figure 18. Relationship between suction and moisture content for undisturbed heavy clay soils.
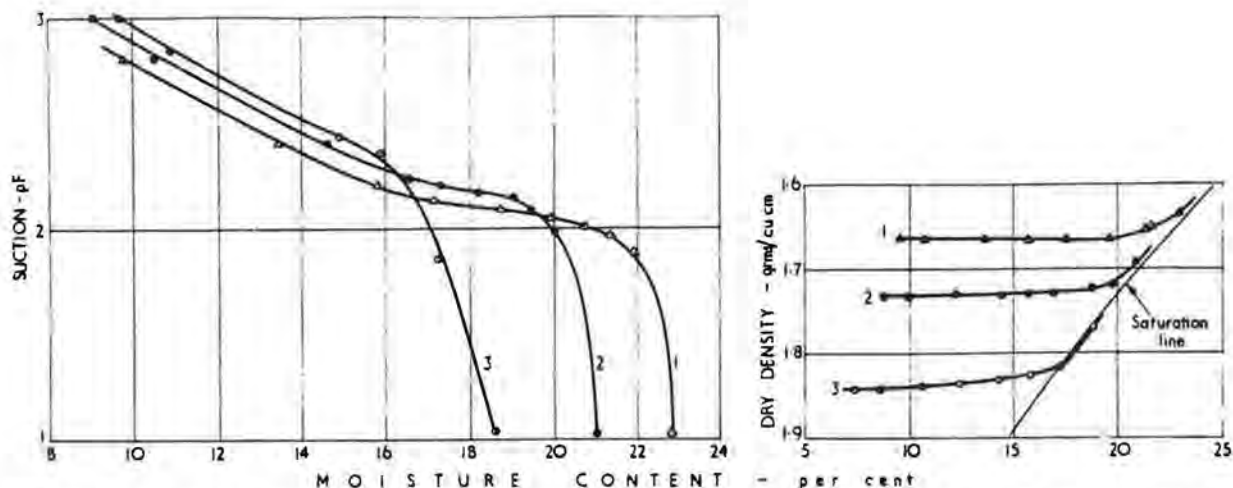
Figure 19.   Relationship between suction and moisture content of a silty soil at three densities.   Inset are the corresponding shrinkage curves.

sents considerable constructional problems in Great Britain, these problems are secondary in comparison with those that can arise with cotton soils in their more extreme climatic environment.

The suction curves for intermediate soils partake of the characteristics of both the incompressible and compressible soils. The curves for undisturbed natural samples of such soils lie between those of the sands and the heavy clays to form a continuous spectrum, the vertical characteristics of the sands at low suctions becoming less and less pronounced as one passes through the sandy and silty clays towards the heavier soils. When heavy clays in the natural moisture condition are remoulded and compacted to different degrees the compacted material consists of aggregates of saturated or nearly saturated clay with comparatively large air voids. Although it is the magnitude of these air voids which determines the difference in dry density between the samples, their presence has little effect on the suction/moisture content relationship as a whole. In sandy and silty clays, however, where saturated aggregates of this type are not present, compaction modifies the particle arrangement and the density of remoulding has an effect on the suction/moisture content relationship. Although by carrying out a series of tests on sandy or silty clay soils at different initial densities a family of curves is obtained, these curves are not strictly comparable with those for an incompressible soil since the curves do not represent iso-density conditions because of the natural swelling and shrinkage of the soil. By carrying out swelling/shrinkage tests simultaneously with the suction determinations, a family of suction curves corresponding to constant density conditions can be prepared. These curves show the same cross-over characteristic as the curves for incompressible soils. A detailed study of the suction/moisture content/density relationships of this kind is likely to be of fundamental importance in studies which are in progress into the interrelationship between suction, shear strength and compaction. Figure 19 shows typical suction/moisture content curves for a silty soil in three states of compaction. The corresponding swelling and shrinkage curves are shown inset. Again for clarity drying curves only are shown.

MOISTURE MIGRATION BENEATH ROADS AND STRUCTURES

In the natural soil the pore-water pressure is determined by the rainfall, evaporation, transpiration from vegetation and the soil permeability. These factors may give rise to a water table whose depth can be determined from a borehole. Under an infinite impermeable surfacing and under uniform temperature conditions the level of the water table alone determines the ultimate distribution of pore-water pressure. In practice if the water table is sufficiently near the surface for the water films to be continuous throughout the profile a linear distribution of pore-water pressure with respect to the water table is reached, that is, x ft above the water table the pore pressure

is negative by x ft of water, and x ft below the water table it is positive by the same amount. Figure 20 shows an example of such a linear distribution measured beneath the concrete floor of a building some 50 ft square. The water table was at a depth of about 9 ft and the equilibrium distribution of pore-water pressure consistent with this depth of water table is shown by a chain-dotted line in Figure 20.

From any known distribution of pore-water pressure with depth the corresponding variation of suction with depth can be deduced using Eq. 1. In conjunction with the appropriate relationships between moisture content and suction, the suction distribution can be converted to a distribution of moisture content.

Beneath an infinite impervious surfacing, the vertical pressure P on any horizontal plane will be the pressure exerted by the wet soil above the plane together with any surface loads. The value of the compressibility factor a can be determined by the apparatus already described. (In the solution of particular practical problems the value of a should strictly speaking be determined by the application of the system of principal stresses to which the soil is subjected in situ and not necessarily by an all-round pressure. However, the small gain in accuracy is hardly likely to compensate for the increased complication of the test.)

During the last eight years observations of pore-water pressure and moisture content have been in progress at several sites in Great Britain representing a

Figure 20. Pore water pressures measured at different depths beneath a building foundation.

range of soil conditions. Measurements have been made under grass cover, under bare soil and under impervious road pavements laid at various times of the year. The earlier stages of these experiments have been reported elsewhere (19). Figure 21 (a) shows the variation of pore-water pressure at various depths under grass cover (Area A) at Site 1 for the period 1951-56. The soil profile at this site consisted of sandy and silty clay strata overlying gravel at a depth of 6-7 ft. The rainfall and water table data over the same period are given at the bottom of Figure 21. Measurements of pore-water pressure made under bare soil (Area C) at the same site are reproduced in Figure 21 (b) and they show the part played by vegetation in removing water from the soil. The manner in which impervious pavements (Area B, E and G) stabilize the moisture conditions in the soil beneath can be seen from Figure 22, which again refers to the same soil profile. In this instance an accurate linear distribution of pore-water pressure with respect to the water table had not yet been realised, partly because of the finite area of the pavements (30 ft square) and partly because of the presence of the coarse gravel layer above the water table. This layer was relatively impermeable to capillary moisture flow and retarded vertical migration of moisture. The influence of these factors on the pore-water pressure distribution was satisfactorily explained using the principle of flow nets. The associated measurements of unsaturated permeability, both vertical and horizontal, were made using an apparatus developed from that de-
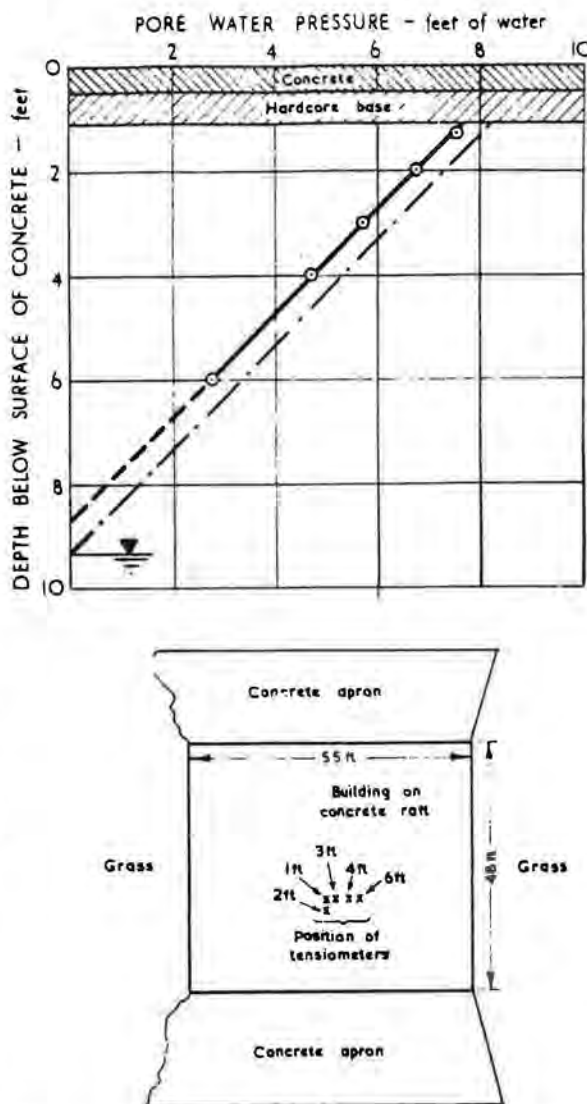
Figure 21. Pore water pressures under grass cover, Area A, and bare

scribed by Russell and Spangler (20) and shown diagrammatically in Figure 23. This apparatus has been found very satisfactory for measuring unsaturated permeabilities in the suction range 0-20 cm of mercury.

In Figure 24, the pore-water pressure distributions shown in Figure 21 (a) have been converted to moisture content distributions using the method outlined above. Owing to the variation of soil type with depth the appropriate values of the compressibility factor a and the appropriate suction/moisture content relationships for each depth were measured and used in making the conversion. Moisture content distributions estimated in this way have been compared with measurements made by boring and sampling at specific times. The comparison shows close agreement (see Fig. 25, which is typical) and confirms that the suction approach can be used with confidence for estimating the ultimate moisture distribution beneath pavements in Great Britain. In these field investigations, the pore-water pressure measurements were made with large numbers of all-glass tensiometers of the type shown in Figure 26 and which were developed for the work. They were found to be reliable and required little attention over a period of years. Research was carried out to investigate the reliability of electrical absorption
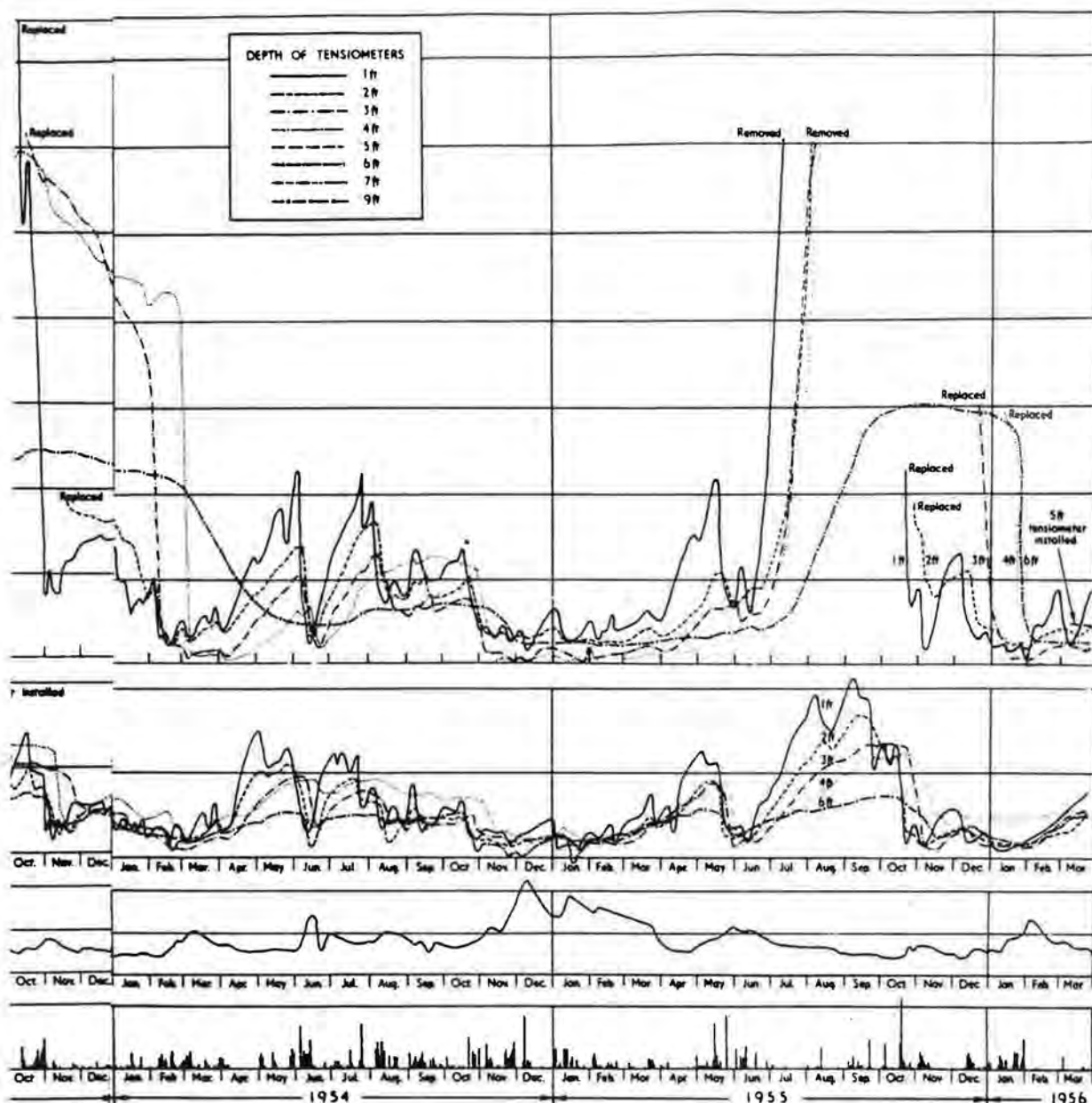
soil, Area C, together with water table and rainfall data at Site 1.

gauges for measuring pore pressures, but the results showed that they would be too insensitive at the low values of negative pore-water pressure generally found under pavements in Great Britain (21).

The combination of suction and shrinkage data provides a valuable analytical method for estimating the settlement or heave of structures resulting from moisture migration, due for example to the covering by foundations of previously exposed soil or to the lowering or raising of the ground-water level. Such computations, made in connection with the site referred to in Figures 21-25, showed that the soil when covered in the driest summer condition by an impervious surfacing would heave at the surface by about 0.2 in. as a result of the subsequent attainment of an equilibrium pore-water pressure condition. For a heavy clay soil the corresponding heave would have been about 2 in.

VOLUME AND MOISTURE CONTENT OF UNSATURATED SOILS

In the foregoing treatment the suction and shrinkage relationships have been con-
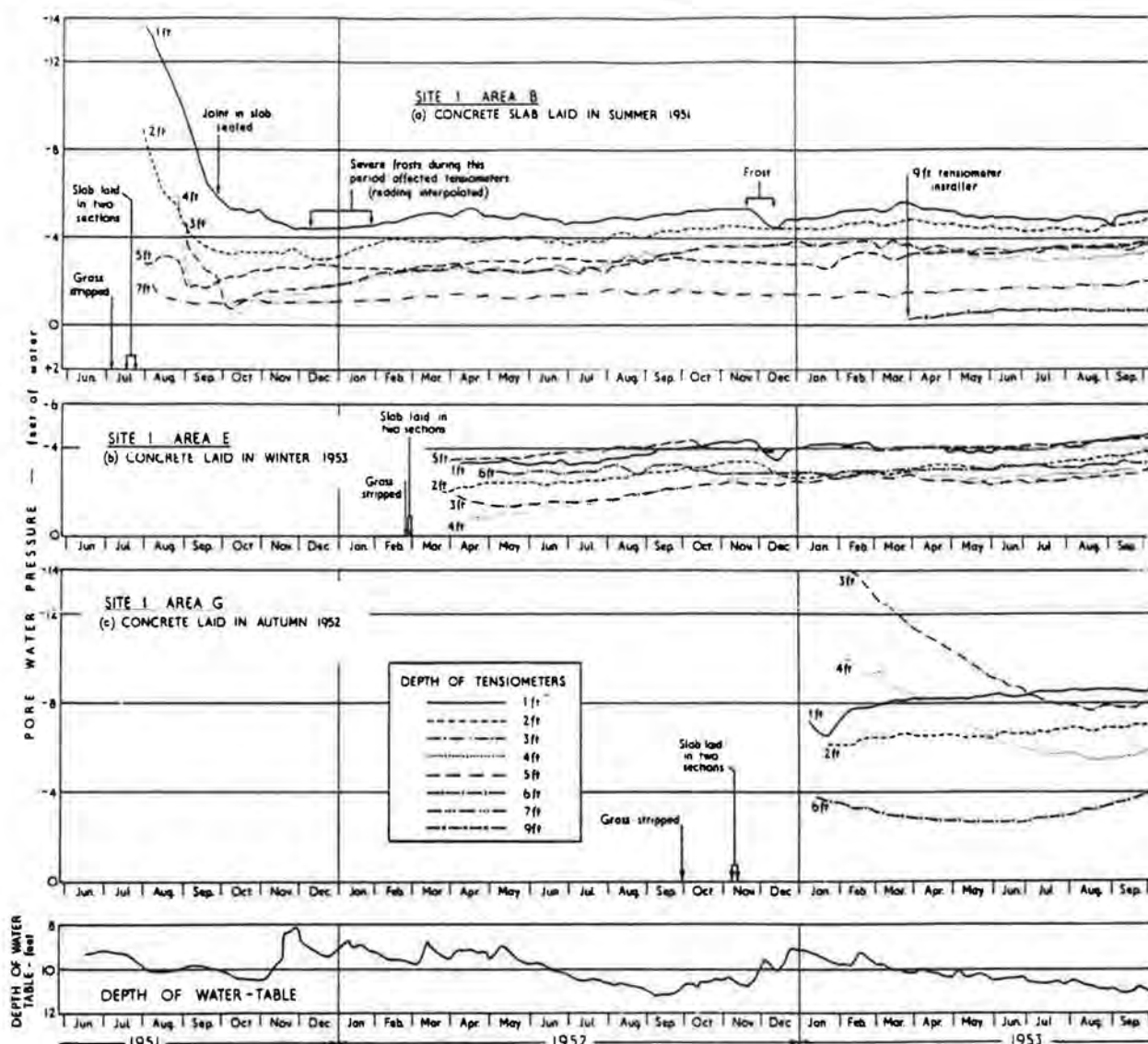
Figure 22. Pore water pressures under centre of 30-ft square concrete

sidered independently although there is clearly a measure of interdependence in so far as reversible changes of suction and volume are concerned.

If the volume of a fixed mass (of dry soil) is V_S and the volume of contained water is V_M, then any small change of the applied pressure p and the pore-water pressure u will do work equal to $p \cdot dV_S$ and $u \cdot dV_M$. The sum of these is the change dF in the free energy of the system, that is

$$dF = u \cdot dV_M - pdV_S \tag{2}$$

From Eq. 2 it may be deduced that,

$$\left(\frac{\partial F}{\partial V_M}\right)_p = u - \left(\frac{\partial V_S}{\partial V_M}\right)_p \cdot p \tag{3}$$

and

$$\left(\frac{\partial F}{\partial V_S}\right)_u = u \left(\frac{\partial V_M}{\partial V_S}\right)_u - p \tag{4}$$

It may further be shown theoretically that

$$\left(\frac{\partial V_S}{\partial V_M}\right)_p = \left(\frac{\partial u}{\partial p}\right)_{V_M} = a \tag{5}$$
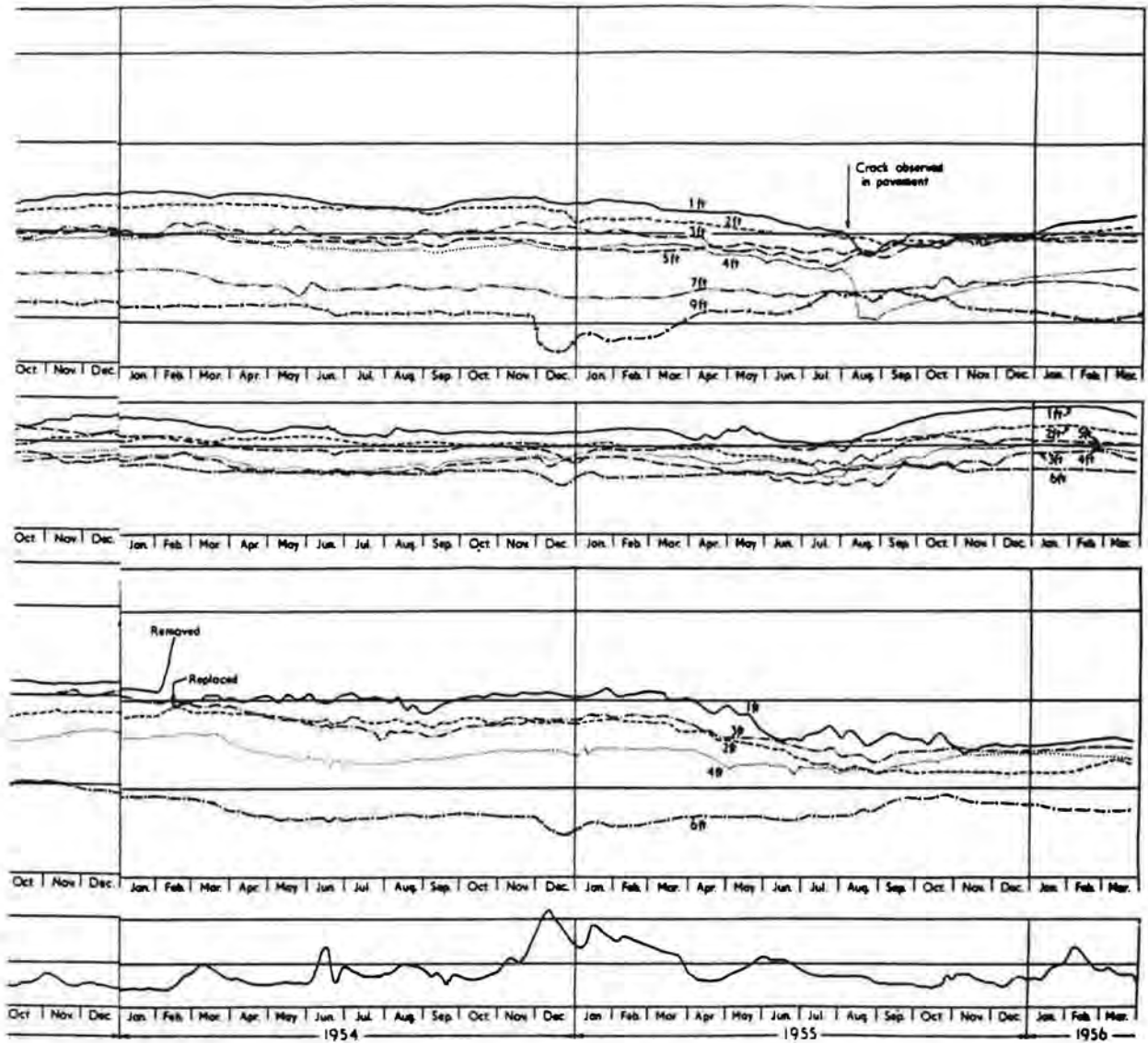
slabs laid at different seasons together with water table levels—Site 1.

where α is also as defined as in Eq. 1 (the equivalence of the shrinkage and direct loading method of determining α is illustrated in Figure 27), also

$$\left(\frac{\partial V_M}{\partial V_S}\right)_u = \left(\frac{\partial p}{\partial u}\right) V_S = \beta \tag{6}$$

If α and β approximate to constants for small variations of soil conditions Eqs. 3 and 4 can be written in the form,

$$s = u - \alpha p \tag{7}$$

and

$$\sigma = p - \beta u \tag{8}$$

These equations can be used to find (1) that pore pressure s (the suction) which combined with zero applied pressure produces the same moisture content in the soil as p and u combined and (2) that pressure σ which combined with zero pore-water pressure produces the same volume in the soil as p and u combined. For saturated soils, from Eqs. 5 and 6, $\alpha = \beta = 1$ and Eqs. 7 and 8 reduce to the normal expression for effective pressure used in soil mechanics, viz., $\sigma = p - u$. It is generally assumed that the effective pressure defined in this latter manner determines both the volume and shear
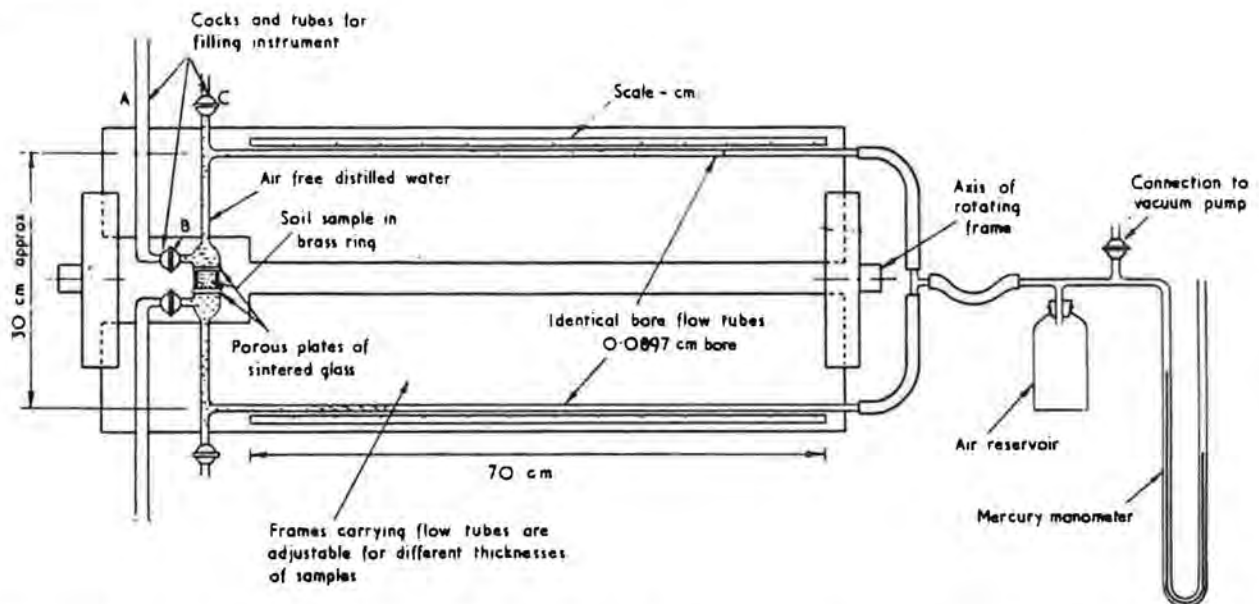
Figure 23. Diagram of apparatus for measuring the coefficient of permeability of soils at low suctions.

strength of saturated soils. It is apparent that for unsaturated soils the volume will be determined more nearly by σ as defined in Eq. 8.

SHEAR STRENGTH OF UNSATURATED SOILS

It is probable that the shear strength of unsaturated soils will be determined by an
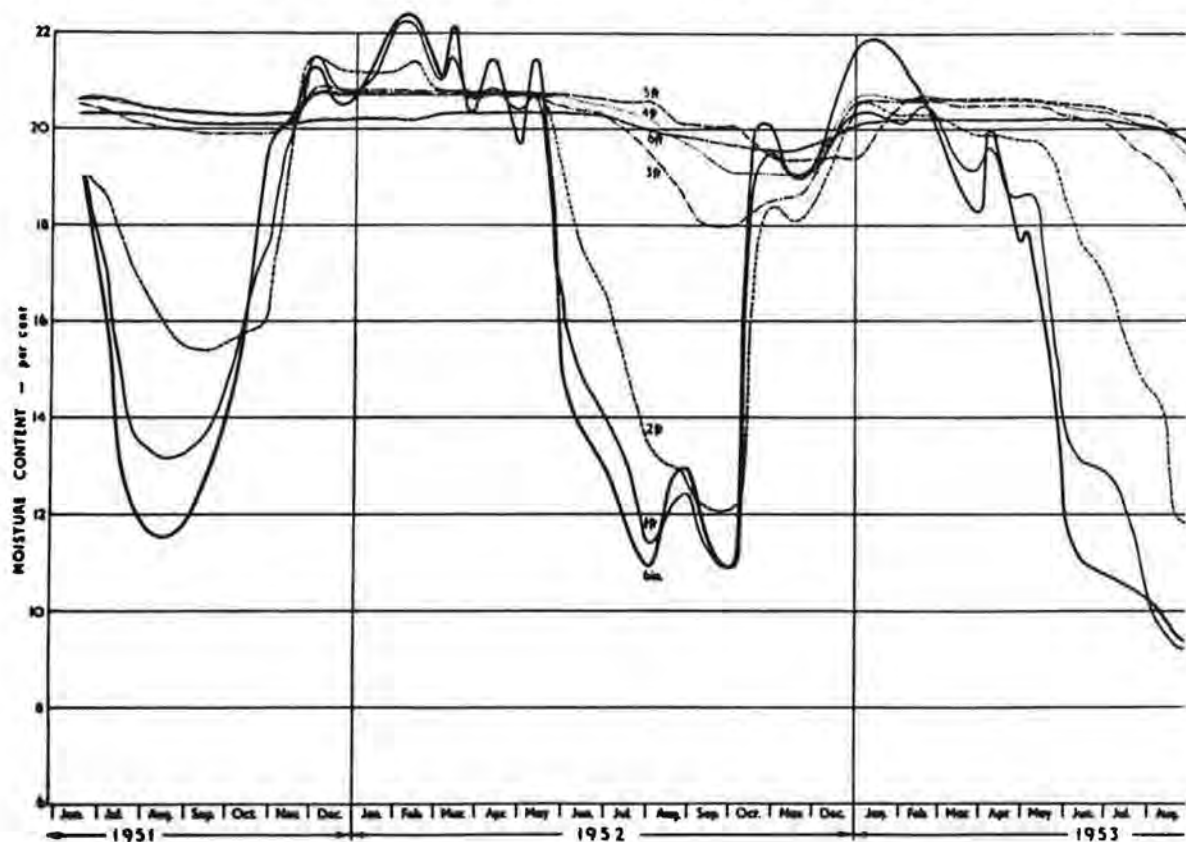
Figure 24. Moisture contents at various depths under grass cover, Area A. Curves deduced

expression similar to that for determining the volume, that is

$$\sigma' = p - \beta' \cdot u \tag{9}$$

where p is the total normal pressure on the shear plane and u is the pore-water pressure on the shear plane.

The pore pressure u will in general be below atmospheric pressure and in principle can be measured by some suitable energy method. In practice it may be inferred from a knowledge of the suction/moisture content relationship for the soil and from the known effect of applied pressure on pore-water pressure.

The extent to which the coefficients β and β' are equivalent can only be determined by experiment, since the shearing process in soil is almost completely irreversible, and is not at present susceptible to a thermodynamic treatment.

The coefficient β' appears to be holding or bonding factor, and is a measure of the number of bonds of water under tension effective in contributing to the shear strength of the soil. Considering the variation of the shear strength of soil with moisture content, as the soil dries the suction increases and the strength of the bonds per unit area of water contact also increases. On the other hand, the number of bonds and the area of each individual bond both decrease as the soil becomes more unsaturated. In this way the product β's may reach a maximum as the soil dries, giving also a maximum of shear strength. At such a maximum,

$$\beta' \cdot ds + s \cdot d\beta' = 0 \tag{10}$$

The maximum strength will occur at suctions less than one atmosphere for coarse sands, β' being zero for such soils when oven-dry. For silts the maximum will occur at higher suctions than for sands and for clays at very high suctions.

Some experimental evidence of the relationship between shear strength and suction has been obtained from laboratory vane tests carried out on completely remoulded samples, Figure 28 (22). The suctions were determined before shearing and when the
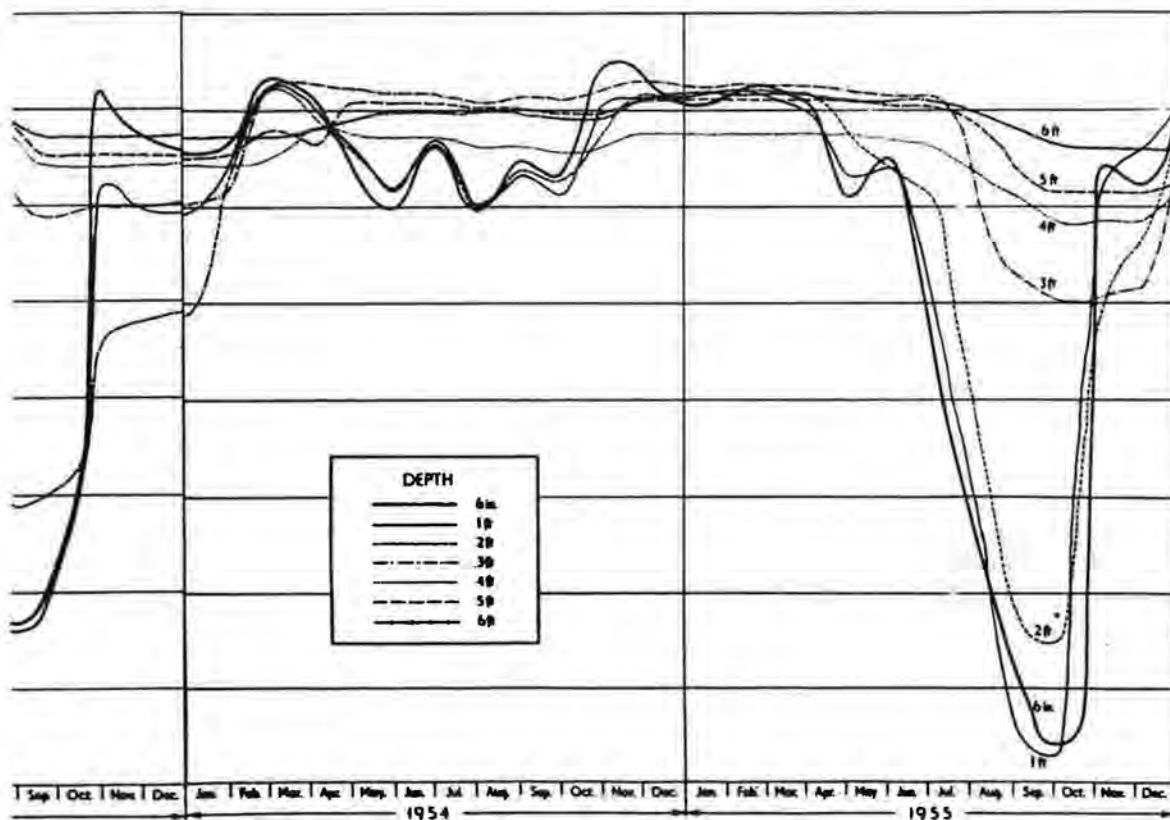
from measurements of pore water pressure and from suction/moisture content data — Site 1.
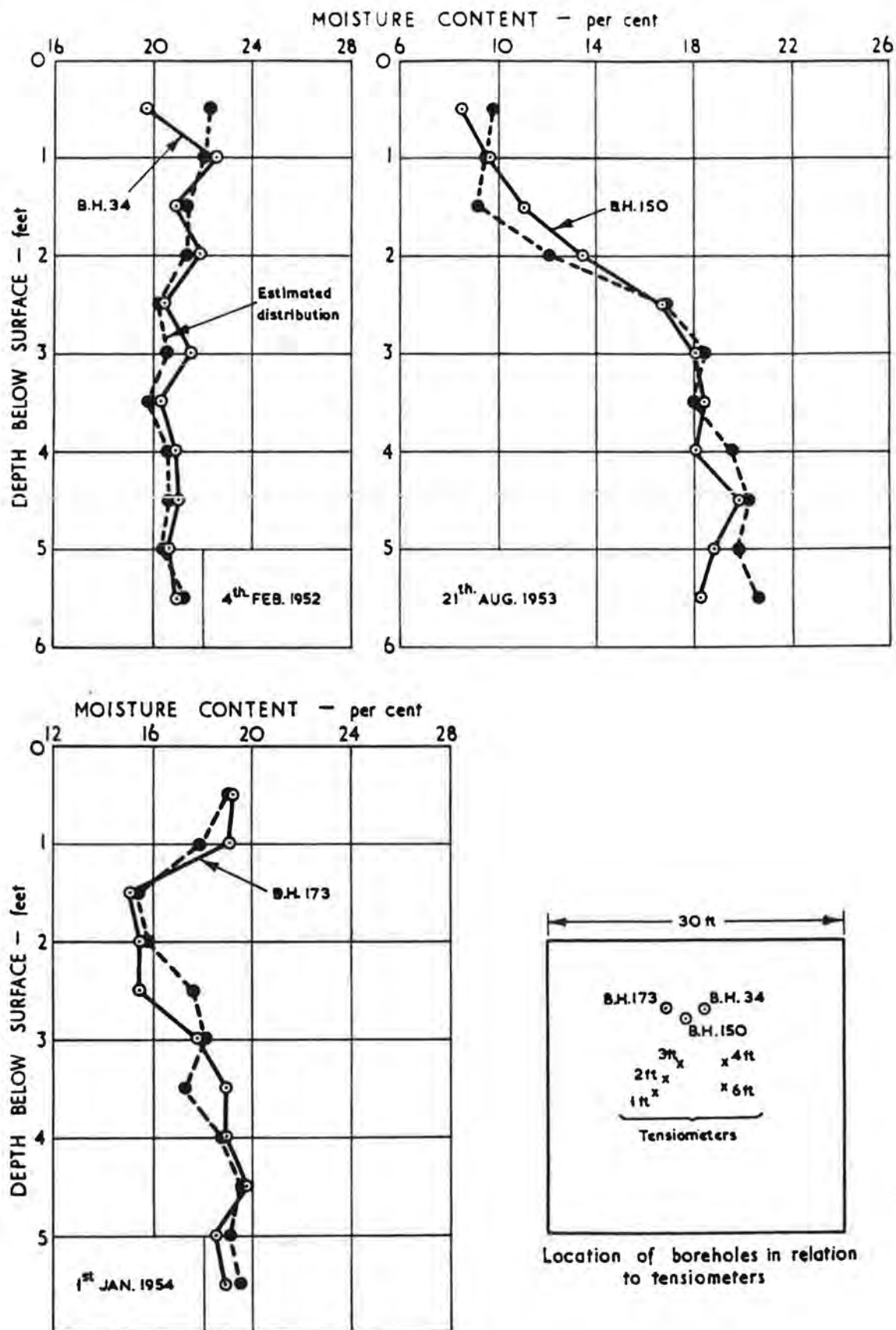
Figure 25. Comparison of estimated and measured moisture distributions at different times under grass cover—Area A.

suction condition of each soil was repre-
sented by a point on the "unique line" of
that soil (see discussion on Fig. 17). The
lighter soils in Figure 28 may have some
frictional strength imposed by the stress
distribution set up by the vane used in the
tests.

CALIFORNIA BEARING RATIO (C.B.R.) AND SUCTION

Studies which have been made of the
California bearing ratio of soils at various
moisture contents and dry densities also
suggest a close relationship between suc-
tion and the bearing ratio of the soil.
Figure 29 shows a family of curves relat-
ing California bearing ratio on a log scale
with moisture content for various constant
dry densities. The similarity between the
shape and characteristics of these curves
and those relating suction (also on a log
scale), moisture content and dry density,
Figure 16, will be apparent. The results
suggest a linear relationship of the type,

$$C.B.R. = C_1 + C_2 \cdot s \qquad (11)$$

where C_1 and C_2 are constants and s is
the soil suction.
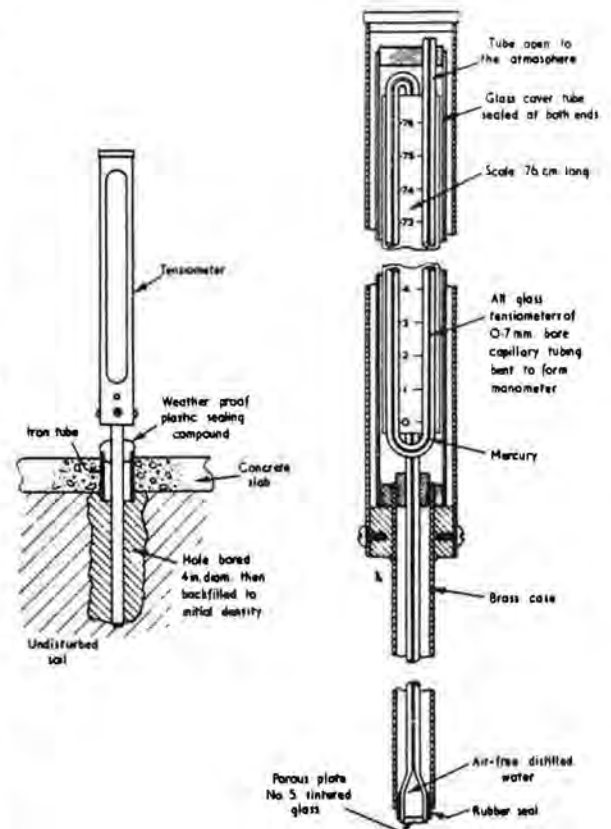
Figure 26. Details of construction of ten-
siometers and method of installation.
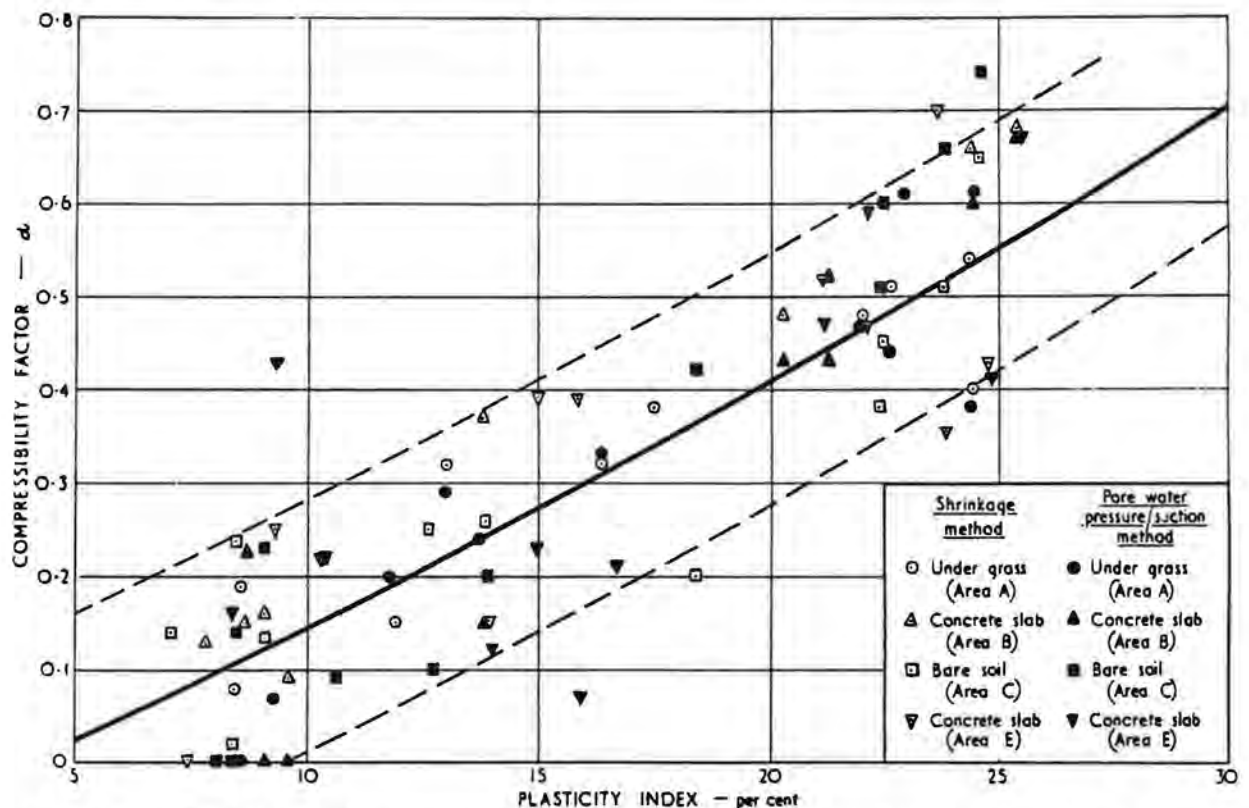
Figure 27. Variation of compressibility factor a with plasticity index of soil using
two methods of determination.
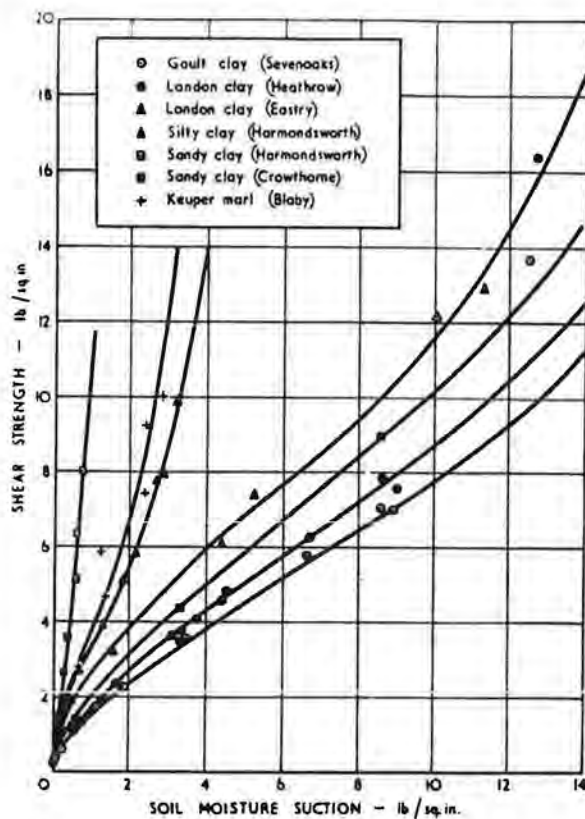
Figure 28. Relationship between shear strength and soil moisture suction for continuously disturbed soil.
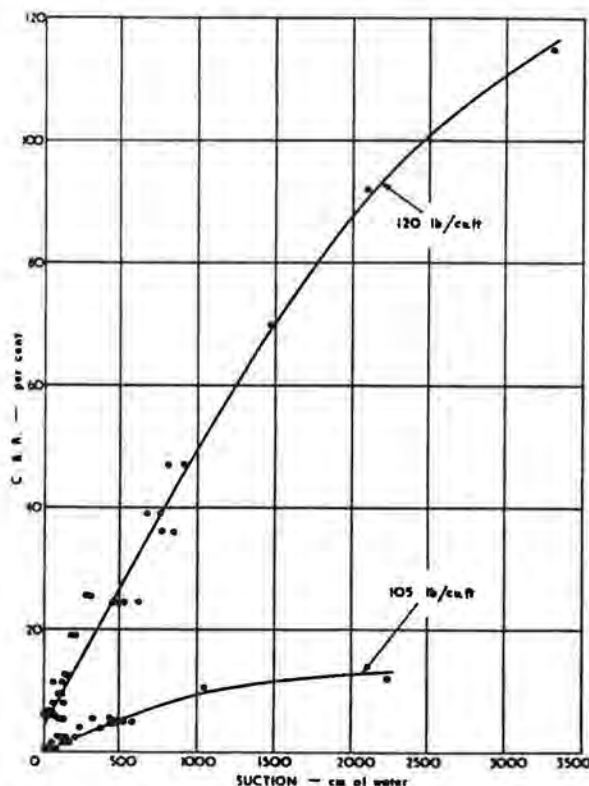
Figure 30. Variation of C.B.R. with suction of a silty sand at densities of 105 and 120 pcf.
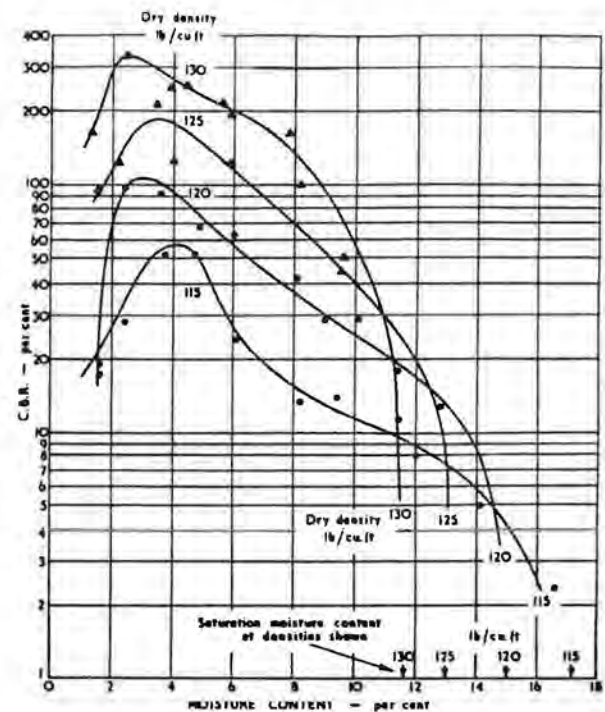
Figure 29. Variation of C.B.R. with moisture content for a sand at different densities.

In the C.B.R. test a bearing capacity failure may occur in some cases. Restraint due to the pot, and incomplete mobilisation of the full bearing capacity at 0.1-in. deflection will in other cases make a bearing capacity analysis inapplicable to the test. The relationship between the bearing capacity of soil, the apparent angle of internal friction, ϕ, and the apparent cohesion, c, is, however, of the form

Bearing capacity = $f_1(\phi) + c \cdot f_2(\phi)$ (12)

This type of relationship applies to both a strip or circular footing. If the apparent cohesion be proportional to the product β's, then Eq. 12 becomes,

Bearing capacity = $f_1(\phi) + \beta$'s $f_3(\phi)$

and is of the same form as the experimental Eq. 11.

The approximate linearity of the variation of C.B.R. values with suction at suctions below one atmosphere, for an unsaturated silty sand (LL 24, PL 22) is shown in Figure 30.

At the Road Research Laboratory it has for some years been the practice in designing flexible road pavements to estimate first the equilibrium moisture content of the subgrade using the method outlined in this paper. The C.B.R. test has

then been carried out at that moisture content and at a density likely to be achieved in the field. Now that means of checking the pore-water pressure are available it would appear more logical to bring the sample to the appropriate pore-water pressure rather than moisture content, since reference to Figure 29 shows that a small error in moisture content may lead to a very serious error in the C. B. R. value when the moisture content approaches saturation. Another factor which is at present under investigation in relation to the C. B. R. test is the effect which pore-water pressure, density, and stress gradients, present in the sample immediately after compaction, may have on the C. B. R. value. Such gradients arise from the effects of wall friction in the mould.

CONCLUSION

The paper summarises the research in progress at the Road Research Laboratory in Great Britain on the application of soil thermodynamics to the design of road foundations.

It is hoped that it will be of interest to those concerned with the more fundamental aspects of "moisture conduction phenomena" as well as to those whose concern it is to solve as expeditiously as possible the problems that arise in connection with highway engineering.

ACKNOWLEDGMENT

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Field Studies on Subgrade Moisture Conditions

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Introductory Remarks by the Chairman

Mach in "Die Mechanik in ihrer Entwicklung" stated: "All our principles of mechanics, as we have shown in detail, are experienced knowledge concerning the relative position and motion of bodies. They could not be, and were not, admitted in the areas in which they are now recognized as valid, without previous testing. No one is warranted in extending these principles beyond the boundaries of experience."

Bodies are usually defined as things that possess mass and extension in space or form. Forces and energies are associated with the mass properties and for many theoretical purposes the extension in space or form is of only secondary importance. This has led to a widespread practice of neglecting form properties and often reducing a body to the absolute minimum, that is, a point in space that is acted upon by forces. For real systems, form is as important as mass and forces interact not only with mass but with forms and are themselves influenced by the latters' geometrical features. For biological systems, this has been demonstrated in a beautiful and exemplary manner by D'Arcy Wentworth Thompson in his classic "On Growth and Form."

Sometimes, in the analysis of soil moisture conditions, we become so much involved in the consideration of the forces that we forget about the geometrical features of the system in which we are interested. It is gratifying, therefore, that Mr. Guinnee in his field studies on subgrade moisture conditions presents evidence not only on the influence of climatic forces and factors, but also on that of geometrical features of the pavement base-subgrade system.

● THIS PAPER is in the nature of a summary of various investigational studies undertaken to obtain information concerning (a) the subgrade moisture content, its change with time and environment, (b) the source of post construction subgrade moisture, (c) the means by which this subgrade moisture travels or accumulates, and (d) the potentials which cause such flow. This paper will also serve as a temporary closure to these projects due to the demands of the expanded interstate program on the personnel involved. This information is deemed necessary to a more complete understanding of subgrade moisture conditions from which a more rational and economical design method might be evolved.

Since these listed purposes are so inclusive it must be understood that they are basically behind each project, even though that project may not have been pursued to completion. The information thus gained serves as a basis for the over-all considerations which will be covered. The progress reports from which this paper has been taken are of considerable volume so that only a few illustrations of each project and some typical project data will be included. The discussion of the results of all projects will be covered in a later portion of the paper.

The various construction projects which have been studied all contain the following basic design features unless otherwise noted. The pavement is of P.C.C. construction 8 in. thick by 24 ft wide with a parabolic crown of $1\frac{1}{2}$ in. at the center. "Dummy" asphaltic filler contraction joints are spaced at 20 ft and the pavement is laid on a 4-in. by 26-ft compacted stone base. The 10-ft shoulders are sloped $6\frac{1}{4}$ in. and the standard ditches are 2 ft below the edge of the shoulder.

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SEASONAL MOISTURE VARIATIONS

A project study was initiated in 1950 to try to determine the variations in the sub-grade moisture due to seasonal changes as well as the extent of long-time moisture accumulation under concrete pavements. As an adjunct, the original moisture data would provide a reference datum for future performance investigations.

The Construction Division requires that pavement thickness cores be taken from newly constructed slabs so that actual thickness measurements can be made to verify wet concrete stick measurements. Since the pavements were thus ported through normal operating procedure it seemed as though these ports might afford an ideal entrance
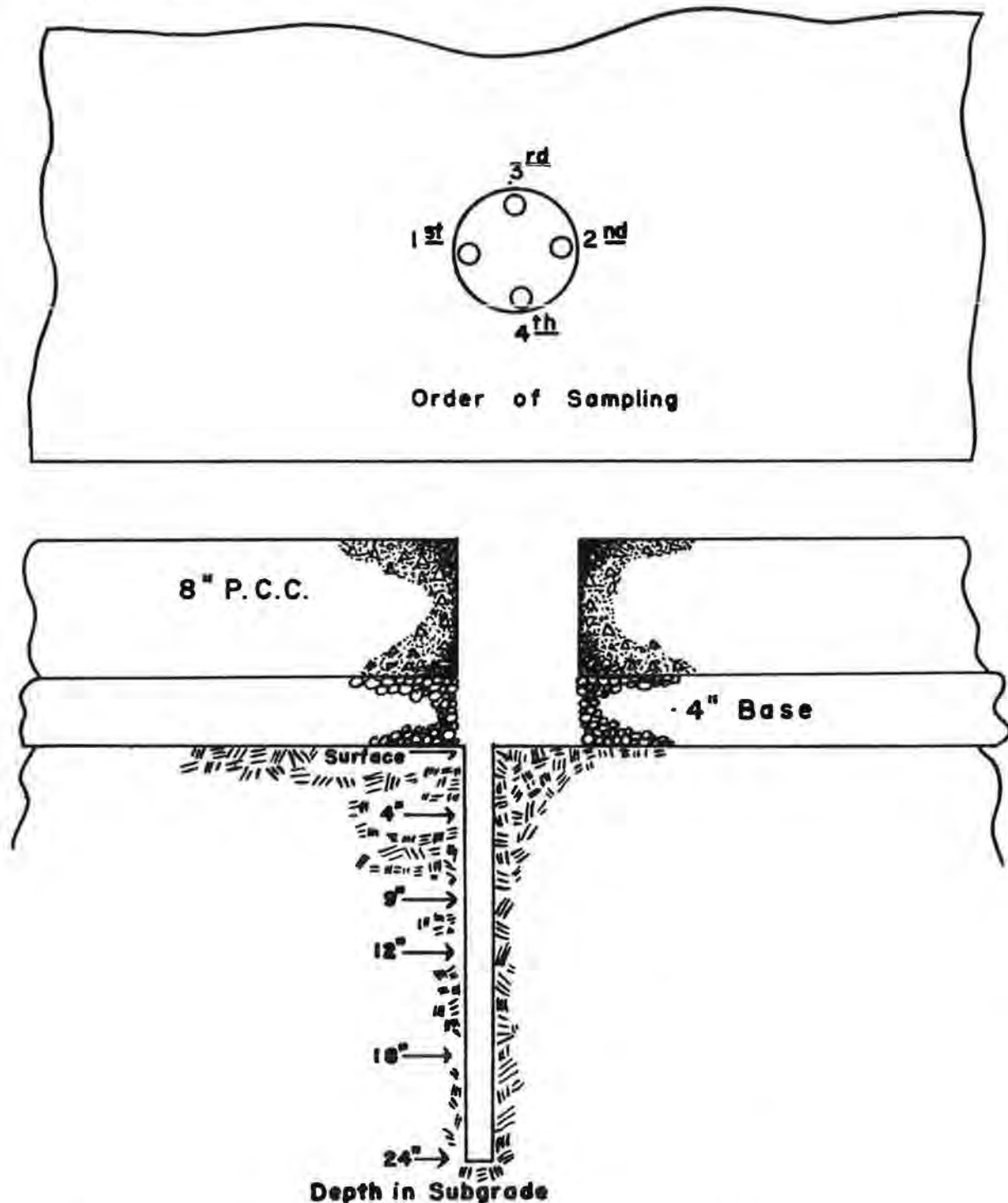
Figure 1. Details of manual sampling through pavement thickness core holes.

for manual subgrade moisture sampling. With the above purpose in mind, arrangements were made for a soils crew to accompany the core drill to sample the subgrade as soon as the cores were removed. All of the locations where the cores were required were sampled to obtain the original subgrade moisture content. The details and the order of sampling are shown in Figure 1. Every attempt was made to return the soil, base, and pavement to its natural condition after each sampling. Similar soil was tamped firmly into the auger hole, the base was replaced and compacted and the core hole was filled with a well-rodded, rich concrete mixture.

Thereafter according to plan, one-fifth of the locations were resampled after three months. These same locations were sampled twice more at three-month intervals until four successive samples had been taken. The second one-fifth of the locations were then sampled for three successive three-month intervals. It was hoped that this successive three-month sampling system would give the seasonal variations as well as the moisture history for four years. On projects where it was deemed of sufficient importance new core holes were drilled adjacent to the original series so that a continuing sampling system could be carried on. The projects selected for resampling were chosen so as to give a representation of different soils. Some new projects were sampled for the original moistures only, thus providing the datum as set forth in the purpose (that is, for possible future investigations of performance).

Under this plan, projects were sampled on a "take what comes" basis providing
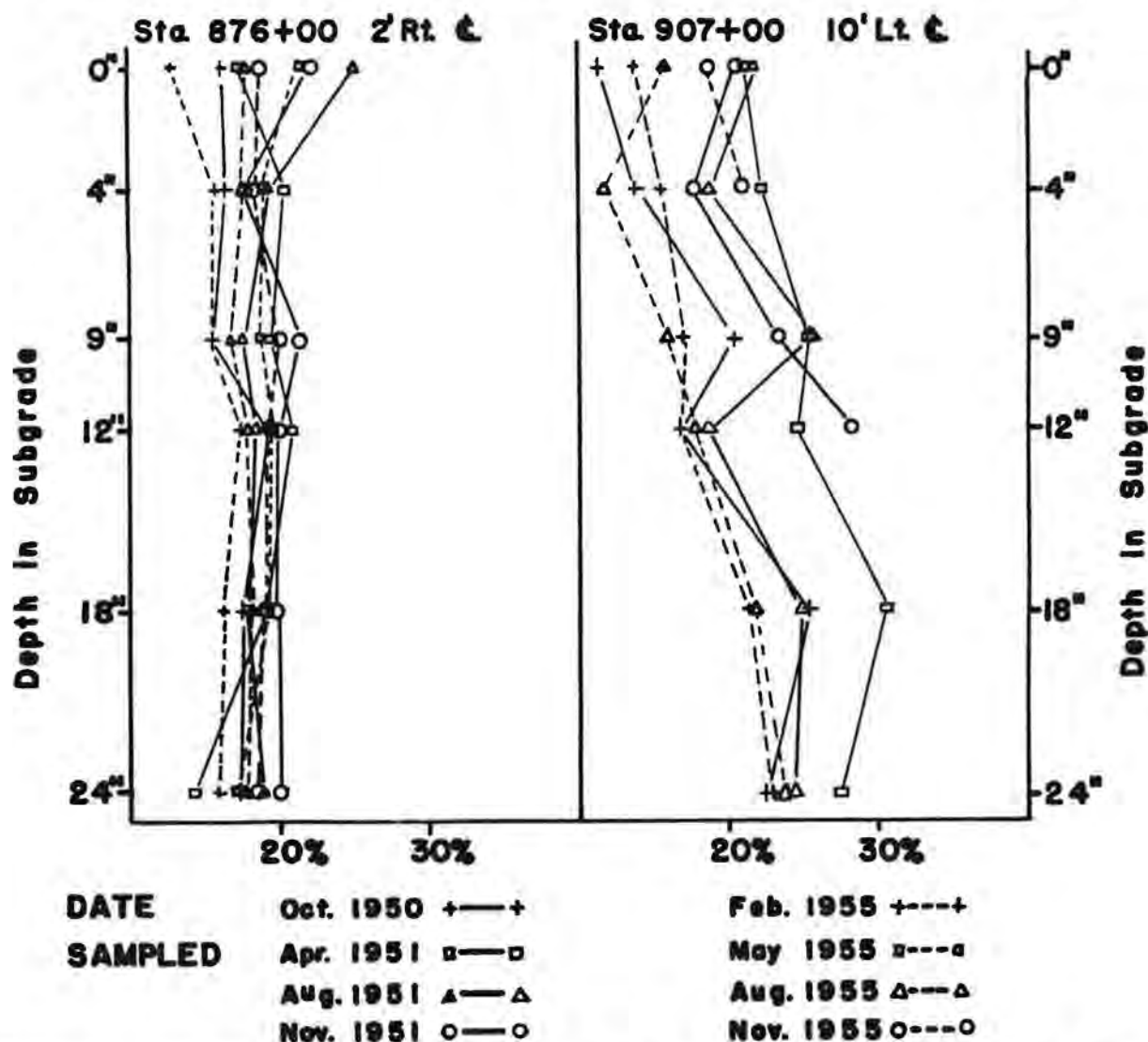
Figure 2. Individual moistures at successive sampling dates for two locations near Columbia, Route US 40.
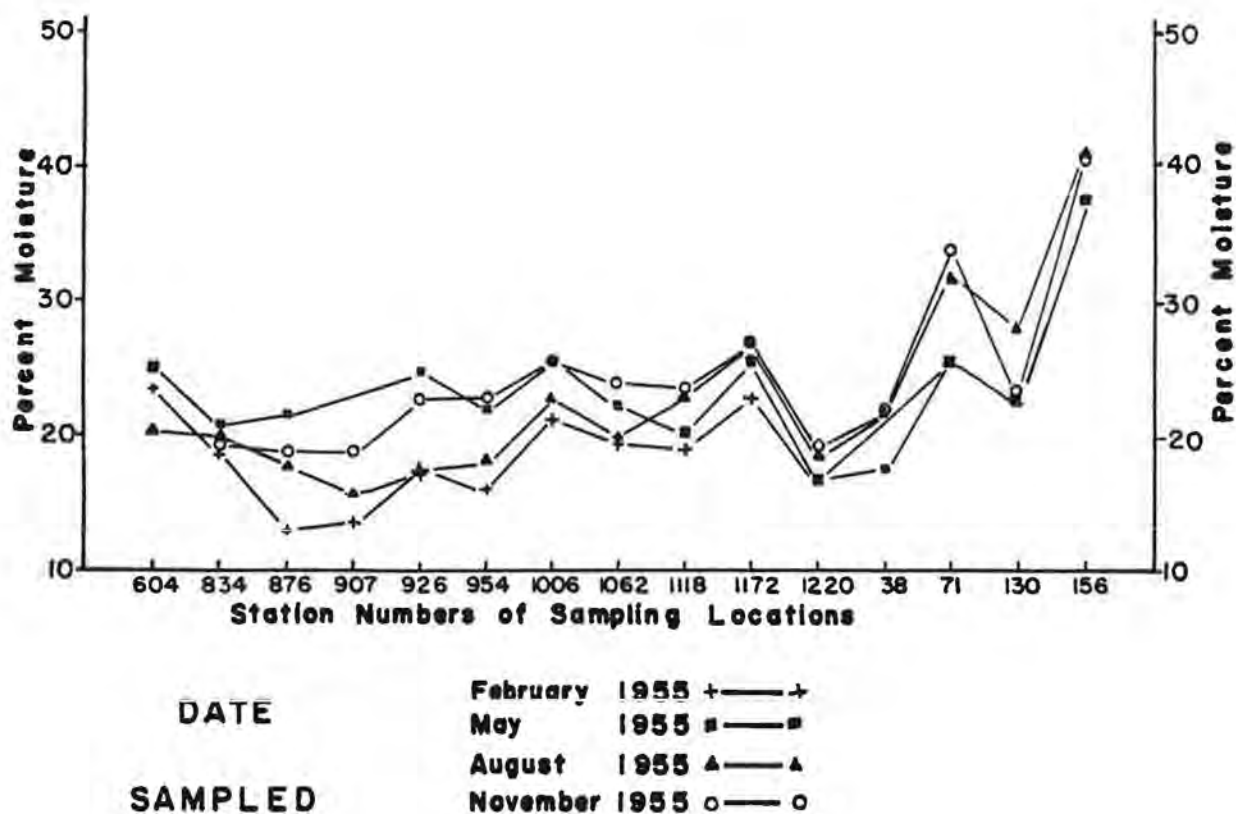
Figure 3.   Subgrade surface   moistures at successive   samplings for the entire project
near Columbia, Route US 40.
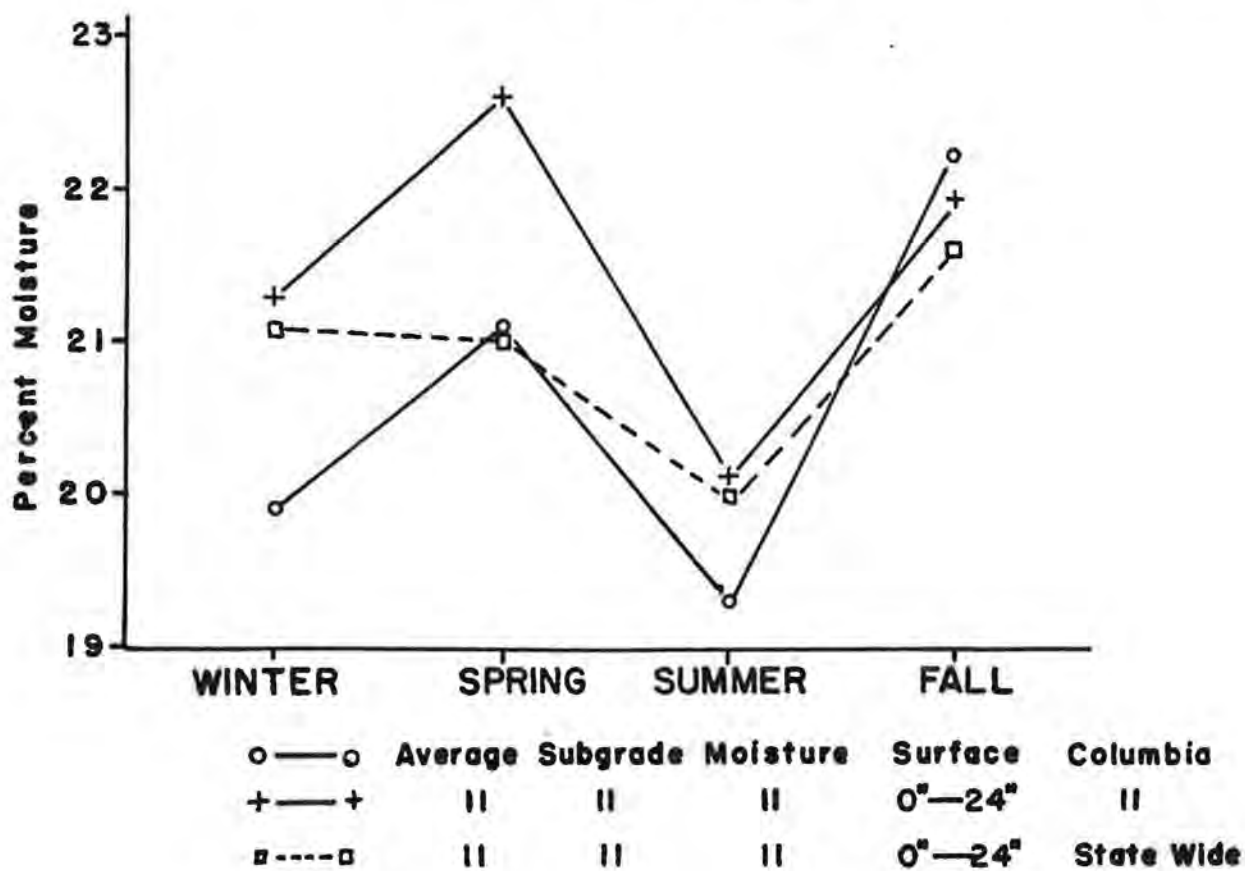
Figure 4.   Seasonal average of the subgrade moisture.

they were of sufficient length and were composed of new subgrade construction. This system thereby provided an automatic randomizing effect on the sampling locations since the core hole sites were selected by the resident engineer with regard to construction only. A minimum of eight cores per mile were required whether any thin pavement was suspected or not.

Figure 2 shows the individual moistures obtained at eight successive sampling dates for two locations near Columbia, Route US 40. The variation in moisture is typical of the various locations of this project. It should be noted that, although four years had passed, the moisture levels in 1955 were no greater than in 1951 and perhaps even somewhat lower in these two illustrations.

Figure 3 shows the variation in the moisture of the subgrade surface along the entire project for successive sampling dates. This longitudinal variation is typical of the several projects studied showing the wide spread of moisture contents which occur along the project even though the difference in characteristics of the soil may be slight (that is, Sta. 1062 P.I. 22.6 Group A-7-6(16) and Sta. 156 P.I. 30.6 Group A-7-6(19)). On other projects where the variation in soil group ranges from A-4(4) to A-7-6(19), the spread of moisture content is correspondingly greater, but when appraised with reference to these characteristics the variations appeared to be reasonable.

Seasonal variations obtained from the averages of seven years of sampling are shown in Figure 4. The small spread in average moisture (less than 4 percent) is probably related to the geographical location of Missouri; not far enough north to year after year be affected by moisture potentials of extreme colds of relatively long duration, nor far enough south to be affected by the relatively high rainfall and temperatures of the southeast or by the low rainfall and high temperatures of the southwest. The actual value of these averages is of little importance since they represent a range of soil classifications. The general trend, however, should be representative of existing statewide conditions.
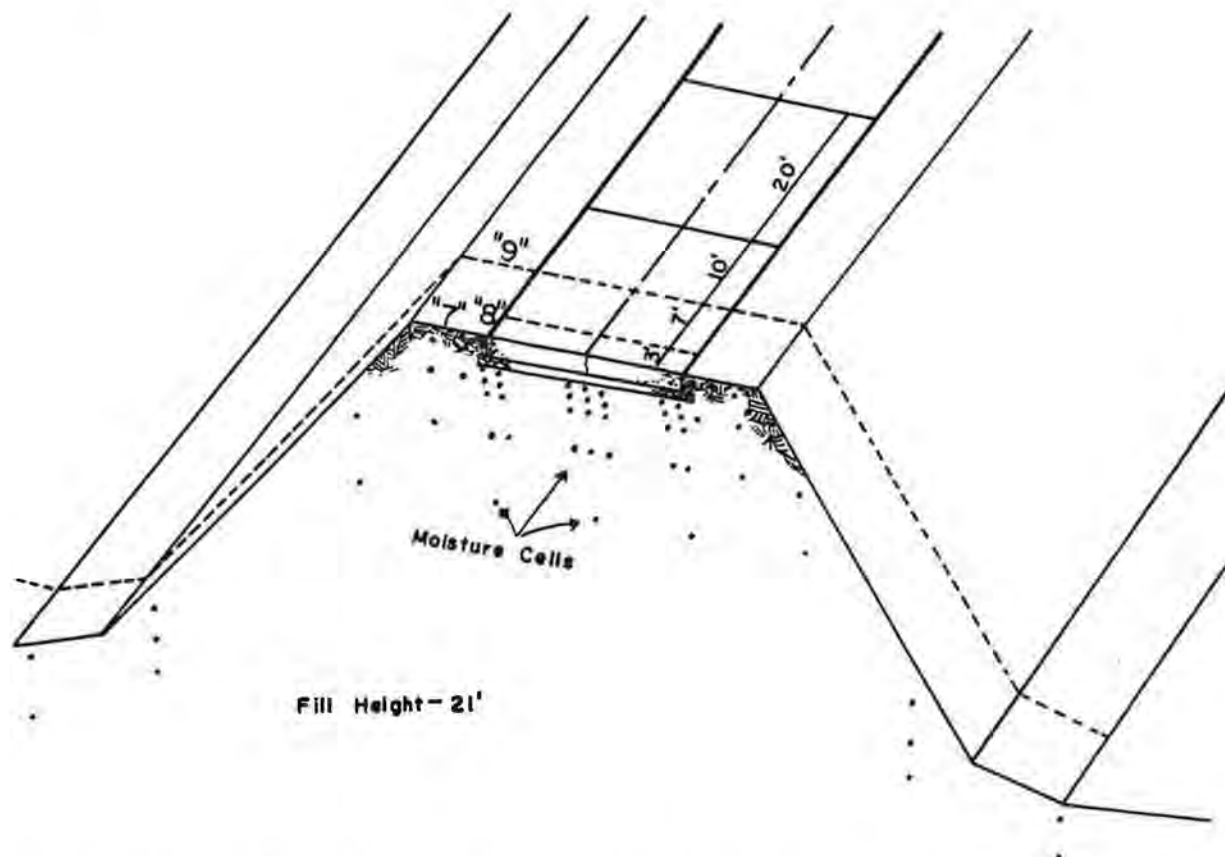
Figure 5. Lines "7," "8," and "9" showing moisture cell installations at 4-in., 9-in., 18-in., 36-in. and 72-in. depths in the subgrade.
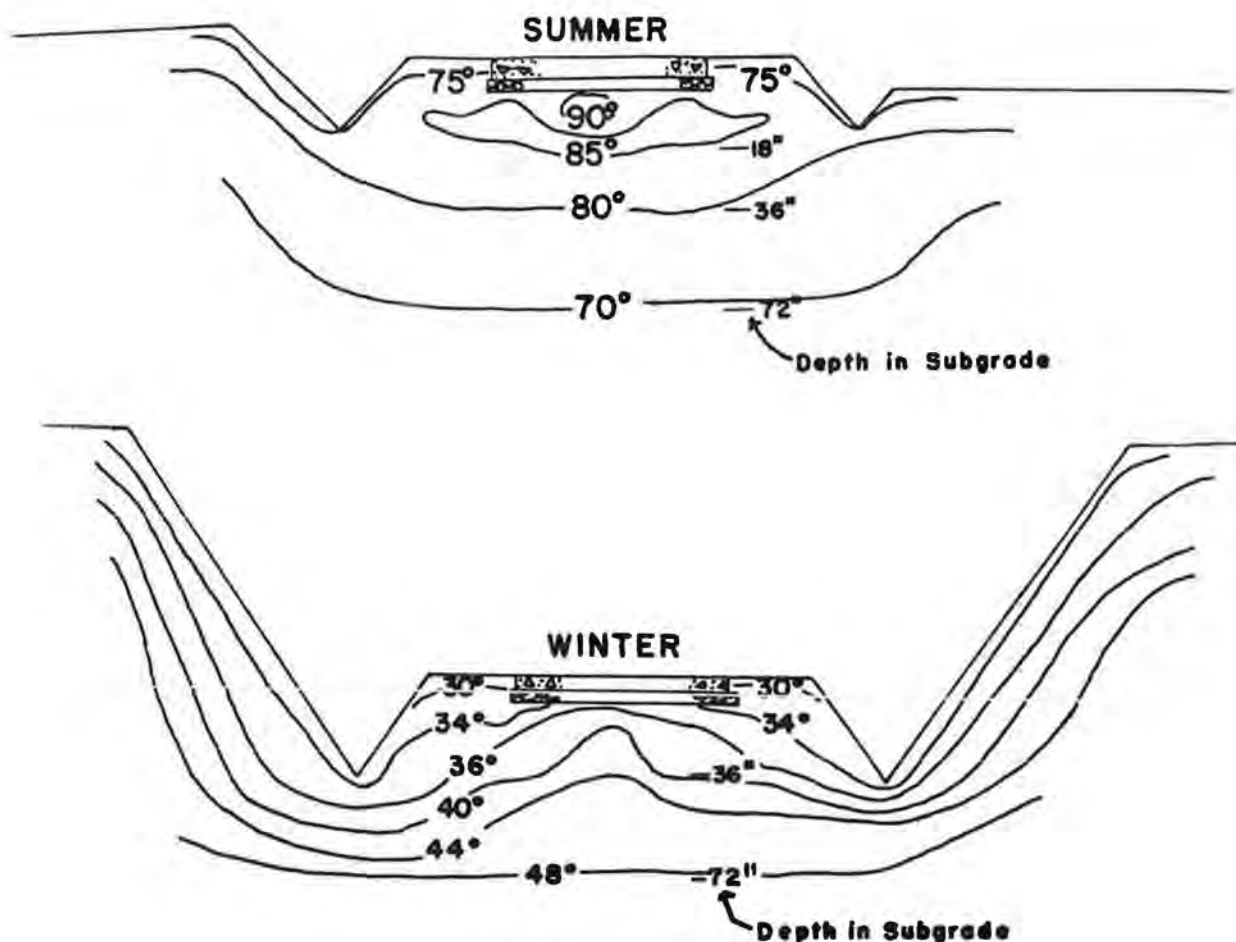
Figure 6. Typical isotherms.

MOISTURE ENTRANCE

An investigation was undertaken to try to determine the main source of supply for subgrade moisture and at the same time to select if possible the moisture cell locations which would be most generally representative of the average moisture level in the subgrade. Approximately 50 plaster moisture cells were installed in each of nine locations similar to those shown in Figure 5, with Lines 1, 2, and 3 placed in side-hill cut, 4, 5, and 6 in a 12-ft cut and 7, 8, and 9 in a 21-ft fill, with Lines 1 and 9 only 1,000 ft apart. The leads from the moisture cells and temperature coils were gathered into two terminal boxes for each set of three lines, one box on each side of the pavement.

Figure 6 shows typical isotherms during the summer and the winter. These isotherms were used in making temperature corrections to the resistance readings of the moisture cells. It was interesting to observe the sheltering effect of the backslopes of the cut section in contrast to the exposure of the fill section.

Typical moisture distribution levels as obtained by the moisture cells are shown in Figures 7, 8 and 9. These moisture levels were discontinuous because of the heterogeneous nature of the soil and because, as must be constantly kept in mind, the interpretation of moisture contents from resistance readings must go through temperature correction and calibration charts both of which may introduce errors into this interpretation. This project has been discontinued because the plaster cells had reached their maximum dependable life, having been in the earth for over five years.

CONTROLLED MOISTURE ENTRANCE

In 1951 this study was set up to obtain additional information concerning the ways by which moisture enters the subgrade subsequent to the base and pavement construction.

It was designed so as to limit or control certain of the ways by which moisture might enter the system. To make the study as complete as possible and yet to keep out many extraneous influences, it was constructed in eight comparable 100-ft sections, each
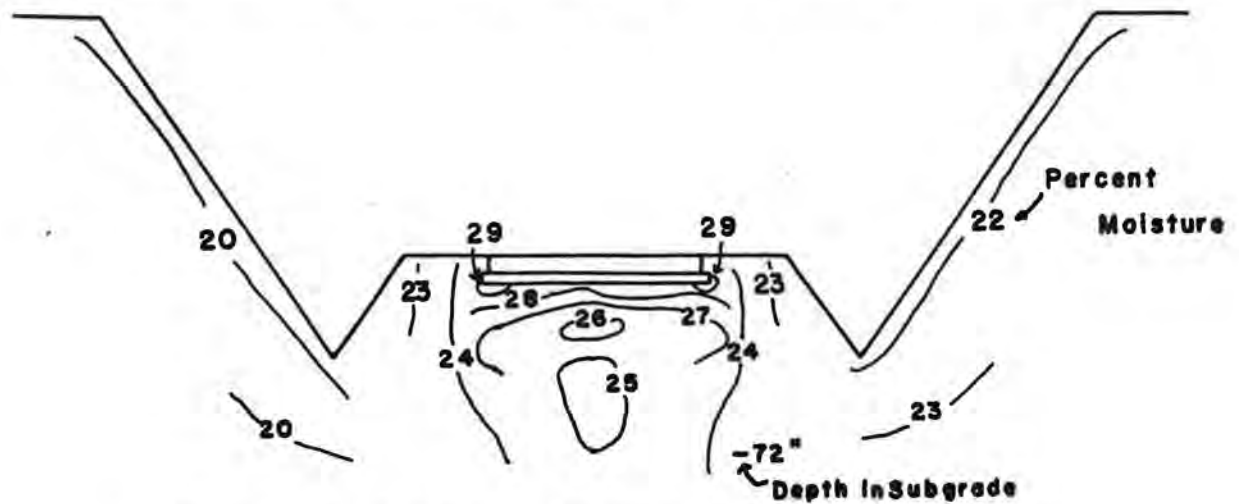
Figure 7. Typical moisture distribution levels on a winter day.
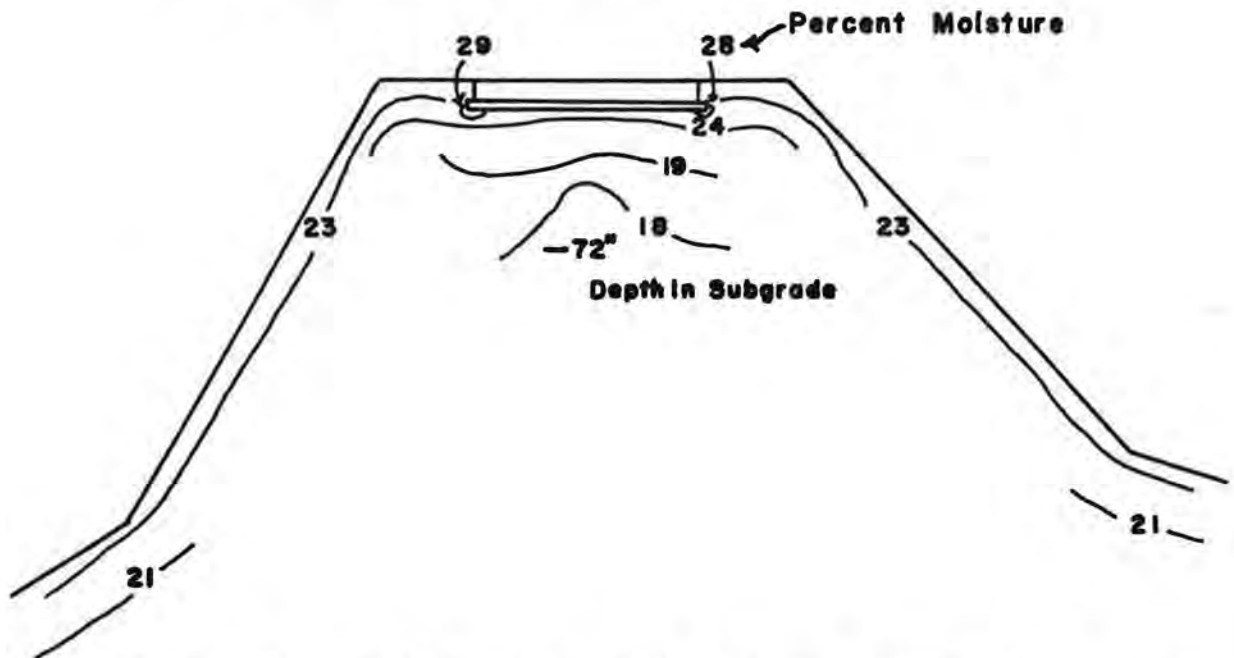
Figure 8. Typical moisture distribution levels on a summer day after a light shower.
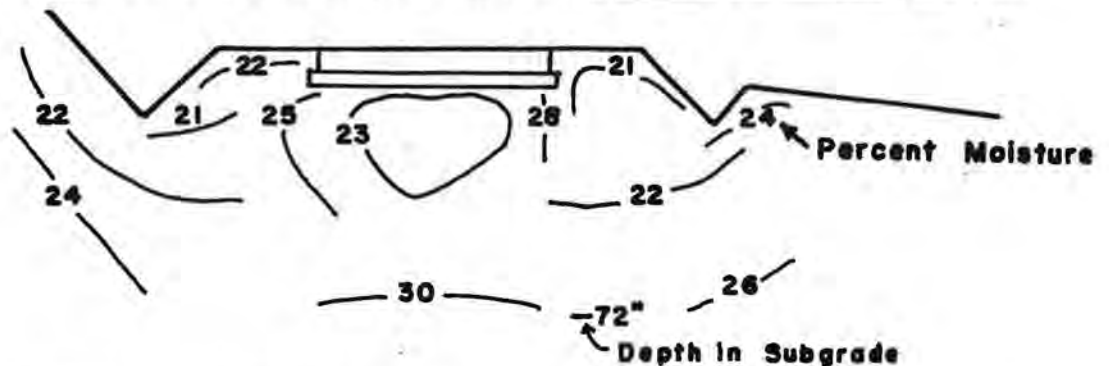
Figure 9. Typical moisture distribution levels on a fall day.
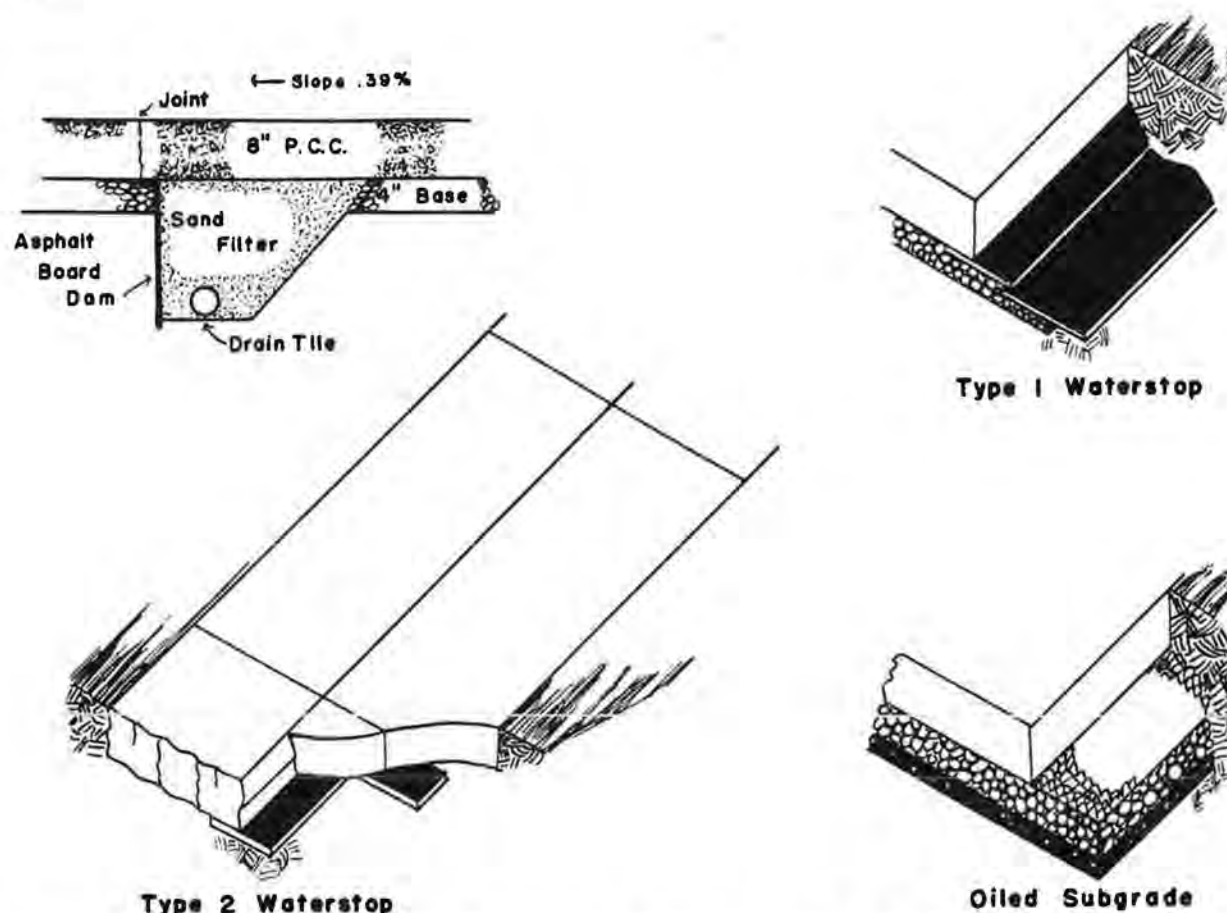
Figure 10. Details of methods of moisture entrance control and of drain construction.

with five contraction joints at 20-ft centers, all on a slight fill and with all the non-experimental design features to be identical with standard practice. As shown in Figures 10 and 11, attempts were made to prohibit the surface moisture from entering the system through the interior joints (Type 2), past the edges or through the joints (Type 1 and 2) or from the base at any point (oiled subgrade). These membranes, designated in Figure 10 as "waterstop," were sealed to the bottom of the slab by the use of an asphaltic emulsion applied just prior to the placement of the wet concrete. The three sections together with a blank section were duplicated on a 4-in. by 26-ft rolled stone base and directly on the subgrade.

Twelve moisture cells were installed in identical groups in the center 20-ft slab of each section to try to check on the extent of moisture entrance at the center joint, transverse joint, or edges.

Supplementally, special underdrains and dams of the design shown in Figure 10 were installed at the downgrade end of each 100-ft section for two reasons. (1) To try to evaluate any differences in the amount of surface water which drained over the subgrade (or through the pavement-base-subgrade system in some manner). (2) To try to stop any excess water from one section intruding upon the next adjacent section. These underdrains were connected to catchments in which provisions were made to measure the drainage.

A graph showing the total accumulated drainage from each of the 100-ft sections is presented in Figure 12. The fact that the base sections drained more water might indicate that they kept more water from entering the system but the average moisture of each section as indicated by the moisture cells showed that the sections on base were wetter than those with no base except for the untreated sections. It is interesting to note that the section with the oiled earth subgrade under the base, even though consistently draining the most water, maintained a lower subgrade moisture level than the other three base sections.

The section with oiled earth subgrade and no base had the lowest subgrade moisture level of all eight sections, consistently 10 percent below the rest.

A comparison of the average seasonal moisture and drainage for the Section 6 which was consistently the wettest, and Section 4, which was consistently the driest, is shown in Figure 13. This comparison shows that even though the drainage per inch of rainfall was at its lowest in the spring, the average moisture level was at its peak for both the wettest and driest sections.

TABLE 1
DROUTH DATA

Year	Total Rainfall in.	Deviation from Average
1952	29.34	-9.45
1953	23.98	-14.81
1954	32.34	-6.45
1955	28.23	-10.56

PAVEMENT CONSTRUCTED ON A VERY DRY SUBGRADE

This study was started in 1953 when it was noted that pavement was being constructed on very dry subgrade, the dryness of which extended in depth. Table 1 shows the extent of the drouth which was affecting Missouri at that time.

In this study subgrade moisture samples were obtained to depths of 24 in. in a transverse line at 3-ft intervals starting at the designated north edge of the slab and extending to the south edge (9 locations with 6 samples each). These original moisture samples were taken from 13 locations about evenly divided between fill, cut, and transition section. After the base was laid a few spot checks were made and the subgrade surface moisture was found to have risen to almost that of the previous underlying soil moisture levels, but still approximately 6 to 10 percent below the plastic limit. On the completion of the paving and shouldering, bench marks were set well back in the backslope and imbedded to 20 ft to attempt to keep disturbance of the bench marks to a
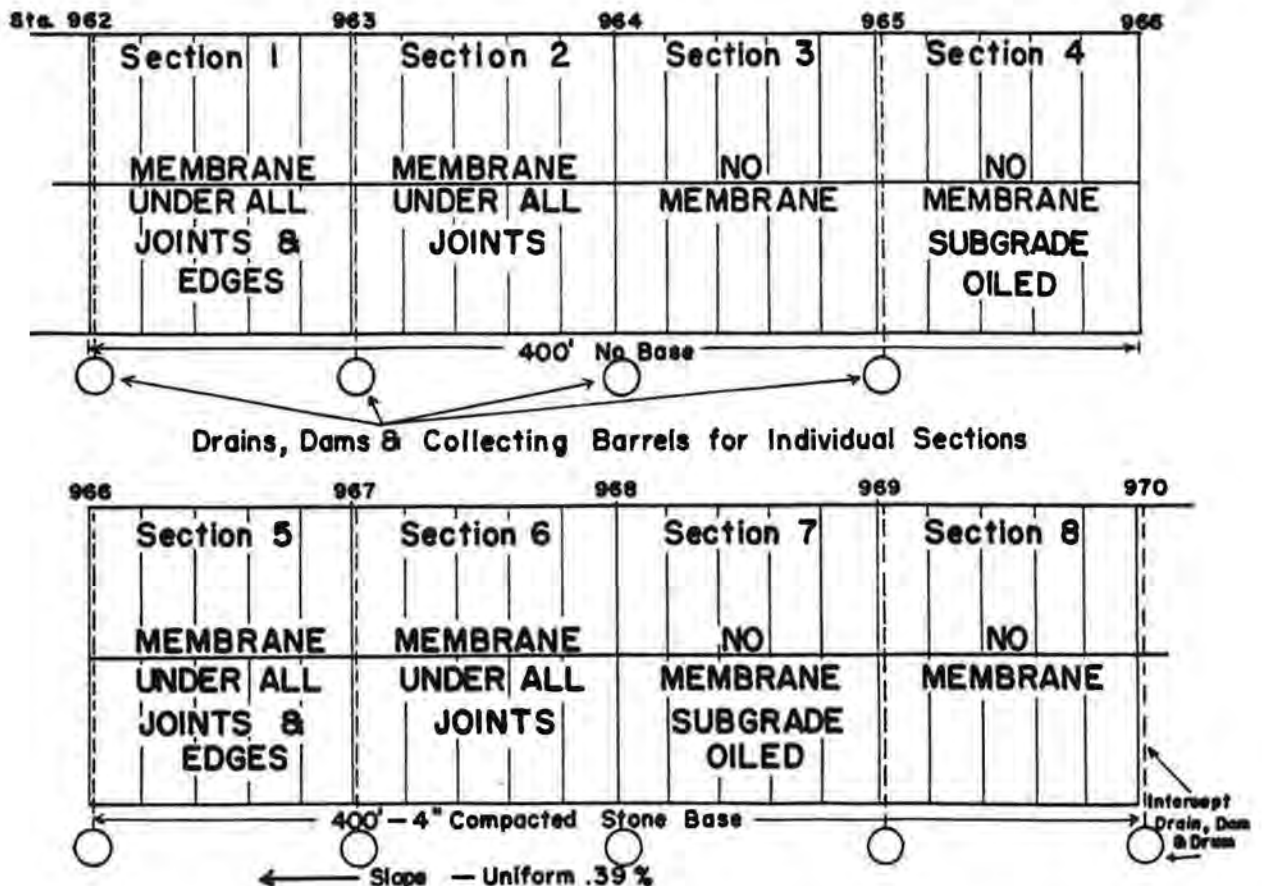
Figure 11. Controlled moisture entrance variations.
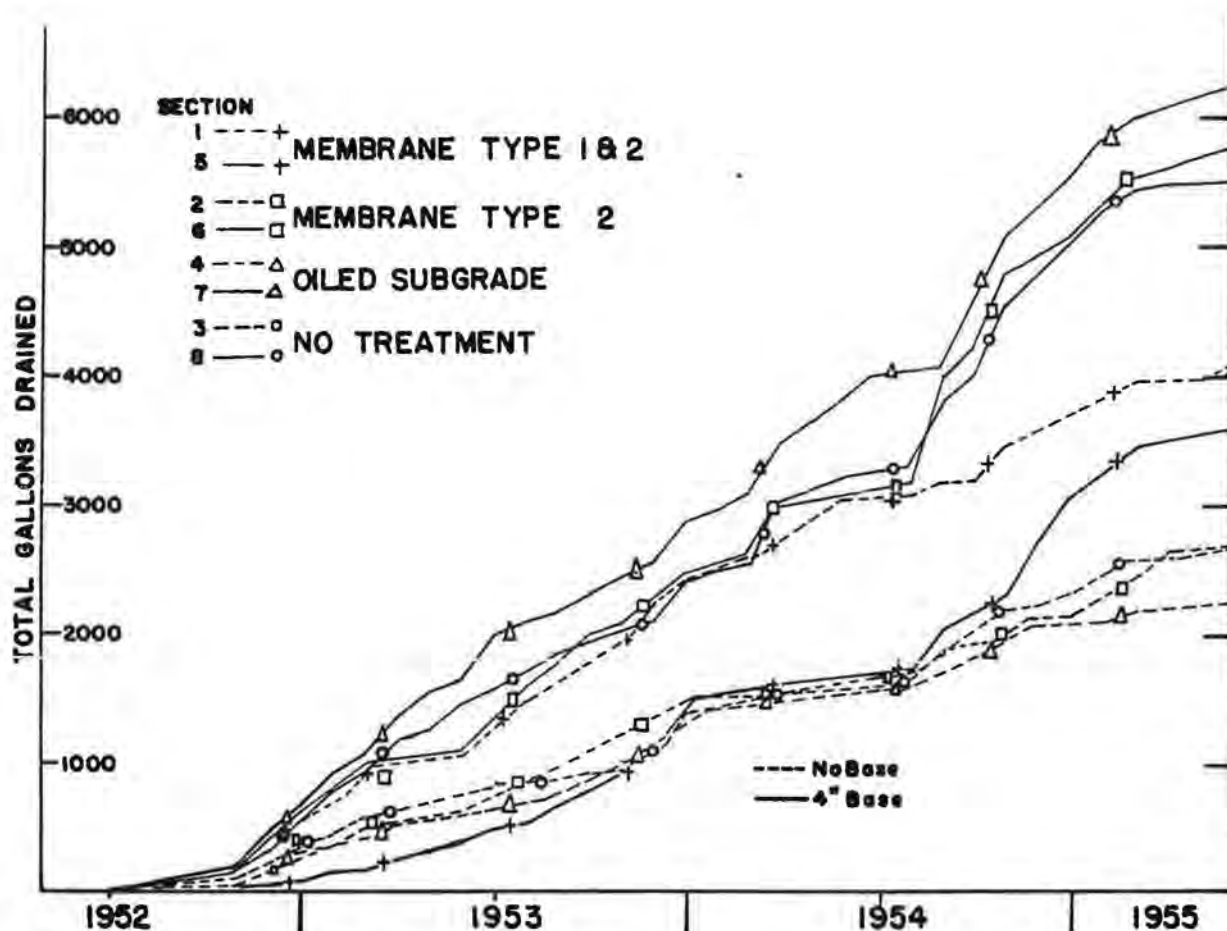
Figure 12. Comparisons of cumulative drainage.

minimum. At the same time permanent marks were placed at six locations across the slab and directly over one of the previously sampled transverse lines. Elevation readings were obtained at these points to provide the original datum. The marks were placed at 4 in. from each edge of the slab, 4 in. on each side of the centerline and at the quarter points of the slab (that is, 6 ft from each edge).

Thereafter tri-monthly subgrade moisture samples were taken through one core hole at each of the locations where the elevations were being checked. The elevations were checked once a month with every third month coinciding with the moisture sampling time. Figure 14 shows the vertical movement, at a typical fill location, of the six points on the slab surface as corresponding to the moisture contents of the tri-monthly subgrade sampling.

As an adjunct to the other companion studies the subgrade moisture data thus obtained were averaged to show the seasonal variation depicted in Figure 15.

DISCUSSION

In a general sense, the foregoing data present a picture of subgrade moisture conditions in Missouri. It must be borne in mind that the majority of these tests and studies were under way during the nearly five years of drouth which plagued Missouri farmers. While it was not evident except in minor cases that this drouth affected the newly constructed concrete pavements, it did cause damage to many flexible pavements and to the asphaltic widening of older concrete slabs. The damage was mainly in the nature of subsidence due to desiccation, especially that caused by the hair roots of vegetation which is not a reversible process.

The data depicted in Figures 7, 8 and 9 show that the main source of surface moisture entrance into the subgrade system is past the edges of the pavement. The bulbs

of high moisture content were apparent more often under the edges of the slab than at any other place and these bulbs also proved to have the widest range of moisture, relative to the rest of the subgrade, at the times of high moisture levels. These spots also evidenced the greatest spread of moisture levels for that portion of the roadbed directly below the pavement. It can then be assumed that the same means of wetting the subgrade soil (that is, past the edges of the slab) is also a means of drying the subgrade under a reversal of conditions.

Information which applies to this discussion but which was obtained from a study outside of this particular group is shown in Figures 16 and 17. It is presented at this time to substantiate the following statements. A more or less continuous channel was discovered next to the vertical edge of the slab. At the time of this study, the crack between the slab and the shoulder soil appeared to be very slight but on excavation the channel with a cross-section as much as 2 in. by 3 in. was found at the lower corner of the slab edge. This opening or channel also extended for some distance under the slab as spaces of $\frac{1}{4}$ in. to $\frac{1}{2}$ in. were visually apparent. Observations were made on all other studies which entailed the opening of the concrete so that the base could be visually inspected. From these observations it was concluded that water flow in the pavement-base-subgrade surface system was no different than in any other system, following the path of least resistance whether it be over, under, around or through the base materials.
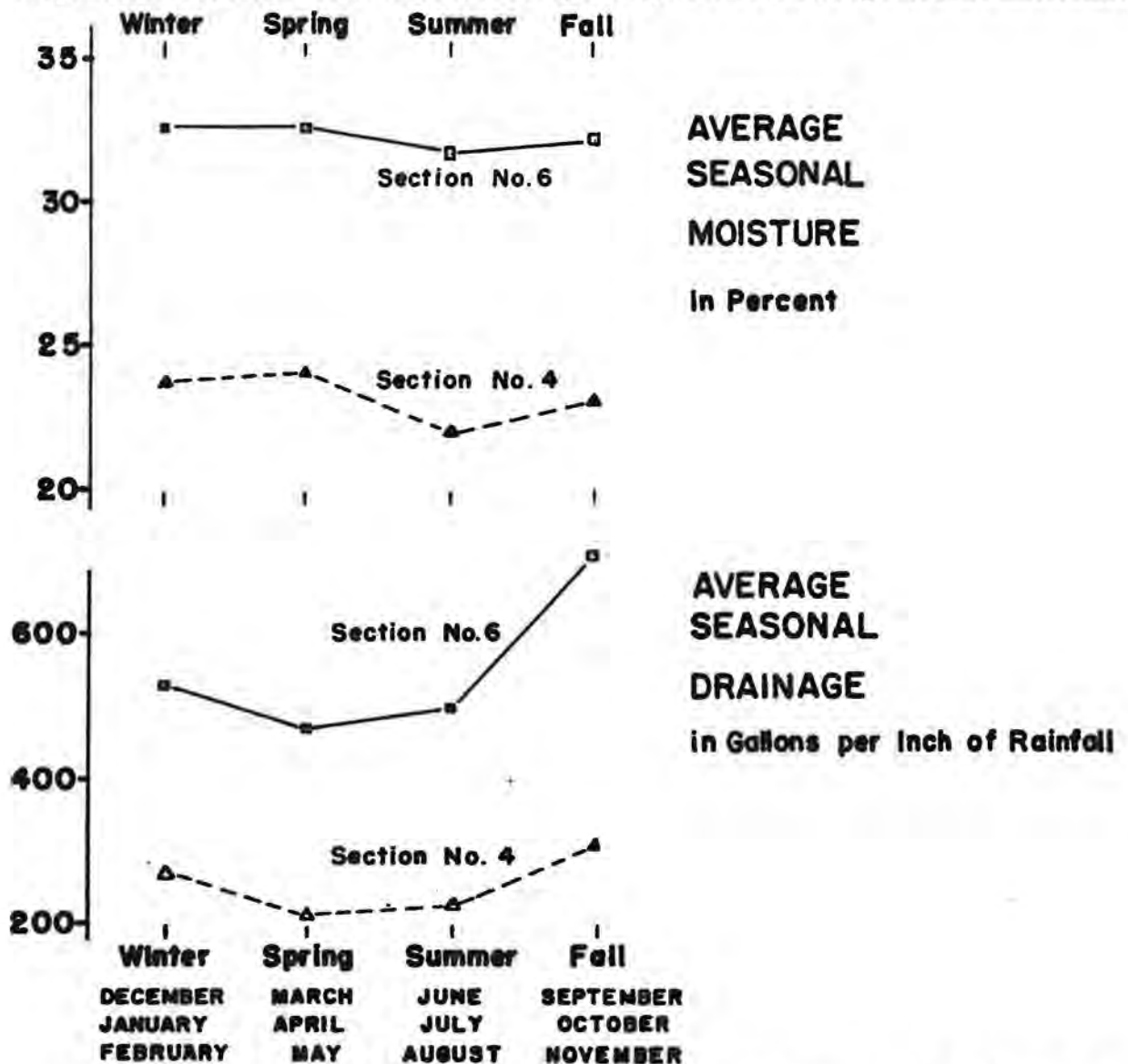
Figure 13. Comparison of average seasonal moistures and average seasonal drainage for two sections.

Cross Section at Sta. 67+09
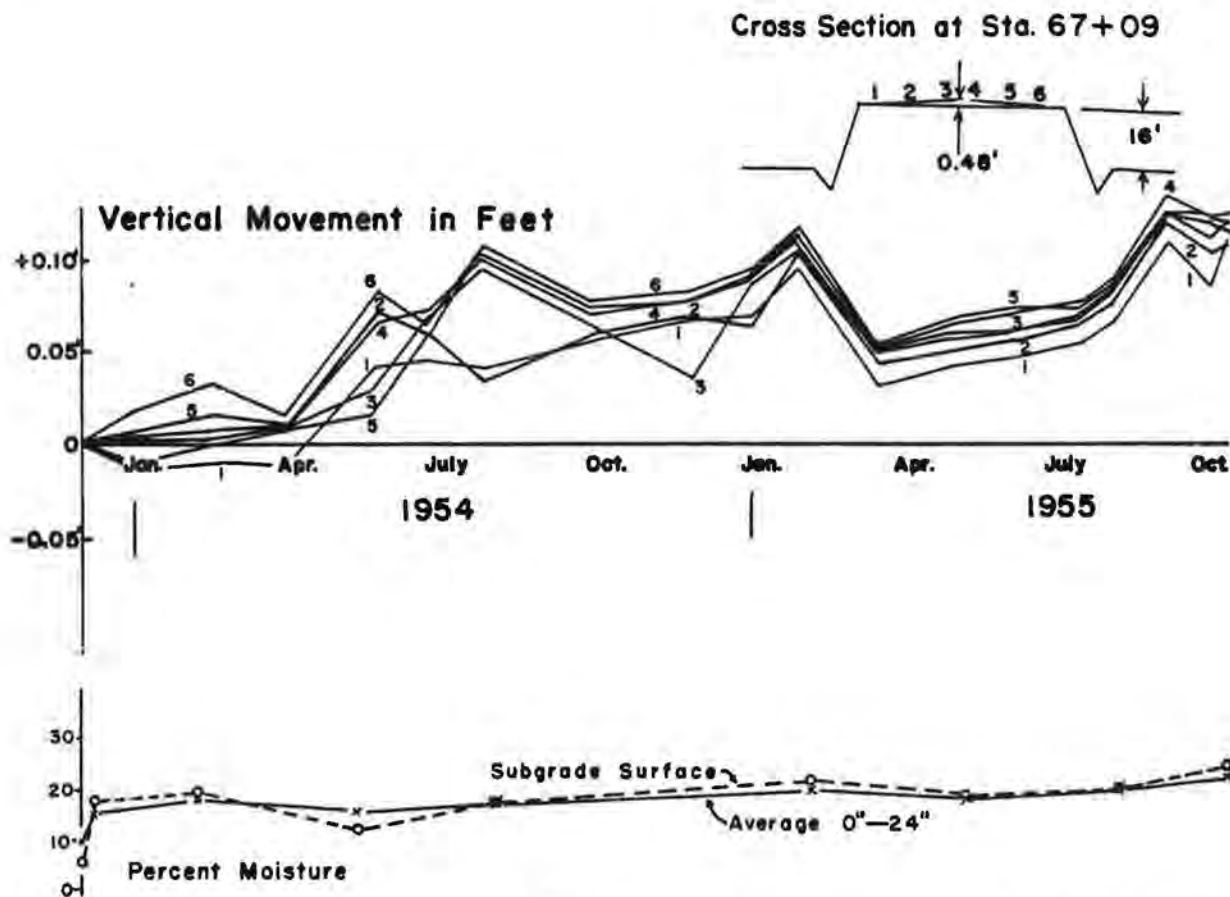
Figure 14. Vertical movement of surface of slab constructed on dry subgrade.

This means of entrance was discounted as a major factor in the appraisal of the ultimate average moisture level of the subgrade system by the data obtained from the "Controlled Moisture Entrance" study. This study showed quite plainly that there were no major differences in the average moisture levels of the sections where the moisture entrance past the edge or through the joints was controlled and the section with no control. The efficacious effect of the oiled earth subgrade was more apparent in the section with no base than the section with base. Since the only preparation was by surface planing and spraying with oil, it is quite possible that the process of placing the base might have somewhat damaged the oiled surface. At any rate the oiled earth subgrade under the base did provide a delaying effect upon the rise in the average subgrade moisture, also a stabilizing effect in that the fluctuation of the moisture level was decreased.

All of these studies have shown that the moisture level of the subgrade rises rather rapidly after construction where no sufficient preventive treatment is provided. A previously reported study (1) substantiates this indication. In many cases the climb of the averages to close to the plastic limit had occurred in three months or less. Lancaster (2) has shown that in his study of flexible construction it took nearly seven years for the average moisture content of those points 8 ft from the edge, to rise
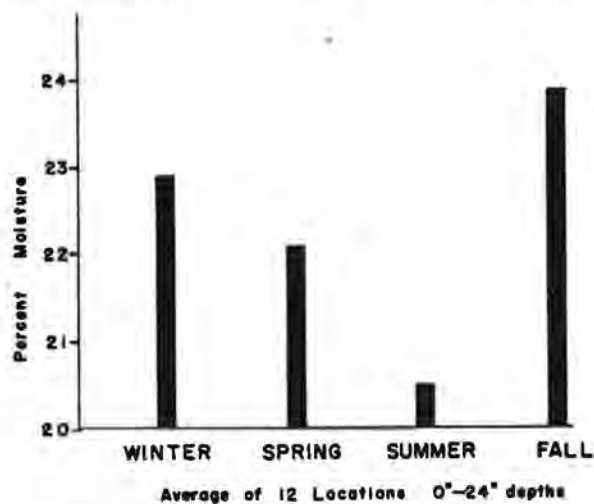
Figure 15. Average subgrade moisture.

to the three-month level of those points 2 ft from the edge.

The seasonal variations in average subgrade moistures were not very great but a more indicative measure of the possible changes of subgrade moisture might be found in the examination of the changes at any particular location. For example, data obtained in the "Seasonal Moisture Variation" study showed that at one location the subgrade surface moisture content varied approximately 25 percent in three months. The fact that there is no great variation in the averages over the seven years of sampling is an indication that prediction of ultimate average moisture levels need not regard seasonal effects. This statement is made with the reservation that it applies only to concrete pavements on base course material in Missouri.

A subgrade in which the average density, indicated by compaction reports, is 100 pcf would have a saturation moisture content of 24.7 percent. Therefore, if a moisture content of 38 percent was found in the top 12 in., the density would have changed to 82.4 pcf, again assuming saturation. This change in density would indicate a vertical expansion of $2\frac{1}{2}$ in. Yet in this case the measured change in the elevation of the slab surface at the adjacent check point was only 1 in. From this it can only be assumed that the resultant expansion was horizontal as well as vertical even though considerations of resistance would seem to indicate otherwise. Although this study indicates considerable vertical movement throughout the project, there was little evidence of critical pavement distress. The most recent measurements of faulting at the transverse joints on this project have been showing a decrease in the total inches per mile of faulting from 47 in. to 40 in. Whether or not this is a true trend remains to be seen.

Calculated theoretical moisture distributions based on the approach of Croney (3), indicate that some differences in basic assumptions must exist (that is, impermeable and infinite cover) to account for the lack of correlation. Nevertheless it is felt that based upon whatever assumption is made, the best time to cover the subgrade would
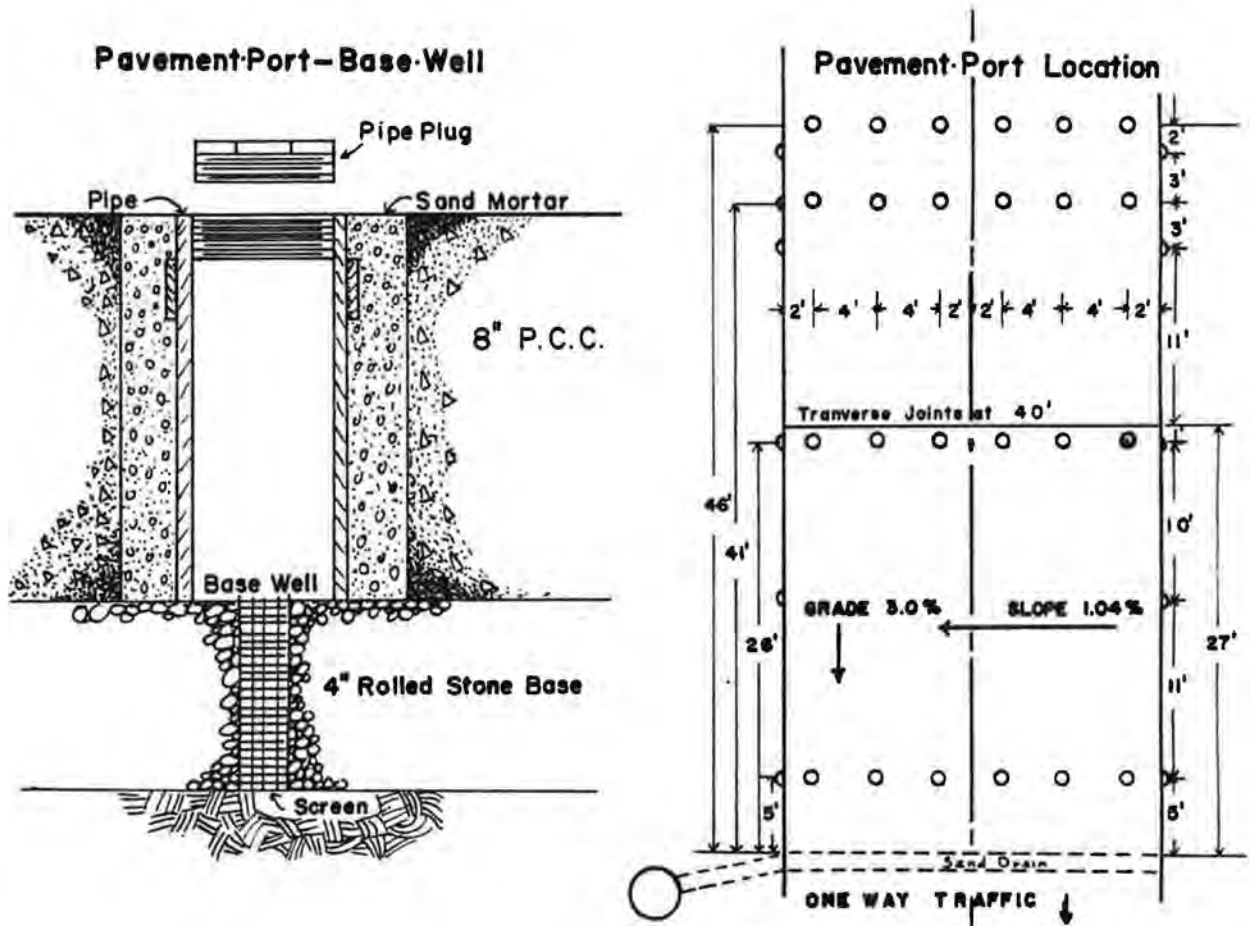
Figure 16. Details of base moisture flow study.

Dye Supplied at Points "F","C", & "A"
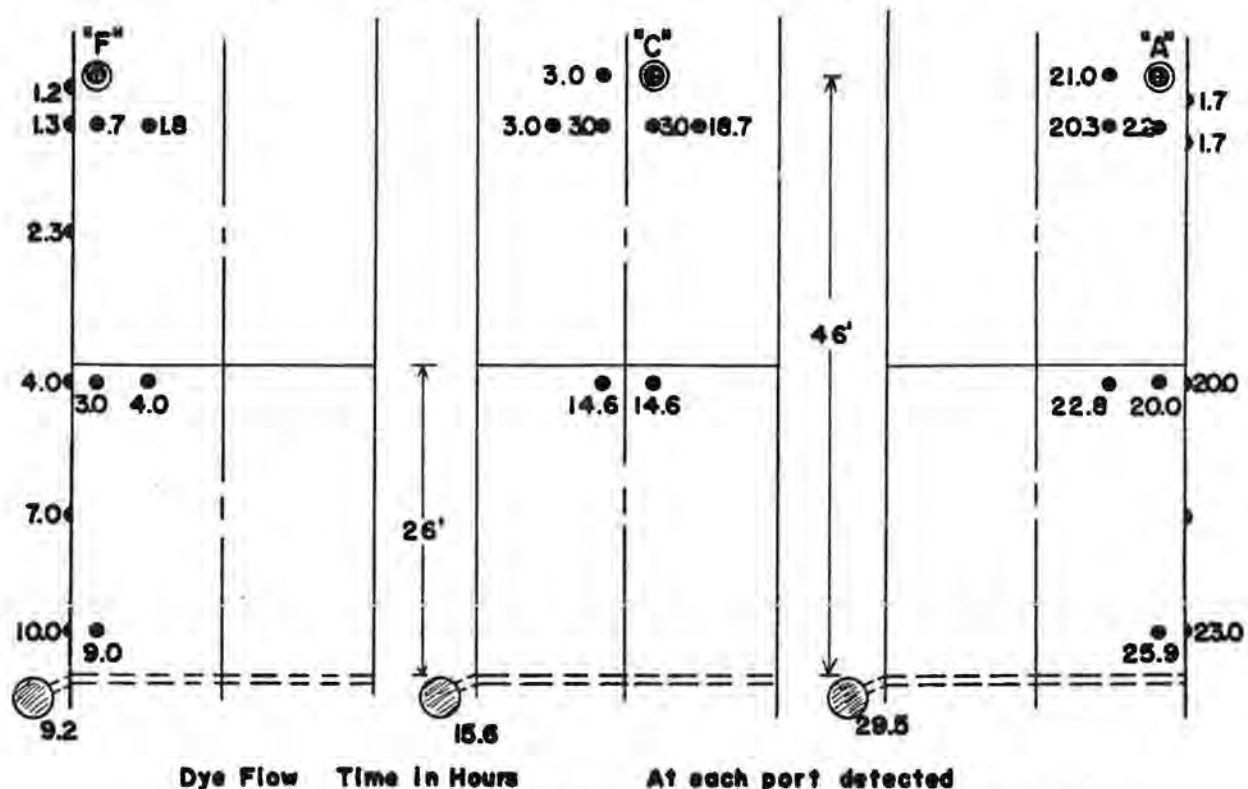
Figure 17. Dye flow times in hours from different points of supply.

be when the moisture distribution curve is at or above the optimum moisture for compaction and yet remains below the theoretical curve as defined above. It would then seem that if the cover could be made to more closely follow the basic theoretical assumptions, the likelihood of the subgrade remaining in a stable moisture condition would be enhanced. If such could be obtained then the engineering design of such roadway foundations could be more economically based on valid supporting values, which could be determined in the laboratory.

CONCLUSION

Since some of these studies may be reopened in the future it would not be proper to list any conclusions now, but instead some indicated questions are presented.

1. What avail (as far as subgrade moisture is concerned) is the sealing of center and transverse joints, if the edges are not (or cannot be) sealed?

2. Is there an advantage in making a base course less permeable so that the subgrade surface would possibly show less variation in moisture content even though its average may be higher than that under a permeable base?

3. Continuous membrane seems to produce a more uniform, although possibly a higher subgrade moisture content. Will the added cost be justified on the basis of long term results?

ACKNOWLEDGMENTS

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Moisture Content and the CBR Method of Design

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Introductory Remarks by the Chairman

The essence of science is generalization or, as Poincaré says, to give the same name to different things. The essence of engineering is to use science, experience and constructive genius toward an economical solution of a specific problem. While there will never be a substitute for constructive genius, considerations of economy move us to expand science in such a way that it will cover more and more of the area for which experience is required at the present time. In road construction, experience still holds a large sway in the adequate understanding of soil and other construction materials and of the effect of climate on the performance and service life of material structures. One of the outstanding pioneers in expanding science into the area that is still essentially dominated by empiricism is Colonel Wooltorton, who has a large and intensive experience as a road builder in various climates. In his long and distinguished career, Colonel Wooltorton has always endeavored to understand scientifically the complex phenomena encountered by him and others and to coordinate them into a logical system as a first and necessary step toward a true science of rational road construction applicable to all climatic regions. In his present contribution, Colonel Wooltorton makes available to us his conclusions on the relationship between the moisture economy in soils and the proper use of the CBR method of design based on long experience and much good thinking.

THE CBR TEST

● THE CBR test involves the compaction of a sample, in a manner specified by one of several standardized techniques, at a predetermined or ascertained moisture content and to a predetermined or ascertained density; and the penetration of the sample, in its existing state or after soaking, by a plunger at a given rate to give a specified deformation under a measured load. The value measured, for use in design, is the load or the resistance of the plunger to penetration. It may be considered as an indication of the strength of the material in the form of its resistance, under the conditions of test, to shear deformation or plastic flow. The measured load is expressed as a percentage of the resistance obtained from a like penetration of a standard material and is referred to as the California Bearing Ratio.

The required pavement thickness is determined from this CBR percentage by a method which is essentially empirical. The bearing ratio value is entered into an appropriate loading curve to give the required thickness.

Originally there was only one curve which became known as the curve for "light traffic" or the 7,000 lb wheel load curve. With accumulated experience a second curve, for "medium heavy traffic," or for a 12,000-lb wheel load, was added (22, 23).

These took the form of the more modern variations shown in Figure 1.

THE DEVELOPMENT OF THE TEST

The test was devised by the California Division of Highways in or about 1929 for the original purpose of comparing base and subbase course materials and only later for the evaluation of subgrades, but it was not until 1940, when the U.S. Corps of Engineers adopted the test as the most convenient one for use in connection with its wartime airfield construction program, that the method was intensively developed.

An extensive program of investigations was put in hand with a view to extrapolating the design curves from the 12,000-lb wheel load to very much higher limits and to check the validity of the curves so obtained by experiment.

As a result of the embracing laboratory and field work undertaken, more is known about this system of testing and method of design than of any other approach. From this research sprung much of the present-day knowledge of the design problem and of the many and involved properties of soil under strain.

As far back as 1946, there appeared, in very different parts of the world (South Africa and Texas), two most remarkable research papers on the various relationships encountered in the bearing value method of design.

The two authors, Kleyn (South Africa) and McDowell (Texas), had adopted the same line of thought and had come to substantially the same conclusions. Their works were, in a most remarkable way, complementary for jointly they covered a very wide range of soil materials thus enabling in conjunction with similar data from elsewhere, for example, Kenya, the deduction of general rules of the behavior of compacted soil under strain.

Figure 1.   CBR-pavement thickness curves for various wheel loads.

Their data were presented by plotting on a family of density-moisture content curves, for various compaction efforts, the iso-lines for such properties as bearing value (after soaking), expansion, air-voids content. The techniques were based on compaction by the impact method and an absorption procedure involving capillary rise. Kleyn (10) used the CBR value as an indication of stability whereas McDowell (14) used the results of the Texas Modified Bearing Value Punch Test.

The combined results of their work with deductions therefrom supported by modern research, carried out for the most part after 1950, are referred to later in this paper.

THE CBR CORRELATION CURVES

The design curves are observed correlationships between CBR values and pavement thicknesses.

Their implication is that if a field or an "in place" CBR value is determined for a base or a not too highly swelling (27) subgrade soil in or under an established, aged and provenly durable pavement (high quality base and wearing course) so designed as to be free from frost action (27), then, for average conditions, the thickness of the pavement above, necessary for achieving such permanency, will generally be indicated by the appropriate curve. And that is all.

The method assumes that a waterproofed, durable and permanent type of pavement is required and that the design and construction of each course will be planned accordingly; but note that the CBR concerned is the ultimate in-place CBR for the undisturbed base or subgrade soil, at some moisture content generally unknown at the time of design and existing in a structural state controlled not only by the way in which the layer was compacted but by the chemical and physical structure developed with time. If climatic conditions are such that the moisture content always fluctuates then the appropriate moisture content will be the maximum occurring under the ultimate range of fluctuation.
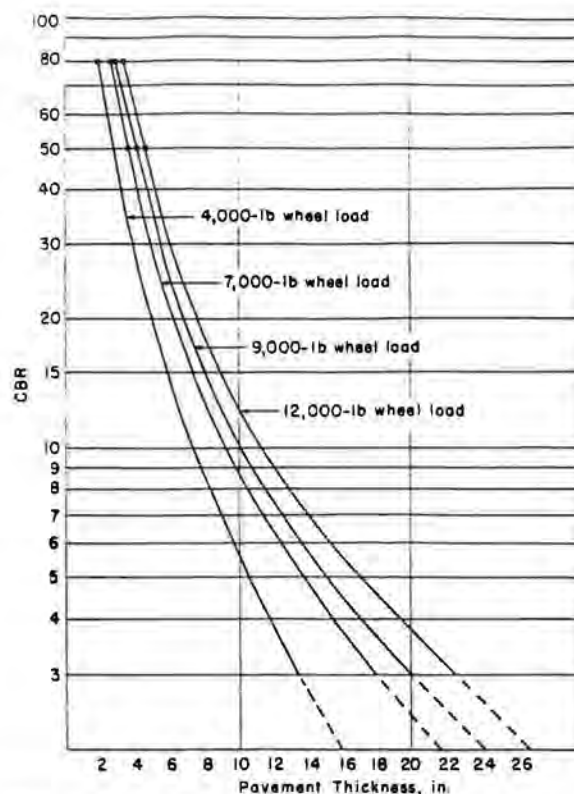
The success achieved in using this method of design depends entirely upon adapting a successful correlation between testing requirements and the ultimate conditions of the prototype.

Testing procedure must be standardized and strictly controlled and the data required and obtained must be planned and interpreted with discretion and considerable acumen.

It is evident that if the conditions governing the penetration test are in any way varied, then the value of the CBR will change and a different thickness will be obtained from the design curves. It is therefore essential that the accepted test specifications should be rigidly adhered to until such time as locally gained knowledge can be collected to justify the validity of any variation contemplated.

Nevertheless the aim must always be to develop a technique which will more and more nearly simulate the structural and controlling moisture content conditions of the subgrade to be eventually reached in the field. When this is achieved it will be possible to introduce a constant factor of safety into the design calculations.

THE DESIGN PROBLEM

The design correlationship, as given by the CBR curves, is thickness versus in-place CBR after a number of years.

The problem is how to arrive at this ultimate CBR value keeping in mind that the road must also be stable when first opened to traffic.

The ultimate in-place CBR, or stability, depends on (a) the method of compaction, (b) the ultimate density, (c) the ultimate maximum or equilibrium moisture, and (d) any structural effects developed in the soil with time.

METHOD OF COMPACTION

Under the original California test method of obtaining design data, compaction was achieved under a static load of 2,000 psi [1] but subgrade experience eventually indicated that the stability of the material compacted in this manner sometimes differed considerably from the stability of the soil after compaction to the same density in the field.

In the meantime and as a result of this procedure of compacting by the static method, the belief grew that stability always increased with increase in density where this is now known to have limitations as can be deduced directly or indirectly from reference (12).

In an endeavor to rectify this discrepancy, between the stabilities attained in the laboratory and in the field, other forms of compacting in the laboratory were investigated by the U.S. Corps of Engineers. This resulted in a modified form of the AASHO compaction test or compaction by impact (1942); more recently this has been replaced, in some laboratories, by compaction by kneading action. There is not a great deal of difference in the stability or moduli of deformation of samples compacted by these two latter methods to the same density at the same moisture content though the results of kneading action compaction have been found to be closer to those attained in the field (26). Both compaction by impact and by kneading action give far more realistic properties, as evidenced by triaxial and shear test data, than static compaction, when compared with the stabilities obtained after compaction by sheepsfoot rollers and rubber-tired rollers. Compaction involving kneading action is believed to produce a soil structure or particle shape and arrangement most nearly simulating those achieved during construction and thus most likely to produce comparable shear strength.

The CBR's obtained for samples prepared by static compaction may be very different from those obtained by the other methods of compaction and they may be very misleading if used as a basis for design.

There is some evidence that the unit pressure exerted during compaction in the field also has some effect on stability.

[1] This pressure was selected as that then believed to give densities most comparable with those found under old pavements.

STABILITY AS DETERMINED BY LABORATORY TESTING OF SAMPLES COMPACTED BY IMPACT OR KNEADING ACTION (12)

Soaked Samples

An analysis of published stability data, for acceptable strains, has shown:

1. For constant molding moisture content, an increase in the density to which a low to medium plastic soil (P. I. from 0 to about 12-15) is compacted is accompanied by an increase in bearing value for densities up to a value corresponding to an air void content which decreases with decrease in the moisture content of compaction after which the bearing value ceases to increase so rapidly and may decrease appreciably. This is illustrated by Figures 2 and 3.

Figure 2. Iso-CBR lines for various conditions of compaction after four days soaking; after (10).
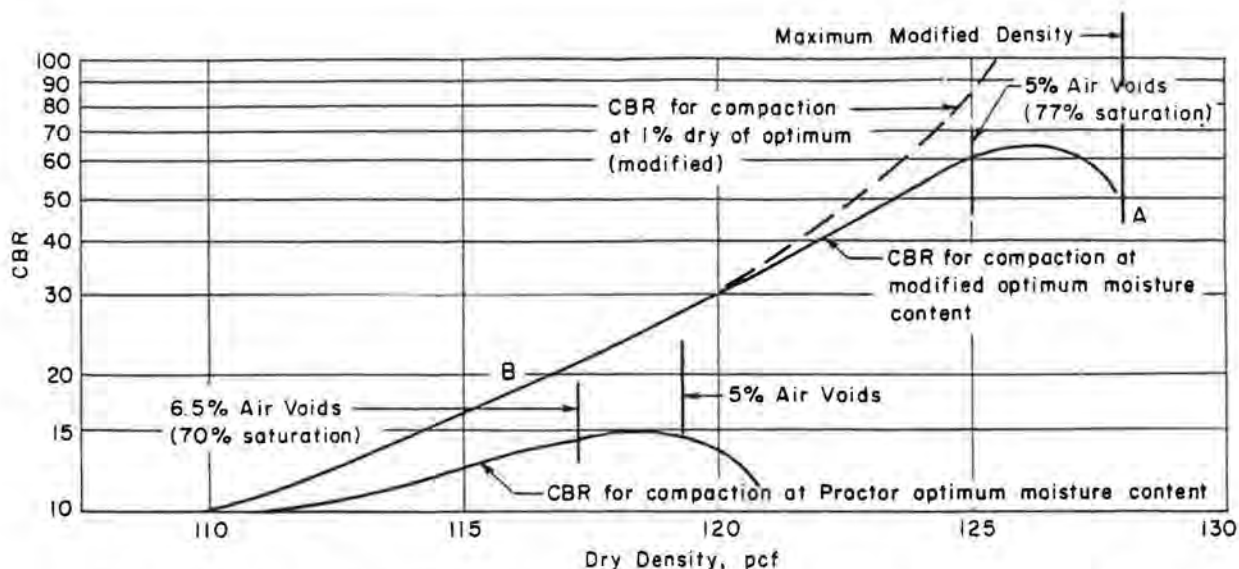
Figure 3. Variation in CBR with moisture content of compaction (data from Fig. 2).

For materials possessing a plastic index in excess of about 12-15, the lines of iso-bearing value change their pattern (see No. 2 below) and the tendency of the bearing value to decrease, for densities in excess of a critical value, seems to fade out as the P.I. increases (see Fig. 4).

2. The maximum bearing value for low to medium plastic soils [2] occurs, for any given compactive effort, at a moisture content of about 3 to 1 percent dry of optimum; while for medium to highly plastic soils the maximum bearing value moves to the wet side of optimum, at a P.I. of 12-15, where the deviation from optimum increases with increasing P.I., and the effect is more pronounced for modified than for standard Proctor compaction (see Figs. 2 and 4).

3. For equal percentage saturation, bearing values increase with density for materials whose P.I. varies from zero to about 15.

Unsoaked Samples of Silty Clay and Sandy Clay Compacted by Kneading Action

1. For constant moisture content of molding, an increase in density caused an increase in stability depending on the moisture content and the range of densities involved (25) (see Fig. 6).

2. For a constant degree of saturation an increase in the density was accompanied by an increase in stability (25) (see Fig. 6).

DENSITY MAY BE CRITICAL

Density may thus be a critical factor in design. A reference to Figure 3 shows, that for the particular medium-plastic soil concerned, an increase in density from 126 to 128 pcf for a sample compacted at modified optimum moisture content the CBR drops from 65 to 50.

When designing for a density, the value required must be sufficient to eliminate the possibility of appreciable consolidation, must be sufficiently high to achieve an economic value of the stability, should in conjunction with its moisture content give a condition of near minimum volume change, should be economically attainable with the equipment available and must not be so high as to lead to the possibility of a decrease in stability

[2] Some soils containing halloysite or fine material of volcanic origin appear to be exceptions in that while the iso-CBR lines are of the form associated with soils having a P.I. of less than 15, their P.I.'s are of the order of 30-35. The explanation may be in the moisture fraction representing the inter-planar water of halloysite or the vesicular moisture of porous volcanic material which are not indicative of plasticity.

accompanying any future increment of densification under traffic or by over-compaction during construction.

Though many high-swelling soil subgrades may lose density with time, if over-compacted, the more general run of materials utilized in good construction would appear either to remain at a near constant (dry) density or evidence a slight increase in (dry) density.

They could remain at constant density because of the constancy of the subgrade moisture content or, if that moisture content increases, by virtue of the grading and plasticity properties of the material or possibly because the superimposed pavement loading was sufficient to suppress and prevent volume change. The slight increase in dry density would most probably be a result of additional compaction under traffic. It could, perhaps, be caused by "thixotropic set" or particle orientation under stress.

If, while using such a soil as illustrated in Figure 2, construction control is such that there is a danger of over-compaction or if there is a possibility of some increase in density under traffic, it would appear advisable to compact at a moisture content slightly dry of optimum.

ULTIMATE MOISTURE CONTENT

Whether it will ever be feasible always to determine with close accuracy the equilibrium or maximum moisture content within the equilibrium range of moisture contents likely to occur in the subgrade, or in any other layer, under all conditions of internal and external climate cannot yet be foretold. It is, however, known that certain research organizations are actively engaged on this problem.

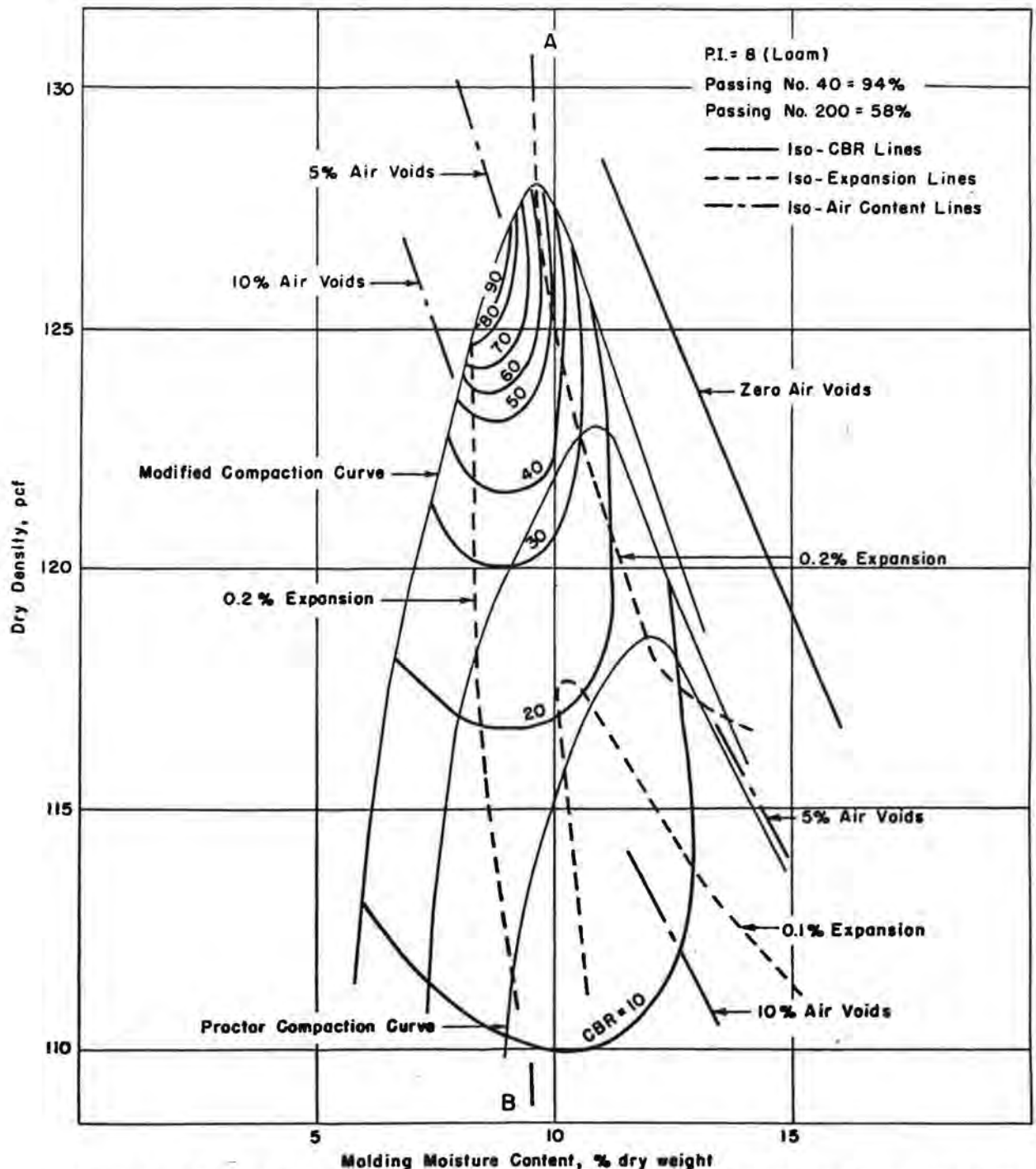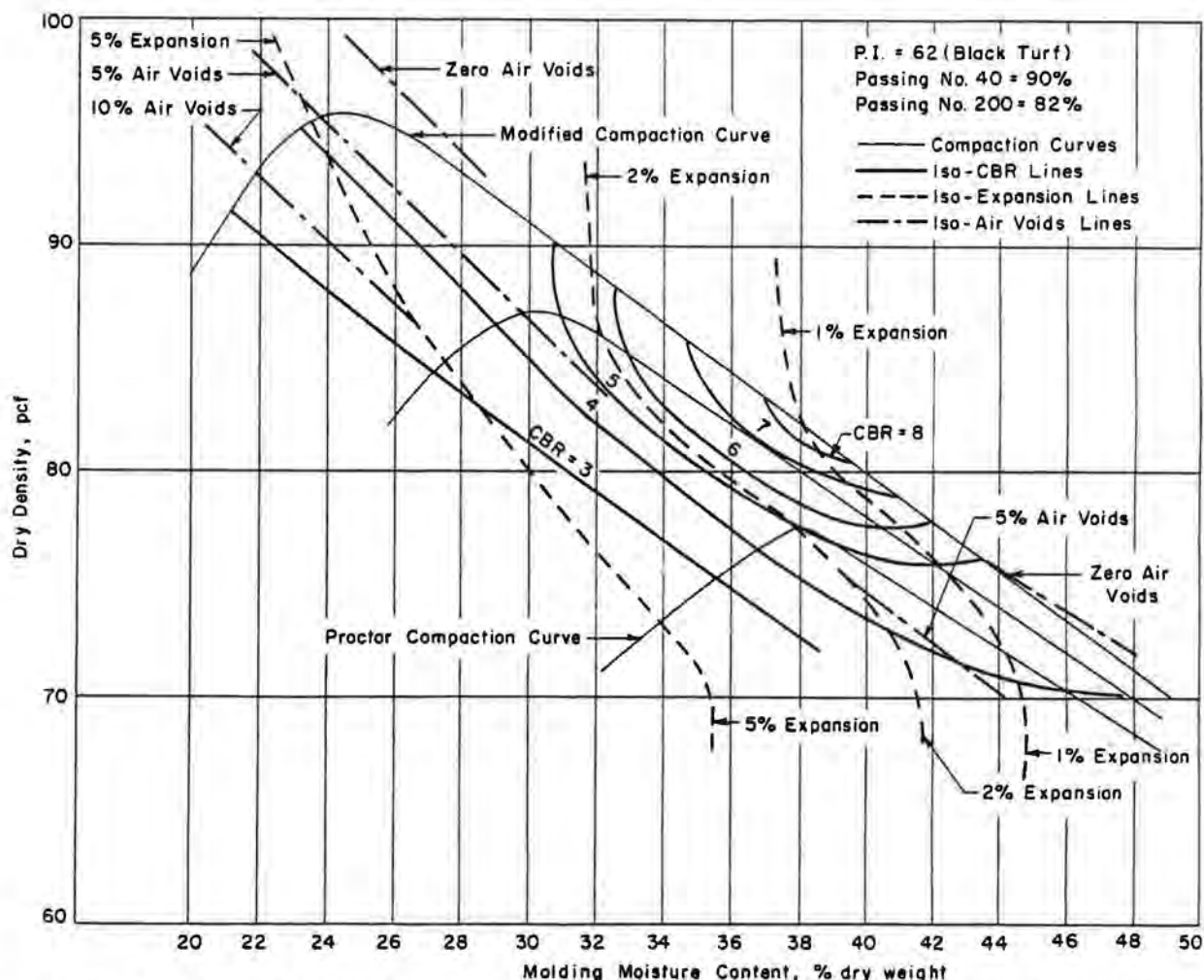Figure 4. Iso-CBR lines for various conditions of compaction after four days soaking; after (10).
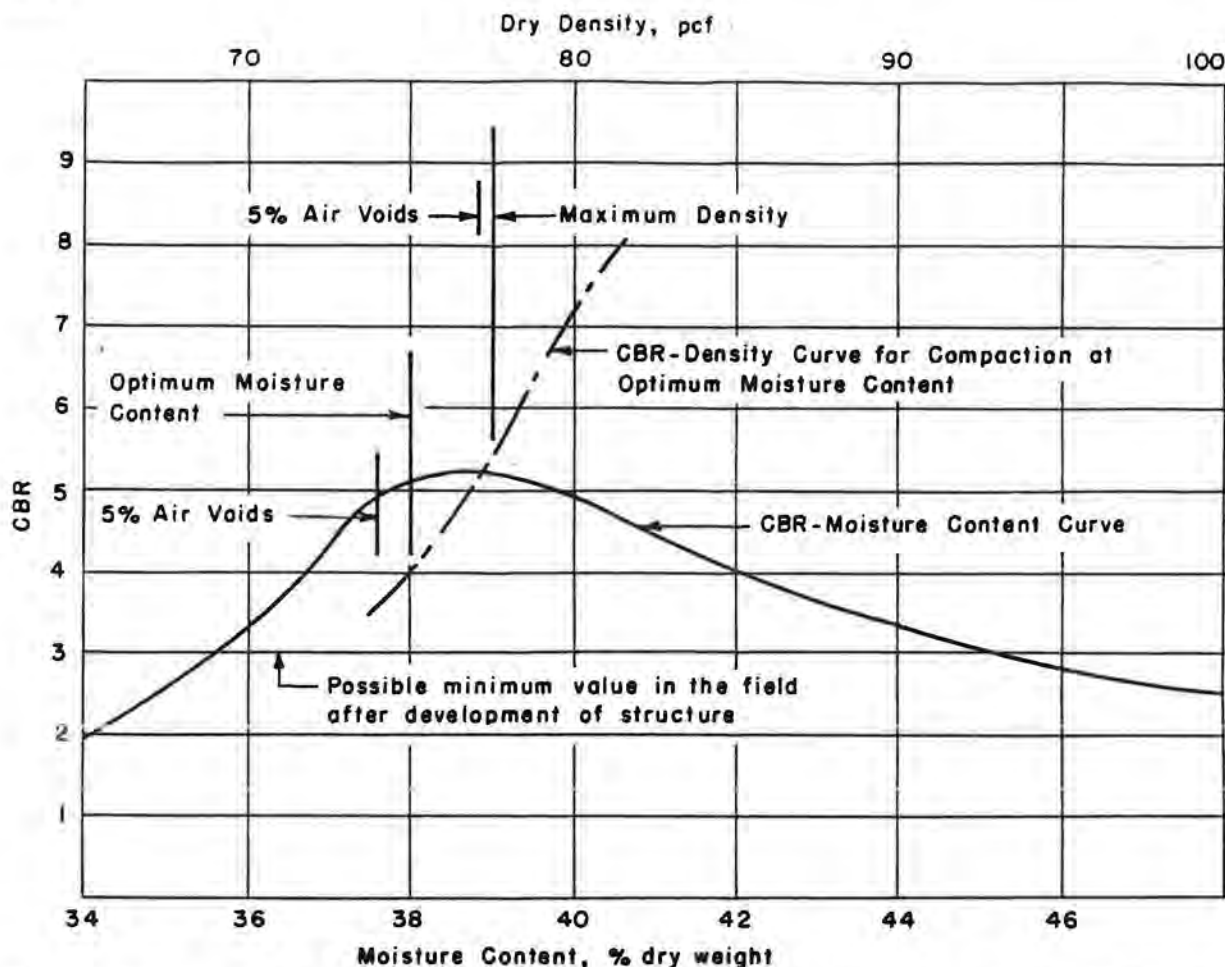
Figure 5. CBR-moisture content and density curves for Proctor compaction (data from Fig. 4).

For certain conditions, as of a high water table, such a forecast is possible, though perhaps laborious, by means of the pF or suction pressure approach (3a) but this method has not yet been proved applicable when the water table is below a depth of about 10 ft.

For other conditions, as for a low water table, there are a number of approximate methods, some of which, in view of the heterogeneous nature of soils, may be found to give a sufficiently accurate answer for predictive purposes no more deviating from the truth than that for any other soil test data. They may, in fact, give far more reliable predictive data than at present surmised if used in the right way and under the right conditions.

Consider the plastic limit guide evolved out of experience. Assume that the soil is not submitted to slaking forces or is able to resist such forces. It appears to be generally accepted that, no matter to how high a relative density a highly plastic soil subgrade is compacted, it will, in time, swell until it ultimately reaches a (dry) density corresponding very closely to Proctor maximum density, that is, for the purpose of obtaining a correlationship between the maximum moisture content and the plastic limit, one should ensure that the material was compacted to Proctor maximum density or has reached a value approaching that density.

For compaction under a given compactive effort, the greater the moisture content of compaction the less the moisture which can be absorbed after compaction and this value reaches a minimum when the moisture content of compaction slightly exceeds the optimum moisture content for that effort.

For more average subgrade soils, the amount of moisture which can be absorbed is, in the absence of any slaking, controlled by the air-voids content at the time of compaction. In more general terms, this air-voids content is, for Proctor compaction,

about $4\frac{1}{2}$ percent as an over-all maximum. This $4\frac{1}{2}$ percent air-voids content could possibly permit of an over-all maximum absorption of about $3\frac{1}{2}$ percent of moisture. On this basis, the maximum moisture content possible would be of the order of (O.M.C. plus 4) percent. This is illustrated in a statistical way by the average curves which appeared in "Engineering and Construction Control of Embankments" published in the Proceedings of the American Road Builders Association in 1941.

In the same set of curves the Plastic Limit and Optimum Moisture Content are connected, in an average way, by a relationship which may be expressed for the range P.I. = 28 to 6 as:

O.M.C. = (1.17 P.L. - 8)

so that the maximum moisture content might be expected to be of the order of:

(1.17 P.L. - 4) percent

A similar expression is deducible from Marwick's points (18a) for British soils.

Expressed as a percentage of the Plastic Limit:

$$\frac{\text{Max. Possible Moisture Content}}{\text{P.L.}} =$$

$$(1.17 - \frac{4}{\text{P.L.}}) \, 100$$

for which when

P.L. = 16 : maximum moisture content = 92 percent P.L.

and

P.L. = 30 : maximum moisture content = 104 percent P.L.

Figure 6. Variation in CBR with compaction effort and molding moisture content for unsoaked samples; after (25).

and these are values of the order found by Kersten (9a).

If the material were originally compacted at Proctor O.M.C. to a density of less than Proctor maximum then the amount of moisture the material could absorb would be greater than considered above.

It would thus appear that in a statistical way the maximum moisture content of the subgrade might be expected to reach ultimately a moisture content which could be represented by the approximate range 92 to 104 percent of the plastic limit with values in excess of 104 percent for certain types of materials and when compaction was less than 100 percent Proctor maximum.

For P.L. of 16, the range would be 14 to 16 percent and for a P.L. of 30 the range would be 27 to 30 percent.

Though for constant density, the CBR, can vary very considerably over a range of 2 to 3 percent of moisture content one wonders whether in soil work a much greater accuracy in testing and during construction is indeed possible.

The real difficulty in interpreting such data lies in being able to estimate the time interval which will elapse before the maximum moisture content is reached should construction be carried out at a lower value. If it is four days or four years, the value of the maximum moisture content is of great importance but should it take forty years to accrue then it becomes of less importance in these returning days of lower standards of construction followed by some of the backward areas being developed in the face of inadequate funds.

Though any firm correlationship between the maximum moisture content and the plastic limit would be most informative, the relationship does not appear to be on such a rational basis as the field moisture equivalent or even the saturation percentage relationship both of which appear to mean something understandable.

An interesting sidelight on the F. M. E. correlationship arose during the study of data for a believed halloysite subgrade soil. It was noted that 0.75 x F. M. E. represented a moisture content 9 percent lower than the modified optimum moisture content or one occurring well off the chart of equi-CBR lines for the moisture content range lying between the compaction curves for modified and Proctor compaction. Such moisture content did not appear to be likely equal to the maximum site moisture content under a pavement.

It was then noted that two of the data available applied to the subgrade under an old gravel road. In this area the rainfall was 80 in. and rain occurred throughout most of the year. The data were actually taken for a rainy period. The measured site moisture contents for those tests were 27 percent and 29 percent only.

The plastic limit was 35 and the Proctor optimum 45 percent. The field densities were 95 percent and 111 percent of Proctor maximum and the F. M. E. was 43.

ULTIMATE MOISTURE CONTENT AND THE SUCTION PRESSURE METHOD OF DETERMINATION

The suction-pressure method of determining the equilibrium moisture content or the maximum moisture content within the equilibrium range of moisture contents likely to occur in any layer of a road structure under an impermeable pavement of infinite dimensions has been developed in England. The method has been described by Croney (3a) and elsewhere. The principles behind this method and the implications of the conclusions reached in its study are not, however, clear at all. The following approach is believed to present an understanding of the principles involved and the conclusions to be reached from such an approach.

Let the total free energy of moisture at a point within a soil profile at equilibrium moisture content and at constant temperature be represented by Δf_S

Then $\quad \Delta f_S = \Delta f_{\sigma S} + \Delta f_{pS} + \Delta f_{oS} + \Delta f_{FS}$

Where $\quad \Delta f_{\sigma S}$ = free energy due to surface tension and radius of curvature of the air-water interface,

Δf_{pS} = free energy due to hydrostatic pressure of moisture adjacent to soil particle surface caused by adsorption forces as well as by any pressure transmitted from external sources,

Δf_{oS} = free energy due to the osmotic pressure developed by any dissolved material,

and $\quad \Delta f_{FS}$ = free energy due to water by virtue of its position in the particle adsorptive force field as well as in the earth's gravitational field.

If "X" and "Y" are two clay particles each surrounded by an adsorbed moisture sheath, as shown dotted, and "a" and "b" are points in this system in which "a" is below the meniscus of the capillary ring moisture but without the adsorptive force fields, and "b" is within the adsorbed water surrounding particle "X", then, assuming equilibrium conditions, the moisture is pure water and there is no osmotic pressure, energy conditions give:
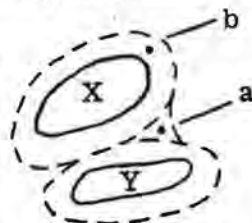
1. For point "a" lying outside the particle force field the energy due to the hydrostatic pressure in the moisture by virtue of its position in the particle adsorption field and that due to the position of the particle in the adsorption field disappear.

Under such conditions:

$$\Delta f_S = \Delta f_{\sigma S} + \Delta f_{pS} \text{ (external forces)} + \Delta f_{FS} \text{ (gravity field)} = 0 \qquad (1)$$

or

$$\Delta f_{\sigma S} = -(\Delta f_{FS} + \Delta f_{pS}) \qquad = -(gph + p_w)$$

where p_w = effective superload pressure due to weight of the moist soil over,

and h = height of the point above the free water surface

or resultant suction pressure = gravity potential - pressure potential

or

$$s = u - \alpha P \qquad (2)$$

where s = suction pressure and is negative,

                   u = gravity potential which may be negative or positive depending on position of the point relative to the ground water level,

                   P = superimposed vertical loading,

and α = a fraction varying between 0 and 1 depending upon the effectiveness of intergranular contact.

2. For point "b" lying inside the particle force field the same general energy relationship holds, that is:

$$\Delta f_{\sigma s} = -(\Delta f_{Fs} + \Delta f_{ps}) \qquad (3)$$

but $\Delta f_{Fs} + \Delta f_{ps}$ now refers to the energies associated with both the gravity and particle force fields.

In British publications the gravity potential appears to be referred to as "the pore-water pressure as determined by the position of the point relative to the water table."

The interpretation appears to imply that, if the water table is 100 ft below a point in the soil profile at moisture equilibrium then the pore-water pressure, or pressure deficiency, across the capillary meniscus (if there is one) would be as high as 43 psi and the radius of the meniscus would be as low as 0.00002 in.

It seems doubtful, however, if capillary water can exist as water in such fine soil pores and it would appear that for such a low water table, frequently exceeded in the tropics, the equilibrium moisture content may well be controlled, as far as the lifetime of a road is concerned, more by adsorbed moisture than by capillary moisture as such. Further, it seems very likely that temperature gradients may, on occasion, influence such equilibrium values to a marked degree to give maximum and minimum equilibrium values of a perhaps different order.

If the pavement is permeable and of limited width there will be further modifications for considerations.

The suction pressure approach to moisture distribution appears to lead to the possibility of confusion arising between the energy with which moisture may be held at a point with the energy available at the point to hold moisture. The difference is, of course, to be represented by the time interval necessary for the distribution of vapor flow to bring about that distribution suggested by energy conditions.

Though it may be convenient to consider moisture as attracted by suction forces, there is no obvious reason to believe that such forces are necessarily responsible for attracting moisture to a point or for controlling the amount of moisture at a point under a pavement when the water table is low.

The energy available to hold water at a point in a profile is made up of the following two components:

Energy associated with the particle force field
or the adsorptive energy

plus

The capillary energy available at the point to
hold moisture when it arrives as may be
modified by any swelling pressure or
any super-load.

The first component has a maximum value as long as the relative humidity is not appreciably less than 100 percent or for suction pressures numerically less than that corresponding to a pF of about 4.0; while the second depends on the shape of the particles, that is, plate or rod-like or spherical, and the density to which the material is

compacted. Where the first component can be represented by a constant, the second is a variable depending upon the geometry of the resulting capillary and pore-space system.

These energies do not so much attract moisture in the sense that they can cause moisture to move over appreciable distances but are energies available to hold moisture when that moisture is ready at hand for adsorption.

The energy available to hold water is thus a constant, subject to a constant temperature, for any particular system and the maximum amount of water which can be held is controlled by that amount of energy.

According to the British approach, it appears that the energy of absorption can be considered to be represented by a particular case of the general formula for the energy of moisture held under conditions of equilibrium, that is, as represented by Eqs. 1 and 2 rather than by Eq. 3 irrespective of the fact that capillary moisture may not exist in the tropics.

The actual energy available for surface adsorption is the hydration energy plus the hydration plus any osmotic energy which limits the amount of moisture which can be adsorbed. (4)

The capillary energy available to retain water is controlled by a statistical treatment of such systems as:
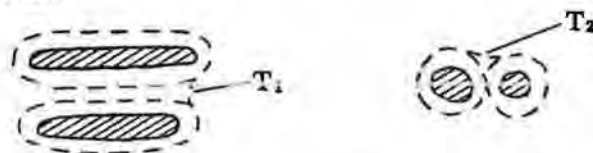
where the amount of capillary moisture possible is controlled by radii r_1 and r_2 and where, in a subgrade soil there would not appear to be necessarily any connection between such radii and the depth of the water table for some appreciable time.

The height to which capillary moisture can rise above the water table is controlled by the maximum tension which can be withstood by water films but water cannot, apparently, sustain a tension exceeding about 1,000 cm (pF 3) or about 34 ft.

More generally, coarse capillary water ceases to exist when the pF is of the order of 1.5 and fine capillary moisture when the pF is about 2.5. There appears to be no evidence that capillary moisture can rise to a height of 100 ft or more to supply capillary moisture under a pavement though, of course, moisture may move to such heights by film and vapor movement to give the same ultimate equilibrium moisture content but this takes a much longer time.

It would, therefore, appear that, for deep water tables, the maximum amount of moisture at any point under a pavement of infinite dimensions is controlled for some appreciable time wholly by the surface energy of the particles and there is no capillary water under conditions of equilibrium at constant temperature.

Moisture movement, at such heights, is in the vapor phase by convection, etc. The gravitational energy of such moisture, is, however, still expressible in terms of:

$$\Delta f = -gph$$

but the free energy equation is that represented by condition three and the amount of moisture, for some very appreciable time, appears to be limited to relationship four.

It would therefore seem that the equilibrium moisture content under a pavement of infinite extent is likely to be in the region of one determined by a pF of about 4 when the water table is very low.

Road pavements are not, however, infinite in width and other phenomena influence the moisture distribution in a transverse direction.

The suction theory presupposes that the pavement is not only impermeable and infinite in extent but that, as a consequence of its extent, the moisture content under the pavement is uninfluenced by horizontal capillary movement, evaporation and the effects of plant transpiration.

Horizontal moisture movement is unfortunately not always negligible in the tropics though its effect is generally found to tail off from a maximum at the pavement edge to

a negligible amount at the road center where suctions of pF = 3.7 have been recorded (ex. 29).

Whereas evaporation and transpiration are important in respect of edge movement and the cracking of the edge strips, horizontal capillarity and permeability of the surface are of the greatest importance as regards pavement thickness.

For the subgrade in the vicinity of the pavement edge, it would be expected that the maximum moisture content would be determinable by the action of the natural forces operating in such an area, where free water was likely to be available, rather than by the depth of the water table.

A soil will, after being fully saturated, drain out, that is, from its coarser capillaries, to a moisture content known as the Field Moisture Capacity, depending in value upon its density and certain other factors, where this moisture content, for a soil in the field, corresponds to that represented by a pF of about 3.0 to 3.2. It is a moisture content which is retained by a soil under a viscous resistance to flow till removed by plant root action.

Most soils reach the F.M.C. in from two to three days after rain while others, as some red soils, reach it within 24 hours even when compacted. Moderately silty soils, however, do not possess a F.M.C. and continue to drain for several months.

The effect of compaction on the value of the F.M.C. is to reduce the volume of the coarser capillaries and to increase that of the finer capillaries whereby the modified F.M.C. would be expected to be increased. In other words, definitions and geometry suggest that the value of the F.M.C. for a compacted soil approaches the moisture content represented by the Centrifuge Moisture Equivalent assuming that constant is determinable. The value of the C.M.E. for the compacted soil would then be that corresponding to a pF of about 2.7. It would, by definition, also be approximately equal to the F.M.E. for that particular density if such a test were possible for the compacted soil in mind where the F.M.E. really implies the presence of excess moisture or some supersaturation.

It is therefore to be expected that the maximum moisture content under a pavement, not less than 20 ft in width, would vary between that corresponding to a pF of the order of 4 at the center to 2.7 at the edges with possible short periods after heavy and prolonged rain when the moisture content would exceed such an edge value.

It is interesting to consider, in a speculative way, the maximum moisture content likely to occur under a pavement in terms of the guide that such a value will not exceed about 75 percent of the F.M.E. when the soil is resistant to any slaking forces which may occur under cycles of alternate wetting and drying.

Three quarters of the F.M.E., for a powdered soil, would then be expected to be representable by three quarters of the suction pressure corresponding to the F.M.E. There appears to be no published correlationship between F.M.E. and suction pressure but on the basis of definition it is essential that the F.M.E. shall have a lower limit of moisture content which can be represented by the F.M.C. or equivalent to a pF of 3. In general, the moisture content would be expected to be higher than given by this pF. Seventy-five percent of this suction pressure gives a pF of about 2.8 or a moisture content a little drier than given by the C.M.E.

It is for consideration whether in the absence of sufficient data, there is any great reason to believe that equilibrium or maximum moisture contents under a pavement are likely to be represented by some constant pF value. As the energy with which moisture is held may depend very much on the adsorptive forces, when the water table is low, it would be expected that such limits will depend in some way on the nature of the clay minerals and the replaceable bases and thus be variables depending upon the chemistry of the soil.

It is also for note that the above discussion emphasizes the value of incorporating membranes into a road structure when such membranes are carried through the road shoulders.

To turn to test data, if the CBR is determined immediately the sample has been removed from soaking, then the bearing value obtained corresponds to that for a supersaturated sample, that is, for one which is at a moisture content representable by the F.M.E. of the sample at its particular density. Under such a moisture condition

the effect of pore water pressure during testing is likely to be of extreme importance. For such moisture contents, the CBR value would be expected to be very low. This suggests that the drainage period adopted between soaking and testing for CBR is of importance and that for low trafficked roads, under favorable climatic and soil conditions, the period might be increased beyond the more standard interval of 15 min. with economic advantage—realizing that for relatively short periods the pavement edges might be overloaded.

The ultimate moisture saturation percentage has been found to vary, in the 4-day soaking test, from about 75 percent to about 95 percent depending upon the soil type, the moisture content at the time of compaction and certain other factors (24) which should include the density to which the soil is compacted.

The amount of moisture absorbed during the soaking test decreases with increase in relative density though the percentage saturation increases.

Field observations have indicated there is little, if any, connection between rainfall and subgrade moisture content when the bitumen surfacing is impermeable; though there is a very distinct trend for the percentage saturation to vary with climate and rainfall (24).

Whether or not the moisture content will increase or decrease with time depends not only upon the moisture content at the time of compaction but upon the moisture content at the time the pavement is sealed which may be a very different value and which may have to be taken into account in the design.

Nevertheless there is a very definite tendency for moisture contents in subgrades to increase, regardless of the depth of ground water level, though with some subgrade soils the process may, because of the characteristics of the soil types, be very slow.

The limited information available (24) suggests:

1. The maximum or ultimate degree of saturation is generally within the laboratory determined range of 75 to 95 percent. [3]

2. The degree of saturation for plastic subgrades tends to vary with rainfall.

3. The degree of saturation tends to be lower in areas of low rainfall (arid and semi-arid regions) than in more humid areas (this assumes that there is no permanent or temporary high water table).

4. The degree of saturation is well below the above range for well graded and drained granular soils. Le Clerc (12a) has specifically drawn attention to the necessity of covering a compacted swelling subgrade, constructed in a stage construction job, with sufficient, perhaps temporary, surfacing to endeavor to prevent moisture absorption and permanent loss in density.

THE EFFECT OF ABSORPTION, AS OCCURS DURING THE SWELL TEST, ON DENSITY AND CBR

Tests show that cohesionless soils (P.I. less than 2) and well graded feebly plastic soils (P.I. of 2 - 6) do not swell appreciably during the 4-day soaking test in which they are contained in a 6-in. diameter CBR mold, and subject to a test surcharge of 10 lb.

Some temporary loss in density will occur in the field during freezing but this is generally recouped under traffic after the thaw.

In general, soaking has no effect on the CBR of cohesionless soils but may have an appreciable effect on the CBR of feebly plastic soils.

When the plastic index exceeds a value of about 6, absorption is accompanied, during the swelling test, by volume change where the magnitude of this change increases as the plastic index increases.

The saturation of finely grained soils, in the field, followed by freezing results in a loss of density.

In general terms, test swell appears to be a minimum on the dry side of modified optimum moisture content for material of low plasticity changing to the wet side of

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[3] The higher limit applies to fine grained soils. Note that the ultimate CBR is not generally determined by a moisture content corresponding to 100 percent saturation.

Proctor optimum moisture content when the plastic index exceeds a value of about 12 to 15 though the limit for pumice and halloysite soils might be greater.

For any specific soil and a constant moisture content for compaction, the swelling for high relative densities apparently decreases with increasing density for materials compacted under a low compactive effort but may increase with density for the same material compacted under a high compactive effort. In this phenomenon, the relationship between the surcharge weight and the swelling pressure for a given void content presumably plays a part.

But whether the swelling decreases or increases with increasing relative compaction, the volume change of a highly plastic soil, is, for high relative compaction, much greater for modified compaction than for Proctor compaction even when, for high swelling clays, the surcharge weight is as heavy as 30 lb. The difference may be of the order of 200 to 400 percent.

The result of this absorption and swelling is that a sample compacted to 100 percent modified AASHO maximum density may drop in (dry) density after soaking to 95 percent relative density or to even a lower value. As would be expected, the CBR decreases in the same way though contrary, perhaps, to general belief this does not necessarily apply to plastic soils compacted under the Proctor compaction effort and soaked for only four days.

The loss in density, which occurs when highly plastic soils absorb moisture under an appreciable surcharge has led to the commonly accepted fact that high swelling subgrade soils cannot usually be compacted to modified maximum density and held at that density. This means that there is apparently no point in compacting them to a density very much in excess of Proctor maximum or, from the point of view of attaining a condition of near minimum swell, of compacting them at a moisture content very different from Proctor optimum. This objection would not, of course, necessarily hold for the material used in the lower layers of high embankments and subjected to considerable surcharge.

One should not forget that the stability of all soils is a function of the molding moisture content and that it may, in fact, be more economic to compact a medium swelling soil under a high compactive effort to take advantage of a somewhat higher CBR after soaking.

Low swelling materials should be compacted under a high compactive effort and, as a general rule, it may be assumed that this is possible with comparative ease.

Many of the early writers as Porter (22), Kleyn (10) and McDowell (14) advocated the use of a bituminous membrane (often under a blanket course) over the subgrade to prevent infiltrating water reaching an expansive subgrade or the damaging of the subgrade from the efforts of alternate drying and wetting. The principle seems to have been introduced by Porter (22) and generally developed by Texas. More recently it has been used in England (18) to protect an exposed subgrade from the effects of rain and in Kenya to protect the shoulder subgrades of an embankment constructed in high swelling Black Cotton soil from the effects of infiltrating water.

SOIL STRUCTURE

With many, though not all, fine grained soils there is a marked tendency for them to develop, through chemical and physico-chemical processes, a "structure" or skeleton reinforcement markedly increasing their stability.

This factor features in the results of measuring in-place stability. It may mean that an undisturbed CBR is considerably greater than that for the disturbed soils at the same moisture content and density.

There is, however, one important thing to remember about soil structures. Some of them are but temporary, that is, while they would influence in-place CBR's measured for material in cut their effect would permanently disappear as soon as the soil was disturbed as it would be when the same soil was used in fill.

DENSITY AND MOISTURE CONTENT

Two factors therefore emerge: (a) Possible considerable loss of stability may re-

sult from overcompaction whether it occurs initially, during construction, or whether it occurs as an increase under traffic with time. This loss may be rendered more severe by any small increase in moisture content.

From the control during construction point of view, the stability of materials of low plasticity is usually very sensitive to the magnitude of the moisture content at the time of molding or during construction. A careless compaction at a moisture content of 2 percent wet (or dry) of the most suitable value may reduce the stability to but a small fraction of the design value.

(b) The ultimate moisture content has to be estimated with discretion to avoid designing on the basis of unsoaked data, when this would be inapplicable in fact, and to avoid designing for the saturation condition when saturation is never likely to occur.

A test sample is normally considered to become saturated after it has been soaked for 4 days but it is known that high swelling soils may go on absorbing moisture for periods of up to 6 months or more (10, 21). Whether this additional absorption and swelling is accompanied by an increase in the percentage saturation does not appear to have been recorded.

On the other hand, it is also believed, if not known that for all soils in all parts of the world the drier the climate the less the moisture the material is likely to absorb in the absence of a high water table.

CAUSE OF INSTABILITY ARISING OUT OF OVERCOMPACTION

It is pertinent to question why no such loss of stability has been recorded as occurring when the prepared sample is compacted by the method of static compaction whereas it is known to have occurred in the field and when samples are compacted by impact and kneading action.

Expressed somewhat differently "for a given initial water content, a reduction in void ratio through a process of consolidation results in a higher compressive strength than that which results if the same reduction in void ratio is achieved through a process of compaction" (13).

Static compaction is achieved under pressures considerably greater than those occurring under compaction equipment and the horizontal squeezing movement in the material which occurs under compaction in a roadbed is absent. In consequence, densities achieved in the static compaction test are obtained under more rigid conditions productive of high interparticle forces. In the field, the same density is achieved by a pushing-into-place action under lower pressures so that the high frictional resistance arising between particles under static compaction to high densities is absent when the same density is obtained under compaction equipment.

Dynamic compaction to high densities may affect stability in two ways. It may do so by reducing the mass strength of the particles through damage to the particle system and it may do so by detrimentally affecting the strength of the soil-water system.

Dynamic compaction may damage the particles as such; and it may likely produce a compacted mass of inferior stability by virtue of a more random system of volumes of particle orientation and the existence of shear planes, produced within the mass by the compaction process, in the vicinity of which the density may be considerably below the average (2).

As regards the soil-water system, it would appear reasonable to suppose that dynamic compaction results, by its molding effect, in a pore water system less favorable to moisture and air movement than occurs under static compaction. The air itself is also conceivably under appreciable pressure. It would then follow that in the region of high relative densities a condition is reached in the process of compaction where the water and air is unable to redistribute itself as would be necessary to avoid pore pressure effects and a "quick" condition eventuates under stress with a loss in stability. This detrimental condition is believed to arise particularly with silts and silty sands which would otherwise lend themselves to easy compaction to high relative densities.

Whether this phenomenon is also responsible for the higher swell pressure determined for samples of materials prepared by static compaction and saturated by exudation than when prepared by kneading compaction (26) is not known.

Compaction by kneading action involves forces more comparable with those occurring during construction and permits some of that lateral movement occurring under compaction equipment. It is thus considered to encourage the formation of a mechanical structure and stability most nearly simulating that produced in the field.

FACTOR OF SAFETY

All engineering design essentially embraces the use of a factor-of-safety which in road design procedure is frequently considered should be of the order of 1.75. Where does that factor appear in permanent design? Is it a constant to be relied upon?

By the very nature of the CBR pavement thickness correlation curves, there is a hidden factor-of-safety but that factor of safety will not apply to design unless the ultimate CBR minimum is at least equal to the value used in design.

To cover the effect of all the imponderables a factor of safety must be introduced somewhere into the design procedure. Unfortunately, however, it cannot yet be specifically introduced as such in design and its actual value is very variable. It may not exist at all. There is some doubt whether the CBR curves do, in fact, give reliable pavement thicknesses for all highly plastic subgrade materials (20).

On the credit side there are the following factors:

1. In the absence of a high water table, the maximum moisture content reached in more normal subgrade material is likely to be less than that occurring after 4 days soaking.

2. The maximum moisture content reached is likely to be appreciably less in an arid or semi-arid region than it is in a more humid region.

3. For any specific moisture content of compaction, the in-place CBR may be very much greater than that for a test sample compacted at the same moisture content and reaching the same ultimate moisture content and density, because of accumulated structure.

On the debit side there are:

1. Some high swelling clays may absorb appreciably more moisture than determined by the 4-day soaking test.

2. Some high swelling clays do not develop a structural aid to stability.

3. Permeable surface courses encourage high subgrade moisture contents.

4. There is, as yet, no full understanding of how stress is distributed through road making materials and how this distribution varies with material type. Recent work in the U.S.A. (6a) suggests that the variation in flexible pavement thickness, required to produce a given stress in the subgrade, may be as much as 60 percent of the minimum thickness required as a result of using different materials in the construction of the pavement.

STABILITY IN RELATION TO STRAIN

One of the most important fields of study, in the endeavor to introduce realism into the CBR method of design, has been discussed by Seed and Monismith (25) with reference to the strains produced by stress in unsoaked samples of a soil material and with emphasis on the meaning which should be attached to such expressions as "failure," "excessive" or "detrimental deformation under stress."

Some authorities consider that failure or excessive deformation occurs under a stress sufficient to cause a strain in excess of 10 percent. Others would appear to believe that such a permissible strain limit is too high and that the limit should be placed at 5 percent. Thinking in terms of permissible pavement distortion would appear to suggest a preference for such a lower limit.

Seed investigated the effect on the stability of a silty-clay soil by placing a limitation on the permissible strains of 1 percent (modulus of deformation), 10 percent and 20 percent and found that:

1. The form of the stress curves for families of density-moisture content curves changed with changes in permissible strain from 1 to 20 percent (see Figs. 7, 8 and 9).

Figure 7. After (25).

Figure 8. Relationship between moisture content, dry density, and stress.
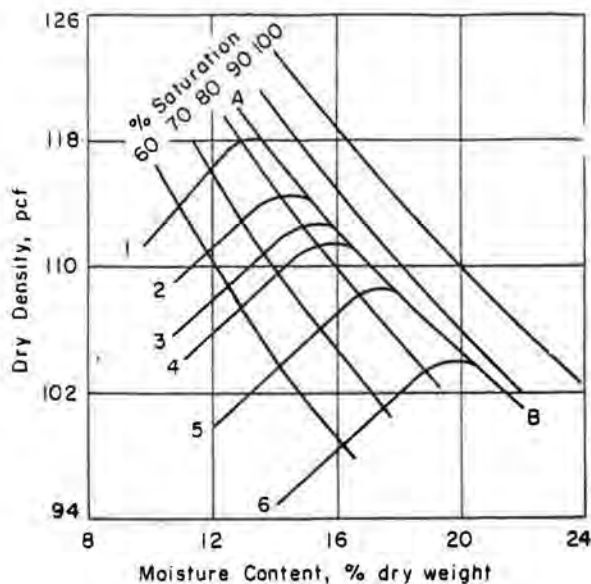
2. The stress-strain relationship for soil material compacted by sheepsfoot and rubber tired rollers were different from those obtained after compaction by the static, impact and kneading methods. They were most closely represented by the results obtained after compaction by kneading action though the results given by impact and kneading techniques did not differ very greatly.

3. It was noted that if the form of failure, when tested by the triaxial compression test, was by defined shearing for moisture contents on the dry side of optimum for any given compactive effort but that at about optimum moisture content and at higher moisture contents the samples bulged considerably while continuing to support increasing load, then failure could be considered to occur under a stress sufficient to cause about 10 or 20 percent strain in the test sample.

The results of the research described showed that, for the particular soils tested and for samples prepared by impact compaction and by kneading action and tested without soaking:

1. "The relationship between density and stability depends on the criterion used to define stability the greater the permissible strain before a sample is considered unstable, the greater is the possibility that an increase in density will cause an increase in stability."

2. "For samples of two soils, a silty clay and a sandy clay, compacted by kneading action, an increase in density at a given water content caused an increase or a decrease in stability (for strains less than 10 percent) depending on the water content and the range of densities involved; however, at a constant degree of saturation, an increase in density always caused an increase in stability."

3. "For saturated subgrade conditions, the higher the density of the subgrade the greater will be its stability." (Note: This presumably refers to samples prepared at
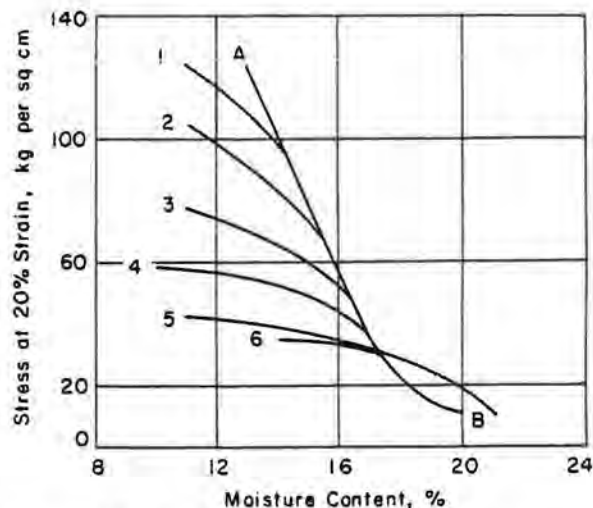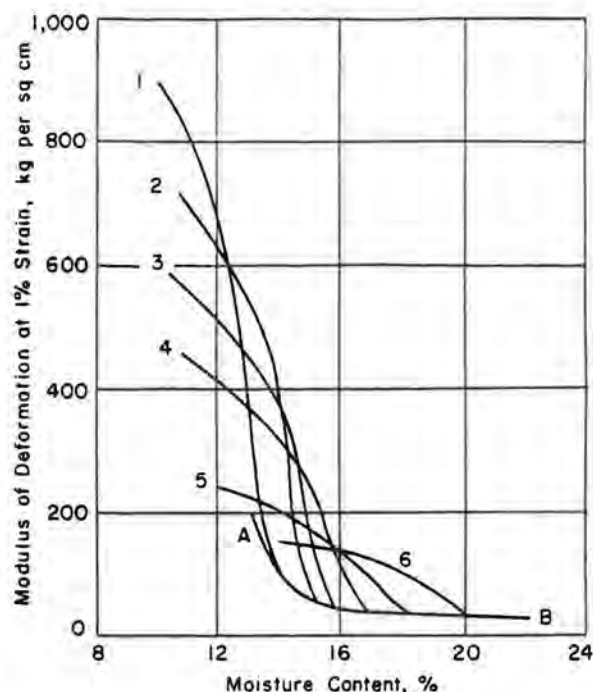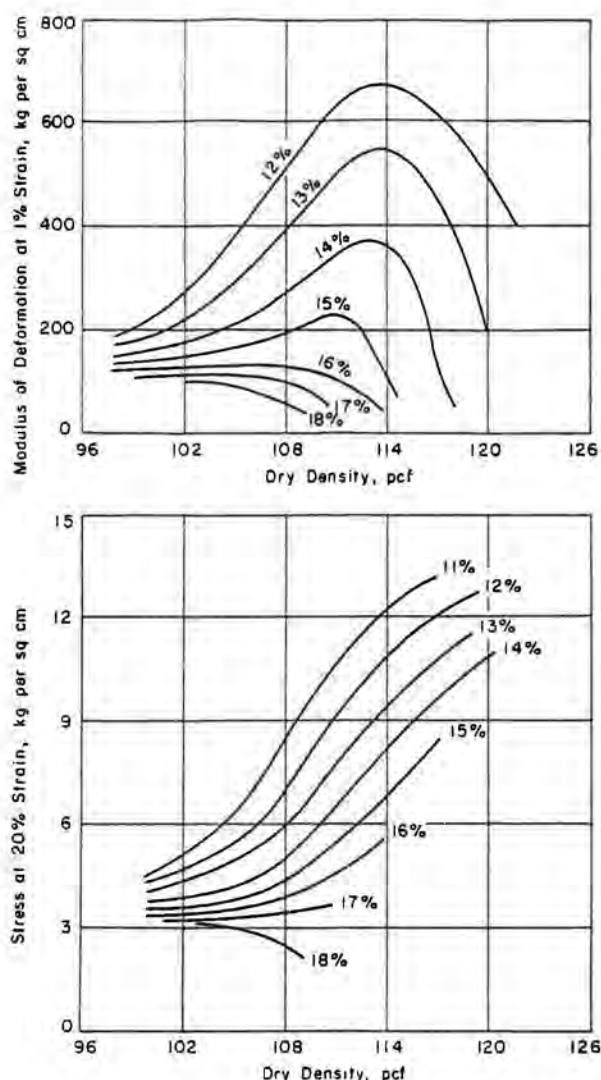
Figure 9. Relationship between dry density and modulus of deformation (above) and between dry density and stress (below) for constant moisture contents.

saturation moisture content.) "However, for partially saturated subgrades, the desirable density for maximum stability will depend on the water content of the subgrade and too high a density may have a deleterious effect on stability."

4. "In designing and constructing pavements resting on saturated subgrades, the selection of the desirable density of the subgrade should be based on the anticipated maximum water content of the subgrade and the density versus stability relationship of the soil."

It will be noted that the observation contained in (2) applied only when strains were less than 10 percent. For strains of 20 percent the authors remarked: "Within the range of densities investigated there is a marked difference between the effect of increasing density on strength and on modulus of deformation. Except for the high water content of . . . . an increase in dry-density in all cases caused an increase in strength . . . . The magnitude of the effect of increasing density, however, decreased with increasing water content."

For subgrades likely to become fully saturated, compaction to the highest practical density is justified though the stability will nevertheless be lower than for partial saturation (see 3 above).

Stabilities measured by the CBR and Hveem Stabilometer tests correspond to those producing a strain appreciably less than 10 percent showing that an increase in density, when soil material is compacted by impact and kneading methods, does not necessarily lead to an increase in stability. It may lead to a decrease.

Reductions in stability, accreditable to overcompaction brought about by small increases in density under traffic, have been recorded for test sections (5, 24) and have been believed to be responsible for certain recorded road failures (ex. 1).

THE VALIDITY AND USE OF THE CBR CURVES

It may be thought that a design based on the CBR method in which the CBR is determined after soaking absolves the designer from any further consideration and worry.

It is the author's belief, after visiting California and studying its literature, that such a view is erroneous. He considers that the CBR pavement thickness relationships were determined from a study of the performance of roads in which the subgrade layers were constructed with the best low cost materials locally available and that the structure, as a whole, was constructed by methods implying (a) high class workmanship and control, and (b) the upper layers of embankments could not, by virtue of good drainage and height, become as saturated as was possible under the conditions controlling the test for determining the CBR after soaking.

Under such a policy there is an implied factor of safety which is not likely to apply when embankments, especially low embankments, and subgrade layers are constructed in inferior highly active A-7 clay material or when workmanship and control are mediocre.

This belief would appear to be supported by Porter's comment (22) that the thicknesses given by the curves apply only for average conditions and are based on a tire pressure of 60 psi; these thicknesses should be increased or decreased up to ± 20 percent depending on (a) tire pressure, (b) quality of base course material, (c) characteristics of imported fill, (d) ground water level and drainage conditions, (e) possible effects of frost action, and (f) frequency of loading.

To this list of provisos should be added (g) the maximum legal wheel-load which is not necessarily the constant it is assumed to be, and (h) the nature and thickness of the surface course (18).

The effects of variations in tire pressure and in maximum legal wheel-load are obvious.

The quality of the base course and subbase course (that is, "imported fill") matereials and the nature and thickness of the surface course are important for they affect the spread of wheel loads and hence the active pressure on the subgrade and other layers. The curves assume that all road making materials spread the load in the same way. A low grade subbase material may not in fact spread the load sufficiently for the thickness given by the curves to be adequate.

As a result of research projects sponsored by the Civil Aeronautics Administration and the Navy Bureau of Yards and Docks (6a), it has been found that the quality of the material used in pavement construction materially affects the distribution of stress on the subgrade due to applied loading and that the comparative effects of various materials can be predicted qualitatively from the triaxial test data.

On the basis of designing to suit the safe loading capacity of the subgrade, it was found, for a particular subgrade for which the transmitted stress had to be limited to 12 psi, that when a static load of 15,000 lb was applied to the surface by a tire inflated to 100 psi, the thickness of various pavement materials required was in the following order:

Crushed limestone [4] base, 1½ in. down and well graded	16 in.
Crushed slag base, 1½ in. down deficient in minus 200 material	17½ in.
Normal gravel, partially crushed 1 in. down and reasonably well graded	21 in.
8-in. normal gravel base and sand subbase	24 in.
Clay-gravel base	26 in.

(The cost does not necessarily follow the same order. In the particular instance quoted, the cheapest section was the 24-in. depth of normal gravel base and sand subbase.)

The CBR of the "soft" subgrade was not given but may be estimated as at about 5 and calling for a pavement thickness of about 18½ in.

This is an important sidelight on the importance to be attached to the meaning of "average conditions." It supports Porter's contention that the thickness, as determined from CBR curves, may be reduced, under favorable conditions, by up to 20 percent and it illustrates the belief of others that the necessity, under unfavorable conditions, of increasing such a thickness by up to 20 percent is an inadequate representation of fact.

In this particular instance, the increase, supposedly mainly necessary as a result of variations from the average of conditions (a) and (b), amounts to as much as 40 percent where the variation from the mean is approximately 24 percent.

Assuming the distribution of stress follows a straight line relationship, then the angle of stress distribution under the applied loading, as measured from the vertical, can be estimated for the materials used as:

Crushed limestone	38 deg.	8-in. normal gravel base	
Crushed slag	36½ deg.	and sand subbase	27½ deg.
Normal gravel	30½ deg.	Clay-gravel	26 deg.

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[4] Limestone is possibly of ideal hardness as regards keying and load distribution under normally used consolidation plant.

According to Maclean (17) the thickness of a layer required to transmit a given loading to a layer below, in such a way that the shear stresses in the lower layer are maintained at a given value, decreases as the modulus of elasticity of the transmitting layer increases.

The characteristics of imported fill, ground water level and drainage conditions control the relationship between the maximum moisture content developing within the subgrade layer and that existing at the time the CBR is determined. They help to control the factor of safety.

Deep frost action leads, during the subsequent thaw, to saturation or even supersaturation of the subgrade and hence may lead to a lower stability than that indicated by test data.

Of the above factors the frequency of loading is, in general, the most important and is, in fact, now possibly considered as of greater importance than was appreciated at the time of Porter's paper.

The greater the intensity of traffic complying with the weight limitations laid down by statute, the greater, in fact, is the equivalent wheel load for which the pavement should be designed.

It is thus clear that the interpretation of the CBR curves is not so simple and that the thicknesses obtained from them are more in the way of a guide to be modified by the designer in the light of his experience and knowledge.

METHODS OF DETERMINING THE CBR VALUE TO BE USED IN PAVEMENT DESIGN

In the earlier days of design by the CBR method, the bearing value selected for use was that obtained for a sample compacted at optimum moisture content to maximum density by the process of static compaction under a pressure of 2,000 psi and then, more commonly, soaked for 4 days. The required pavement thickness over the layer for which the sample was representative, was then obtained from the appropriate light traffic (7,000) or medium heavy traffic (12,000-lb wheel load) correlation curve. Some minor adjustment to the thickness required over a subgrade was permitted under specific circumstances depending largely upon the experience and judgment of the designer for magnitude and justification.

The method of static compaction was then replaced by that of impact or kneading and the CBR more frequently determined was that for compaction at optimum moisture content to a density corresponding to modified AASHO maximum density after soaking though the majority of laboratories later adopting this method of design followed the Proctor technique.

Although the bearing values for subgrade soils were obtained for a sample compacted to 100 percent maximum density, specifications would appear to have seldom required compaction in the field to such a density though compaction at near optimum moisture content was considered essential.

But after a while it was realized that the value of the CBR determined in this way was not necessarily the most suitable value as regards stability and economy or in respect of volume change and subsequent distortion. It was also appreciated that the density used for determining the CBR had to be reproduced in the field.

A number of alternative methods of obtaining a suitable CBR value have thus been developed.

Some of the methods used for determining an acceptable value of the CBR are given below.

Granular Soils in Base, Subbase, or Subgrade (35 Percent or Less Passing No. 200 Sieve; P.I. Less Than 12 to 15)

Method 1. An elaborate approach, recommended for use until such time as the general characteristics of the material are known, is to plot the iso-CBR lines for soaked specimens on a family of compaction curves (using 6-in. diameter samples in the compaction test which can then be used for the penetration test to determine the CBR) and then to select, from such a plot a moisture content and density for compac-

tion which will give the maximum CBR or an economic value of the CBR to be used in design where the criteria for selection of moisture content and density must be such that they are obtainable with comparative ease with the equipment and other resources available. Such a plot is illustrated by Figure 2.

Method 2. As the above method is laborious and as it is known that granular materials can usually be easily compacted to high relative density to give a high CBR value after soaking, it is generally abbreviated to determine a CBR relationship with density for a constant compaction moisture content equal to modified optimum moisture content or to one slightly dry of modified optimum moisture content[3] to enable the maximum CBR attainable to be used in design if so desired.

The CBR value most commonly used in design is that obtained from this relationship for a relative compaction of 95 percent maximum density though, with the exception of certain cohesionless soils that do not readily compact to higher densities, there is, in general, no reason why higher relative densities should not be specified.

The relationship is illustrated by Figure 3.

It is unwise to adopt this method without having previously determined the typical curves given by Method 1 because it is not always possible to recognize soils acting as granular soils on the basis of mechanical analysis alone.

Silt-Clay Soils (35 Percent or More Passing No. 200 Sieve; P. I. Greater Than 12 to 20)

The procedure is somewhat different for the non-granular and cohesive materials of the silt-clay group for with such materials the magnitude and effect of swell has also to be considered.

Most methods are but developments of Porter's realization that design must be based on the density and moisture content ultimately pertaining in the established road, that is, after both properties have reached equilibrium or an equilibrium cycle under field conditions.

Middlebrooks (19) was somewhat more specific: "The proper moisture content and unit weight for compaction control of a soil with a marked expansion characteristic are not necessarily the optimum moisture content and unit weight determined by compaction control tests but have been found to be equal to the moisture content and unit weight of an expanded sample after the soil is compacted and saturated."

Hveem (7), using a different testing technique for stability, carried this approach to its logical conclusion and developed a method of design in which, using a suitable method of compaction and varying moisture contents for compaction, he ascertained the thickness of pavement required for both reasons of stability and overcoming the effects of swelling pressure. The moisture content which gave the same thickness of pavement for both stability and overcoming the swelling pressure gave him the moisture content for compaction.

The data used are illustrated by Figure 10.

It is known that fine cohesive soils compacted under a high compactive effort will not generally retain their density of compaction in the presence of moisture even when appreciably surcharged. They will absorb moisture and swell and in so doing their stability will drop to a low value. As has been previously discussed, this does not apply to all highly plastic soils though it probably does to the majority of such materials and especially to average clay soils.

For such materials, the maximum CBR (after soaking) and the minimum swell occur when they are compacted to maximum density at a moisture content close to Proctor optimum though in view of the low CBR values pertaining and the flatness of the CBR curve the moisture content of compaction may be varied quite appreciably without having very much effect on the thickness of pavement required.

It is this outlook which controls the general form of the test methods used for such materials. Though the methods to be described are attractive, it is not at all clear

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[3] Any saving in water to be added to a soil is particularly welcomed in tropical areas. (As a matter of convenience it is advisable to saturate thoroughly some pumice soils and leave overnight before compacting.)

that they carry for highly plastic materials the factor-of-safety to be expected from the methods more common to granular soils.

Method 3. This method, based very directly on the above observations, has been advocated by Kleyn (11).

Six-inch diameter samples are used for obtaining the Proctor compaction curve. They are then soaked and used for determining a CBR-moisture content curve. The maximum CBR so obtained is used in design and a somewhat wider tolerance in the moisture content for compaction than is allowed with better materials is permitted during construction.

The plot obtained is illustrated by Figure 5.

Kleyn based this approach on a commonly held belief that the sensitivity of saturated samples to molding is believed to be sometimes more a function of the test procedure than of the material tested. This contention, though common, and apparently supported by the results of triaxial testing is certainly not held by all authorities many of whom place great stress on the importance of moisture control.

Method 4. Provided construction can be arranged to take place during a relatively dry period and that drainage conditions will be good the CBR values may be determined for unsoaked samples.

This method involves estimating—from local knowledge or other research—the

Figure 10. After (7).

ultimate or maximum moisture content likely to occur eventually in the subgrade layer.

Design is then based on the CBR obtained by penetrating unsoaked samples molded at such a moisture content and compacted to a density corresponding to 5 percent air-voids content. Construction, of course, provides for compaction at that moisture content and to the density determined as described.

The above method has been suggested by Maclean (18) presumably for silt-clay soils.

Note on Subgrade Layer

The subgrade layer is the layer of material lying immediately below the subgrade and extending to include the depth affected by climate and stress caused by traffic. It varies in thickness from about 6 to 24 in. depending upon the climate and the nature and volume of traffic. The moisture content for compaction and the desired density will depend upon the considerations discussed above.

In general, the subgrade layer will be constructed in the same material as used for the embankment below. It will differ from the embankment in the additional care in control over the moisture content of compaction and possibly in the density to be achieved. The thickness will be determined from considerations of stability and climate. In areas of deep frost penetration it may be necessary to import a material more resistant to frost action than that used in the embankment proper.
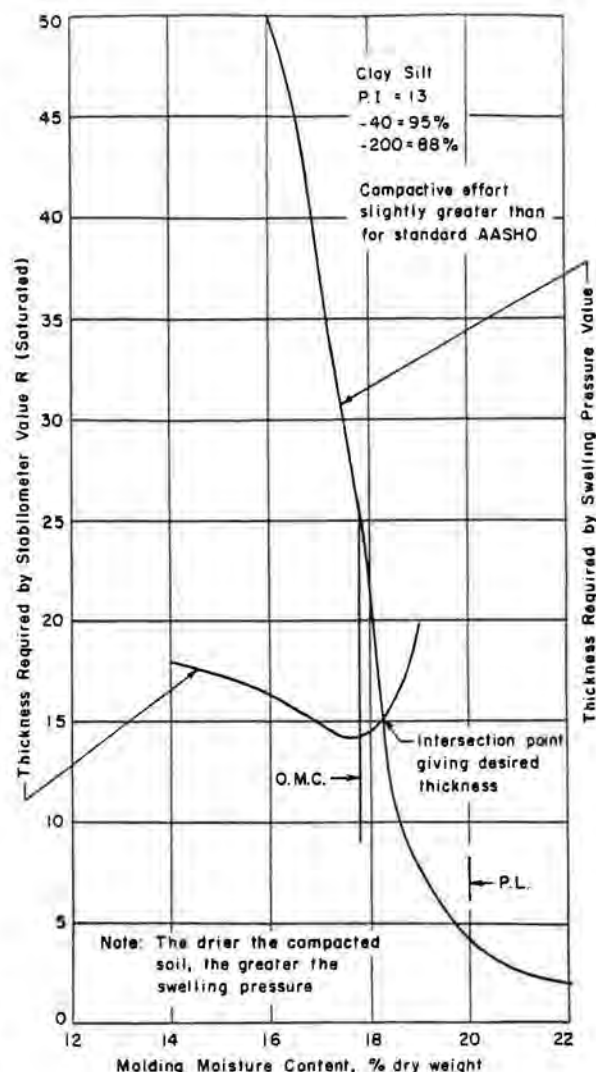
DETERMINATION OF CBR FOR SPECIAL PURPOSES

Subgrade in Cut

When subgrade is in cut, it is common to determine the CBR for the unsoaked and undisturbed condition provided the subgrade is unlikely to be damaged by construction traffic and is unlikely to dry out or be damaged by weathering before being covered by a base or subbase course.

If there is any likelihood of the subgrade becoming saturated by rain before it can be adequately covered then this method is no longer valid and design must be based on CBR's obtained after soaking.

Depending upon the results of testing, it may be more economic to scarify to a depth of about 7 in. and recompact to some satisfactory density giving a higher CBR value.

Embankments

The reasons for compacting embankments, below the subgrade layer, are to prevent detrimental settlement and to aid in providing stable slopes through the inherent stability of the compacted material.

According to Maclean (18), little settlement is likely to occur in embankments if the density achieved during construction is such that the air content does not exceed 10 percent.

The minimum densities required depend on (6): the soil type, the height of embankment, the design slopes, and the condition of exposure.

Minimum values recommended by the Highway Research Board (6) to satisfy these requirements are given in Table 1.

Close moisture control is not usually required during compaction.

The amount of necessary moisture content control will be determined by the desire to (a) avoid a condition of low stability, (b) avoid an uneven and drainage impeding layer surface caused by rutting, (c) obtain the greatest resistance to water-absorption when the sides of the embankment are likely to be subjected to wetting by flooding, and

TABLE 1

RECOMMENDED MINIMUM REQUIREMENTS FOR COMPACTION OF EMBANKMENTS

Class of Soil	Condition 1 (not subject to inundation)			Condition 2 (subject to periods of inundation)		
	Height of Fill (ft)	Slope	Compaction (% AASHO max. den.)	Height of Fill (ft)	Slope	Compaction (% AASHO max. den.)
A-1	Not critical	$1\frac{1}{2}$:1	95+	Not critical	2:1	95
A-3	Not critical	$1\frac{1}{2}$:1	100+	Not critical	2:1	100+
A-2-4	Less than 50	2:1	95+	Less than 10	3:1	95
A-2-5	Less than 50	2:1	95+	10-50	3:1	95-100
A-4	Less than 50	2:1	95+	Less than 50	3:1	95-100
A-5	Less than 50	2:1	95+	Less than 50	3:1	95-100
A-6	Less than 50	2:1	90-95(a)	Less than 50	3:1	95-100
A-7	Less than 50	2:1	90-95(a)	Less than 50	3:1	95-100

Remarks: Recommendations for Condition 2 depend upon height of fills. Higher fills of the order of 35 to 50 ft should be compacted to 100 percent at least for part of fills subject to periods of inundation. Unusual soils which have low resistance to shear deformation should be analyzed by soil-mechanics methods to determine permissable slopes and minimum compacted densities.

(a) The lower values of minimum requirements will hold only for low fills of the order of 10 to 15 ft or less and for roads not subject to inundation not carrying large volumes of very heavy loads.

will thus depend, to some extent, on the natural moisture content of the material as excavated and on the nature of the equipment available for compaction.

If flooding is likely, then the material should be compacted at a moisture content as near optimum as is feasible.

If flooding will not occur and (a) the material is excavated and compacted dry of optimum, then no moisture control is necessary though naturally the soil must be wet enough to be compacted economically, (b) the material is excavated wet of optimum then it should be allowed to dry out to a moisture content of between optimum and 3 percent wet of optimum where the higher limit applies to the more plastic materials.

The more uniform the moisture content of compaction, the less likelihood there will be of surface distortion. For designing a pavement to be constructed over an existing embankment built on a stage construction basis, the CBR is frequently determined for the unsoaked condition.

Subgrade Investigations

During investigations into the strength of an existing subgrade which has been down for some years, the CBR is generally determined for unsaturated undisturbed samples.

It may be noted that undisturbed time-cured cohesive samples generally absorb but little extra moisture and only then with difficulty. They tend to give higher CBR values than those determined by the more normal test involving compaction at site moisture content to site density. The difference between the two values may, however, be low for clay soils and tends to increase with decreasing plasticity. For low plasticity material, the value for the undisturbed sample may be of the order of twice that determined for a sample after compaction to modified maximum density and soaking.

Determination of Pavement Thickness in a Stage Construction Project

If it is desired to determine the pavement thickness required for the bituminization of a graveled road and if it is not desired to recompact the existing surface course or its subgrade but to use the existing surface course as a subbase, then it must be remembered that it is possible that the existing subgrade is not at its maximum moisture content. As part of a planned stage construction project, it is likely that the moisture content of the subgrade layer at the time of its compaction and the density to which it was compacted are known but the CBR corresponding to such data can only be used in pavement design if it is known that the subgrade was covered after compaction by a surface course of a thickness corresponding to the surcharge to be expected from the completed bituminized pavement thickness, that this surcharge was maintained and that this (temporary) surcharge was applied before the moisture content of the subgrade had an opportunity of increasing as under the action of appreciable rain.

If initial data are unavailable or unreliable for the reasons enumerated above, then the CBR to be used in the pavement design may be estimated from samples made up to reproduce site moisture contents and densities and then saturated for four days or after they have been brought up to some other desired moisture content based on local observations before penetration. This method may give only an approximation of the CBR value sought as any hysteresis, due to wetting and drying cycles which have occurred since construction, would imply that the wetting curve for the undisturbed subgrade would not follow that applicable during the test. Nevertheless, if the CBR be determined for the saturated condition any error is likely to be small. The CBR so obtained may be checked against that obtained for an undisturbed sample after soaking or being brought up to some other desired moisture content.

Failure Investigations

The determination of the CBR for use in checking the design of a road already bituminized, as might arise during the investigation into the causes of a pavement failure, presents a problem as the moisture content at the time of compaction and the density to which the subgrade layer was compacted would often be unknown.

Certain assumptions are necessary and one commonly made is that the subgrade

layer has reached its maximum moisture content and this is likely to be so in the instance of a failure.

To reconstitute a sample in the laboratory to duplicate site conditions of moisture content and relative compaction at the time of the investigations may or may not give an approximation of the site CBR—much depends upon the properties of the soil.

The most satisfying method of estimating the CBR is by penetrating an undisturbed sample or by means of the site CBR test.

Variation in Specifications Arising Out of Some Construction Difficulty

Experience shows that it is sometimes necessary to design the pavement thickness for construction at optimum moisture content to some fraction of the maximum density or even to some fraction of the maximum density at a moisture content other than the optimum favored by the Materials Laboratory. The applicable CBR for use in design will not, of course, be that determined for compaction to maximum density at the favored optimum moisture content. In both instances the CBR attainable during construction may be greater or less than that ascertained by standard test and in the latter instance the difference between the laboratory determined and the site attained CBR's may be considerable.

The chart of iso-CBR lines referred to under Method 1 will give the design CBR for the density[6] reached after compaction at any moisture content of compaction within the range of moisture contents covered by the chart.

NOTE ON SELECTION OF A SUITABLE COMPACTION DENSITY

As has been seen the density required is predetermined by considerations of settlement, strength and volume change, where the density required expressed in pounds per cubic foot will vary with the grading of the material used. This density cannot always be safely estimated, in the absence of test data, in terms of a relative compaction or a percentage of the maximum density determined under some standard method of compaction.

McDowell (15) and Burmister (3) have called attention to the unreality of such terms as relative compaction which is based on the "fallacy that zero percent compaction can represent a unit weight of zero for any soil."

The use of such expressions, as occurs in some specifications may cause overcompaction of clays and undercompaction of granular soils.

When full testing for suitable density is impossible, for the want of time, McDowell has recommended as a guide:

1. For clay soils: Compact to a maximum density as determined by $58 + \dfrac{DL}{3.9}$ where values of 5 to 10 lower are acceptable.

2. For granular base materials: Compact to a minimum density of $58 + \dfrac{DL}{3.9}$

where D_L = loose density of the material as determined for clean sands and granular materials by rodded unit weight test (ASTM Designation C 29-42) and for other soils by determining the dry weight per cubic foot of the soil shrinkage pat (molded at liquid limit) and correcting for any plus No. 40 material which, under field conditions, will be floating soil.

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[6] It may be noted that it is not, in general, possible to compact a soil at the design optimum moisture content to a density appreciably greater than the relevant maximum density and that the difference possible decreases as the compactive effort increases. This is despite site data purporting to show this having been achieved. What actually happens is that either the compaction was attained at a moisture content less than the specified optimum or the density measured was that applicable after the compacted material had been allowed to dry out and shrinkage has occurred. If the densities are measured after some drying out has occurred, it is impossible to say, from the data more normally available, whether the specifications have been met or not.

EFFECT OF CLAY MINERAL AND REPLACEABLE BASES ON DENSITY AND STABILITY

The maximum density and stability of a finely graded soil depend upon the nature and amount of the clay mineral or minerals present and upon homoionic variations of those minerals but the manner in which these variations occur is as yet unknown in general terms.

Data presented by Lambe and Martin (12b) and in many of Winterkorn's papers suggest that the effect of ionic modifications of a highly active clay mineral on the maximum density and stability may be considerable.

DETERMINATION OF PAVEMENT THICKNESS FROM THE CBR CURVES

The CBR-pavement thickness correlation curves are used in a number of ways varying from the hit-and-miss method of selecting a 7,000-lb, a 9,000-lb, or a 12,000-lb wheel load curve, according to the judgment of the designer, to the elaborate methods used in Wyoming (24a) and Colorado (12c).

In the former state, factors are given for rainfall, water table depth, frost action, drainage and repetitions of one-way traffic over 20 years expressed in equivalent 5,000-lb wheel loads. The sum of the values given to the factors determines the appropriate CBR curve for use.

In the latter state, factors are assigned for frost penetration, moisture conditions and commercial traffic in vehicles per day. The sum of the assigned values gives the CBR curve for use in design.

Similar considerations feature in the Michigan method (18b, 18c) and that adopted by the County Roads Board of Victoria, Australia since 1945 (28).

Of the many ways of using the CBR curves, as adopted in different parts of the world, a method envisaged in the original California procedure is emerging as the most acceptable method for those areas where frost action is not of prime importance. It is based on a straightforward correlationship between pavement thickness and CBR value through the medium of the volume of commercial traffic. It is justified by the known fact that commercial traffic is considerably more damaging to a bitumen surfaced road than private passenger traffic and that commercial traffic generally uses the same traffic lane when there is more than one traffic lane in each direction.

As has been noted, California used, in the days when the state utilized the CBR method of design, two correlation curves—one for "light traffic" and one for "medium-heavy traffic." Steel based his Group Index method of design on "light," "medium" and "heavy" traffic volumes. Missouri (4) adopted this approach and developed it to provide for various ranges of commercial traffic volumes using the road each day. England (18) has since advocated the use of a similar set of curves.

The validity of this approach follows as a logical deduction from American wartime experience in the construction of landing grounds.

The American Corps of Engineers developed the CBR design method for the purpose of applying it to runway construction but they soon appreciated that it would be thoroughly uneconomic to use the design thickness given by that method for runways only likely to be used for a few months or even days. They therefore collected data and plotted the percentage of design thickness required against "coverages" necessary to cause subgrade failure (16), see Figure 11.

Runways are designed to carry the heaviest loads using them and the life of a runway so designed corresponds to approximately 5,000 coverages where 5,000 coverages corresponds to some 150,000 passages by such vehicles.

The maximum legal wheel load in England and the U.S.A. may be taken to be 9,000 lb, and the 9,000-lb wheel load
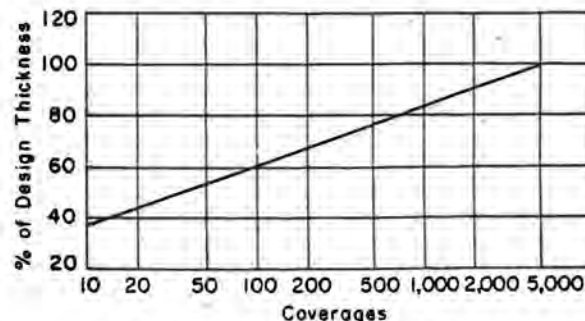
Figure 11. After (16).

TABLE 2

General Classification	England No. of Commercial Vehicles per Day	Missouri No. of Commercial Vehicles per Day	Classification	Approximate Equivalent CBR Wheel Load Curve, lb
Extra light	0-15	Less than 50	Light duty	4,000
Very light	15-45	-	-	6,000
Light	45-150	50-150	Medium duty	7,000
Medium	150-450	150-300	Heavy duty	9,000
Heavy	450-1500	More than 300	Extra heavy duty	12,000
Very heavy	1500-4500	-	-	15,000
Extra heavy	More than 4500	-	-	Under consideration

curve is used for an average traffic volume of about 250 commercial vehicles per day. Assuming that 10 percent of these commercial vehicles transmit wheel loads of the order of the legal limit of 9,000 lb, it might be assumed that such a carriageway would be expected to last 150,000/25, or 6,000 days which is of the order of the 20 years for which permanent road pavements are designed.

The outlook of this form of road design is thus consistent with American runway experience.

If the traffic on a runway were increased 100 percent, the increased thickness'required would, on the above basis, be about 7 percent. If road traffic were increased 100 percent, the design curve for this approach, would be the 12,000-lb wheel curve which gives thicknesses about 10 percent in excess of those determined by the 9,000-lb curve.

Similarly, if runway traffic were reduced by 50 percent the minimum runway thickness would be of the order of 90 percent of the thickness required for 5,000 coverages. In road design, on the basis of traffic volume, the corresponding CBR curve would be the 7,000-lb wheel load curve and the 7,000-lb wheel load curve gives thicknesses about 10 percent less than does the 9,000-lb curve.

The use of such traffic volume curves in road design is thus justified in principle by American experience in regard to runway design.

CLASSIFICATION OF TRAFFIC FOR PAVEMENT DESIGN

It has not always been easy, in the past, to understand what was implied by references to "light" or "heavy" traffic. With the publication of methods of design providing for factors to allow for such variables as rainfall, drainage, depth of water table, frost action, traffic, expected increases in traffic and the relative destructive effects of various wheel load groups (3b, 12c, 24a), the meaning to be attached to the terms "light," "medium" and "heavy" traffic has gradually clarified. It is now obvious that the expressions not only refer to traffic volumes but are, to some extent, relative to the particular area in which they are applied. A "light" traffic under one set of conditions may well be a "medium" traffic under less favorable climatic and drainage conditions.

Thus the California curve for "light traffic" is the 7,000-lb wheel load curve which corresponds to the Missouri curve for "medium duty." In some traffic ranges pavement thicknesses would be greater in Missouri than those required in England for the same kind of traffic. In England the 15,000-lb curve would be used for traffic in excess of 1,500 vehicles a day, whereas in Colorado (12c) it could be any curve between 9,000 lb and 13,000 lb depending upon frost and moisture conditions.

Traffic is generally limited, in the United States, by statute to maximum wheel loads of 9,000 lb. In England the limit is 4 tons for a 4-wheeled petrol-driven vehicle.

For the purpose of designing the thickness of the road structure, only those wheel loads in excess of 4,500 lb are normally considered in the U.S.A. when designing on the traffic volume basis. In England, the tendency is to include in the traffic count all buses and commercial vehicles excluding only light delivery vans and 3-wheelers though sometimes the design traffic is specified as of those vehicles per day exceeding 3 tons in loaded weight (3c).

The intensity of such traffic is obtained by a traffic count of such vehicles or is estimated from a percentage of the total traffic count. Percentages used vary from the more normal 10 to 15 percent of the total traffic in well developed areas to 25 percent as used in Colorado (12c). In undeveloped areas, as in the Commonwealth, it may reach as high a figure as 80 percent.

The number so obtained is then increased by a percentage of development expected to occur during a period of commonly 20 years and the average of the two values is taken for use in design. It may well be that in a fully developed area, there will be no appreciable increase in traffic and that no adjustment of the present traffic count is necessary.

To convert traffic data into equivalent 5,000-lb wheel loads, when that basis is used for determining pavement thicknesses, various factors are introduced including one for a correction for the average number of axles per vehicle.

On the above basis for measuring traffic volumes and using the British classification breakdown, traffic may be classified as regards effect.

Table 2 gives the Missouri classification for comparison together with the corresponding CBR curves used in design in both England and Missouri for the appropriate traffic volume ranges quoted.

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Hydrophobic Earth as a Means of Moisture-, Thermal-, and Electric-Insulation

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Introductory Remarks by the Chairman

During the last twenty-five years, Soil Stabilization has developed in the Western World into a definite well organized branch of Engineering Science. The first comprehensive statement of the principles and practice of this science is found in Volume VI of Jerome Alexander's "Colloid Chemistry, Theoretical and Applied," Reinhold Publishing Corporation, New York, 1946. Its development since is reflected, though not completely portrayed, in Bulletin 108 on "Soil and Soil Aggregate Stabilization" of the Highway Research Board. Little is known about the parallel development in the Soviet Union, although such development could be expected since the Russian interest in soil stabilization was well shown by the publication in 1938 of a collection of papers on soil stabilization in book form under the auspices of the Central Road Administration at Moscow. In the foreword to this book, the acting director of the Research Institute for Road Construction makes among others the following statement: "This institute and its Leningrad branch give special emphasis this year to Soil Stabilization. This problem, however, is so large and of such importance that it will hardly be possible to solve it with the means and talent available to the central institute and its branch organization. We believe that for the solution of this most important problem in road construction all scientific workers in this field must work together in close and friendly union. Only thus will it be possible to study this problem under the widely varying conditions existing in our great federation. It is necessary to organize laboratory investigations on a broad scale, and at the same time to experiment on the roads themselves with greater boldness. We road builders are still lacking in Bolshevik verve and boldness. Without large and bold experimentation, the problems of soil stabilization cannot be solved."

We are grateful to Professor Kolyasev and to Mr. Holodov for presenting an up-to-date picture of the method of approach and of the results obtained in the Soviet Union in one segment of the science of soil stabilization, namely in the water proofing of soils.

● IMMENSE ENGINEERING construction work is in full swing in the Soviet Union. Residential and industrial premises, power stations, factories, railways and highways, bridges, installations for reclamation and electrification of agriculture are erected all over the country in ever increasing numbers.

The natural base and the building materials for all these engineering works, as well as for their various constructive elements, are provided by rocks of the earth surface usually known by the name of soils.

All engineering constructions together with their natural bases (soils) are subject to the action of water, temperature, electricity and pressure. This action normally varies with time in intensity and direction. These influences shorten the life of buildings and in some cases make the ground unfit for engineering purposes.

To increase the resistance of bonded systems (concrete, stucco, bricks, plaster, etc.) against moisture, thermal and electrical forces, and to supply such resistance properties when necessary to dispersed systems like soils, ash, slag, peat, etc., a series of measures has been taken. The latter consist in changing the physicomechanical

factors of the said materials, mainly their hydrological characteristics by decreasing water absorption, filtration, swelling and wetting.

The problems of artificially decreasing wettability, water absorption and filtration of soils are treated by a comparatively new branch of physical chemistry making use of the hydrophobization methods.

The purpose of the present investigation is to elucidate some problems of the theory and practice of soil hydrophobization and to describe methods of obtaining and applying friable hydrophobic materials.

Up to the present, several methods of securing friable hydrophobic materials (hydrophobic earth) have been developed, as follows:

1. Treatment of the soil, ground, peat with surface active agents using an intermediate reagent (1a).

2. Treatment of the cinders from heat and power plant furnaces with a solution of bitumen in green oil (2).

3. Grinding the air-dried soil adding copper salt of abietic acid (copper abietate) (13).

4. Treatment of the soil with paraffin and resin vapours, vapours of silicon organic combinations, siliconates of heavy metals and salts of heavy metals of synthetic fatty acids (3).

The fundamental principle of all these methods consists in covering the hydrophilic surface with hydrophobic material.

The main point in the methods of soil and ground hydrophobization is the problem connected with the nature of building up and fixing the hydrophobic covering on the surface of the treated material particles.

The first indispensable requirement for providing the hydrophobic cover on the particles of the dispersion phase is the introduction of the corresponding hydrophobizing reagents into the treated material (soil, ground, sand or peat). Such reagents may be chemically resistant (cinders, paraffin, resin, abietates of copper, iron, aluminum) or chemically non-resistant surface active agents, such as sodium salts of carbon acid-soaps, siliconates of sodium, and potassium.

Most characteristic of all the methods developed is that of soil and ground hydrophobization by means of surface active agents using intermediate reagents, applied in the form of water solutions. We shall therefore discuss this method in detail.

The introduction of the hydrophobic reagent into the soil is followed by the phase interaction between the hydrophobizer and the treated material. The hydrophobizer introduced into the soil enters into contact with its solid phase and with the dispersion medium. In some way it is detained, i.e., absorbed, by the treated material. According to the manner in which the reagent is absorbed by the treated material, it is possible to distinguish the six following types of the ground-soil absorption power (4):

1. Mechanical absorption power;
2. Biological absorption power;
3. Chemical absorption power;
4. Chemical adsorption;
5. Physical adsorption; and
6. Physicochemical or interchange adsorption.

We shall not consider here the methods which evidently do not solve the given problem, such as the mechanical absorption power, i.e., the capacity of soils and grounds as of any porous body not to pass particles which are larger than the capillary bores of the systems, or the biological absorption power, which is connected with the activity of living organisms.

Chemical absorption power of soils, according to Gedroyz (4), is expressed in that the anions of diluted salts, which produce together with cations of the soil solution insoluble or slightly soluble salts, will leave the solution in the form of the corresponding salts. The resulting deposit will mix itself with the solid phase of the soil as a mechanical admixture.

Chemisorption is a non-reversible physicochemical process as a result of which the anions or cations, existing in the dispersion medium, are fixed on definite valence links of the mineral dispersion phase crystal grid thus forming hydrophobic combinations.

Physical adsorption is caused by the tendency of any dispersion medium to decrease its free surface energy. The reduction of the free surface energy may result from:

1. The increase of the substance concentration in the layer of dispersion medium directly adjoining the particles of the dispersed phase (positive adsorption). These phenomena are described by the Gibbs adsorption equation.

2. The coagulation of soil and other particles of colloidal dimensions into larger aggregates.

Physicochemical or interchange (reversible) adsorption consists in that the soil and ground are able to exchange a certain part of cations existing in their solid phase solution for an equivalent number of cations existing in the contacting solution. A dynamic equilibrium is always present between the cations of the solid phase of the soil and the cations of solution.

Up to the present time, the hydrophobizer fixation was preferably obtained by means of chemisorption with a preliminary orientation of the hydrophobizer molecules after Langmuir without paying attention to the processes of adhesion (5, 2).

Thus, Rebinder (5) assumes that chemical fixation of polar groups, or the chemisorption, is the most reliable type of sorption, providing a most reliable linkage and a correct orientation of the reagent hydrocarbon part. Kostrikov (6) developed a hydrophobization theory based on the equilibrium of energetically active centers of the soil mineral surfaces (O^{2-}, Ca^{2+}, CO_3^{2-}, OH^-, K^+, etc.), which are formed while the mineral is being reduced to fragments.

The way of balancing the non-compensated electric charges of the mineral surface ions by means of organic cations is preferred by this author for the following reason. The clayey part of highly dispersional soils comprises mainly the minerals of the kaolinite groups, hydromicas and montmorillonite, which in their basal planes contain a certain number of negatively charged ions O^{2-}, OH^-, etc. Thus, according to the opinion of the author, the neutralization of negative charges prevailing in the ground-colloidal system requires the application of organic cations. In this case, a typical ionic sorption will take place resulting in the reduction of the surface energy of the system.

We presume that in his considerations the author of this theory does not take into account that the surface energy results from the specific position of the phase molecules and that the mechanical destruction of the crystal cannot bring the destruction of the molecules with the building of the ion O^{2-} or OH^-. Besides, the O^{2-} ion is a strong oxidizing agent and consequently cannot remain in a free state for a long time (i.e., quietly await the introduction of hydrophobizer). The OH^- ion is univalent and, similarly to K^+, Na^+ and other ions, is unable to provide a reliable chemical linkage with the mineral and with the hydrophobizer. It should be remembered that the forces of covalent and hydrogen linkages are several times weaker than the valence forces and that they do not ensure the chemical conversion of the substances.

Adam (7) has shown that the energetically active centers do not occupy more than 10 percent of the particle surface. Consequently, this theory refers only to the hydrophobization of the basal planes and at the best to the 10 percent of the energetically active part of the mineral surface which can never secure the desirable effect of hydrophobization.

The investigations of Kostrikov (6) have proved that up to 90 percent of the hydrophobizer introduced may be extracted from the soil by means of organic solvents.

Holodov (3) has shown by his experiments that the reagents introduced in the form of water solutions, before drying up, may be almost completely washed out.

Thus, the theory of balancing the non-compensated links cannot be considered as satisfactory.

Undoubtedly, chemisorption phenomena may take place during the hydrophobization of the grounds. For instance, Shvedov (8) has proved that between the galenite mineral (PbS) and the ethyl xanthate ($C_2H_5 - OC\overline{S}SK$) a reaction of chemisorption may arise on condition of the latter's incomplete oxidation (8):

$$PbS' \left]{\overset{Pb}{\underset{Pb}{\Big\backslash\!\!\!/}}}SO_4 + 2C_2H_5 - OCSSK \longrightarrow PbS\left]{\overset{\nearrow Pb-SSCO-H_5C_2 + K_2SO_4}{\searrow_{Pb-SSCO-H_5C_2}}}\right.$$
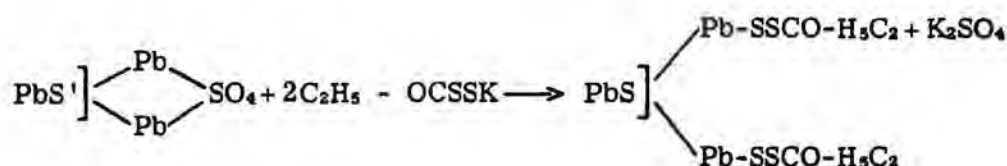
However, at the same time prior to interaction the mineral had been electro-neutral and deprived of non-compensated chemical linkages.

All theories of the hydrophobic covering by chemical fixation provide adequate explanation of the occurring phenomena within one complete monomolecular layer of adsorbed molecules, which may be used in foam flotation of ores, but they do not explain the hydrophobization by means of paraffin, copper siliconates, cinders, etc. The theories do not take into consideration that the monolayers are not stable and are difficult to obtain.

The processes of hydrophobizing soils by means of different reagents have been investigated rather thoroughly at the Soil Physics Laboratory of Leningrad Agrophysical Institute.

The most common case of hydrophobization is the hydrophobizing by means of surface active agents of the type of sodium salts of carbon acids (with the use of an intermediate reagent) of such soils, which possess interchange absorption power and whose absorbing complex is saturated with calcium, magnesium, potassium, hydrogen and other cations. (It should be noticed that the humic acid part and the zeolite part of the majority of soils are cationites.)

While introducing into such ground a solution, e. g., of copper sulphate, the following reactions of the cation interchange will take place between the soil absorbing complex (SAC) and the soil solution:

$$\left[SAC\right] \cdot Ca\,Mg + 2CuSO_4 \rightleftharpoons SAC \cdot 2Cu \xrightarrow{+CaSO_4} + MgSO_4$$
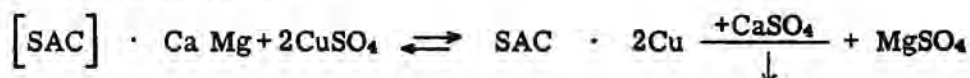
While introducing soap solution into a soil which had been treated with copper sulphate, the following reactions will occur:

1. $MgSO_4 + 2R - COONa \longrightarrow (R-COO)_2\,Mg + Na_2SO_4;$

2. $CuSO_4 + 2R - COONa \longrightarrow (R-COO)_2\,Cu + Na_2SO_4;$

3. $\left[SAC\right] \cdot Cu(Ca_1Mg) + 2R- COONa \longrightarrow \left[SAC\right] \cdot 2Na$

$$+ (R- COO)_2\,Cu\,(Ca_1Mg),$$
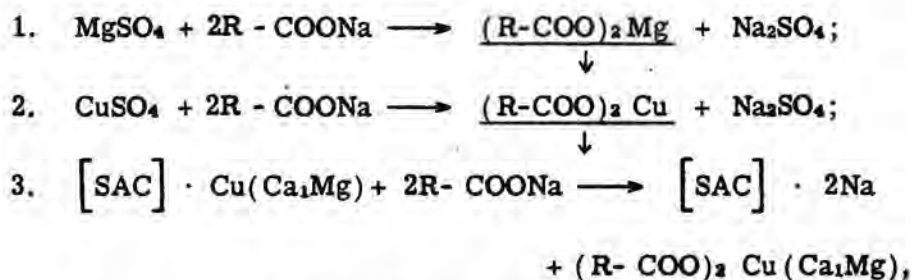
where R is the hydrophobic radical.

Thus, out of the soil solution will precipitate copper, calcium, magnesium and other waterproof soaps. (A chemical absorption of reagents, after Gedroyz (4), will take place.) The deposit will be in the form of a mechanical admixture to the soil. It should be noticed that the reactions involved in the formation of the waterproofing soap proceed mainly stoichometrically.

The investigations of Kolyasev, Jutchenkov, Holodov and others have shown that for obtaining the proper effect of hydrophobicity the soil particles should be completely covered with hydrophobizer.

Practically, the uniform distribution of hydrophobizer on the surface of particles is provided by mechanically mixing the treated material with the introduced reagents until a homogenous mass is obtained. Consequently, the mixing of the soil with the reagents introduced is the second necessary technological requirement.

In the process of mixing the soil with the deposit of the waterproof soap the latter is adsorbed by the surface of the particles as a result of molecular interaction (physical

adsorption, case 2). It is to be assumed that the adsorption of the amorphous deposit of the waterproof soap does not depend on Gibbs' adsorption equation.

To ensure the hydrophobic effect after having introduced and mixed the soil with the reagents it is necessary to eliminate the hydrate films from the surface of the hydrophobizer and the soil particles. Practically, this is achieved by means of drying the material.

In the process of drying only humidity is removed from the treated soil, while all the products of the interchange between the salts of the soil and the soap solution, as well as the products of the interchange between the soap solution and the soil absorbing complex, remain in the treated material either as a mechanical admixture or in adsorbed state as a result of physical adsorption (e. g., calcium soap), or in the interchange state in the soil absorbing complex (e. g., sodium).

While removing the hydrate films from the surface of the particles during the process of drying, the force of interaction between the particles of the ground and and the soap (adhesion) will grow as the distance between them decreases and, finally, a direct contact will appear between the hydrophobizer and the mineral. This statement has been proved by the experiments of Krotova (9). While removing the hydrate films from the surface a "drying adhesion" of the hydrophobizer takes place. Consequently, thorough drying of the treated soil is the third necessary technological requirement, ensuring, on one hand, a more reliable fixation of the hydrophobizer and, on the other hand, the removal of hydrate films from the surface of the hydrophobic covering. The presence of hydrate films would permit rewetting of the ground.

As shown in Table I, the medium thickness of the hydrophobic covering, which prevents the ground from being wetted, is about 60-70 m μ and does not depend upon the length of the applied reagent molecules.

(The length of molecules from C_{16} - C_{18} is assumed to be 24 Å, while the length of molecules from C_7 - C_8 is assumed to equal 12 Å.)

According to the experimental data the rate of applying the hydrophobizer expressed in percent of the soil weight (C) may be determined by the following equation:

$$C = K \cdot S_s \cdot h \cdot \rho \ 100\%,$$

where K is a factor depending on the relation of kinetic specific surface to the static one. For soil with a specific surface up to 1 m^2/g, "K" may be taken as 1.

S_s - specific surface of the soil in cm^2/g.

ρ - specific weight of hydrophobizer.

h - thickness of hydrophobic covering in cm.

TABLE 1

THICKNESS OF HYDROPHOBIC COVERING (hÅ) AT MINIMUM DOSAGE OF REAGENTS (C%) ENSURING THE HYDROPHOBICITY OF TREATED SOILS

Kind of Soil	Specific Surface (Ss m/g)	Dosage of Reagent in Percent of Soil Weight (C%)	Thickness of Hydrophobic Cover (hÅ)	Hydrophobizer	Cation	Number of Molecular Layers (n)
Sand	0.02	0.12	600-650	Fatty soap	Cu	25 - 27
Sand	0.07	0.50	800-900	Fatty soap C_{18} - C_{18}	Fe	33 - 37
Light loam	0.20	1.00	500-600	Naphtha soap	Fe	21 - 25
Medium loam	0.31	2.00	600-700	Resin soap	Cu	25 - 30
Medium loam	0.31	2.00	700-720	Synthetic fatty acids C_7-C_8	Cu	60 - 70
Clay	0.99	3.00	300-400	Resin soap	Cu	13 - 17

Thus, the hydrophobic covering obtained on the soil particle surfaces may be considered as a volume system of hydrophobic films, having the character of an independent phase, and according to Schwartz and Perry (10) being nothing else than a layer of hydrophobic color on a mineral surface.

Hence the hydrophobicity of the particle surface will be determined by the hydrophobicity of the reagent combination, which consequently enables us to foretell the degree of hydrophobization that will be achieved by treatment.

The general requirements to be fulfilled by the hydrophobizing reagents may be formulated as follows:

1. Absence of wettability and solubility in water;
2. Considerable adhesion to the mineral surface; and
3. Easy and uniform distribution in soil mass.

The first sign of hydrophobicity is a great reduction of the water holding power of the material, increase of drying rate, and decrease of equilibrium humidites. Figure 1 shows the drying rate of thin layers of the original and the hydrophobized soil, the soil having a specific surface of $S_S = 900$ cm^2/g.
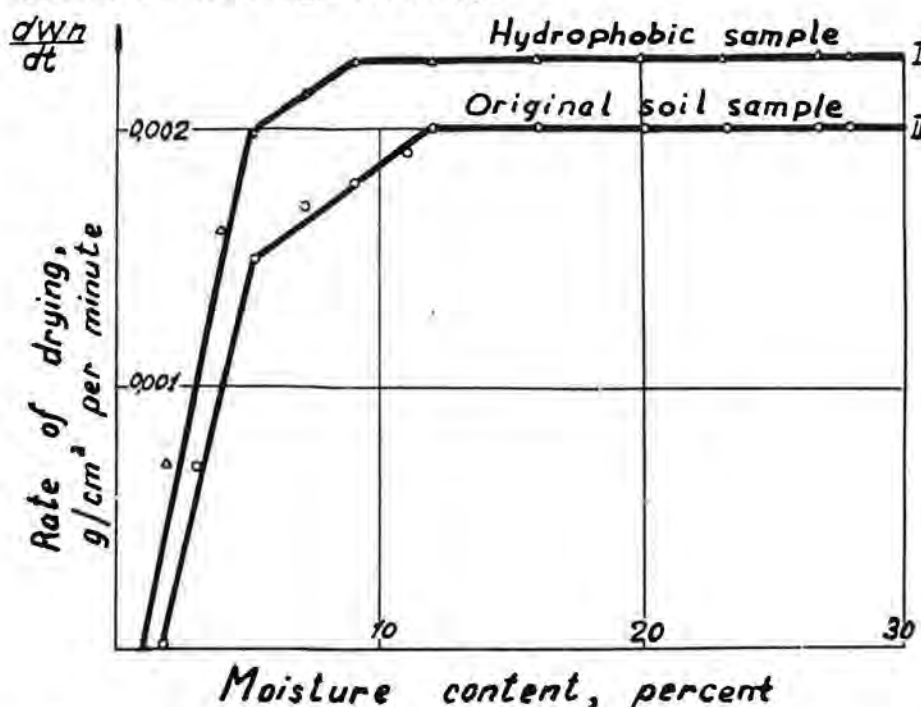
Figure 1. Rate of drying a natural soil and its hydrophobic modification (sandy-loam, Ss = 900 cm^2/g). Drying conditions: t^0 = 22 C, W = 0.3 percent. Equilibrium moisture of the soil: original—1.60 percent; hydrophobic—0.93 percent.

As shown in Figure 1, the drying rate for the hydrophobic soil (curve 1) during the period of constant drying rate is somewhat higher than for the original soil. The duration of the constant drying rate period for the original sample is 3 percent less than for the treated sample.

The first period of falling rate of drying for the hydrophobic sample is shorter than for the original soil. The second critical point both for the original soil and for the hydrophobic sample is at a humidity of 5 percent. The equilibrium humidity, set at the parameters shown in the diagram, equals 1.60 percent for the original soil sample and 0.93 percent for the hydrophobic sample. According to the curves it is found that the hydrophobic sample completed its drying in 280 minutes, while the sample of the original soil continued it for 330 minutes.

Table 2 shows the equilibrium humidities for different soils treated with different hydrophobizers. As shown in Table 2, the equilibrium humidity for the hydrophobic soil equals 34-58 percent of the equilibrium humidity of the initial material.

The treatment of soil by one of the previously discussed methods, according to the scheme:

TABLE 2

EQUILIBRIUM HUMIDITIES OF ORIGINAL AND HYDROPHOBIC SOILS OVER 84 PERCENT SULPHURIC ACID

Kind of Soil	Specific Surface (S_S m^2/g)	Hydrophobizer	Cation	Equilibrium Humidity in Percent of the Absolutely Dry Soil Weight		$\dfrac{W_1}{W_2} \cdot 100\%$
				Initial (W_1)	Hydrophobic (W_2)	
Sand	0.02	Fatty Soap $C_{16} - C_{18}$	Cu	0.39	0.13	34
Sand	0.07	Resin Soap	Fe	0.69	0.39	56
Loam	0.14	Naphtha Soap	Fe	1.37	0.66	48
Loam	0.20	Fatty Soap $C_{18} - C_{18}$	Fe	1.60	0.99	58
Loam	0.30	Resin Soap	Cu	2.27	1.26	55

1. Introduction of one or two interacting hydrophobizers into the soil;
2. Uniform distribution of hydrophobizer by means of mixing;
3. Drying of treated material;
4. Grinding in a mill;
5. Sifting through a sieve with holes of diameters between 0.5 and 0.25 mm, provides a dry powder whose particles are not wetted by water. This sort of powder has been named "hydrophobic earth" (1a).

Hydrophobic earth is a singular kind of material combining in itself both unwettability and friability. It possesses considerable porosity and has an interconnected capillary pore space.

The unwettability of the particle surfaces ensures to the hydrophobic earth some additional properties: capillary rise of water does not occur in the hydrophobic earth for a considerable length of time and the earth is capable of withstanding various hydrostatic pressures. Therefore, the hydrophobic earth like other kinds of hydroinsulation may be used for protecting engineering works from the action of water and from water filtration through the enclosing constructions.

The numerical value of the anticapillary pressure in the hydrophobic earth depends both on the mechanical properties of the initial material and on the reagents used.

The experimental determination of the hydrostatic pressures which the hydrophobic earths are able to withstand, was carried out by means of glass tubes (dia 1.8 cm). The tube walls were paraffined at one end. The paraffined end of the tube was bound with gauze and filtering paper. The hydrophobic earth filled the tube to a height of 3 cm. Through all the experiments densification of the earth was accomplished by means of a rod which transmitted a pressure of one kg/cm^2.

The results of some experiments are shown in Table 3.

As shown in Table 3 the anticapillary pressure in finely dispersed hydrophobic earth is approximately 1.25 m and probably may be increased. The anticapillary pressure has been estimated according to the formula of Deriagin (11).

$$\Delta \rho = \frac{\sigma \cdot \text{Cos } \Theta \cdot \text{So}}{\delta} ,$$

where:

$\Delta \rho$ - anticapillary pressure in centimeters of water;

σ - surface tension of liquid in erg/cm^2;

Θ - marginal angle of wetting;

So - specific surface of porous body in cm^2/cm^3;

δ - porosity equal to the ratio of specific and volume weights to specific weight.

It has been assumed that the marginal angle of wetting was Θ = 106 deg (paraffin).

According to Table 3, such theoretical evaluation is not justified, because not only the hydrophobizer, but also the cation included in the latter, as well as the mechanical properties, influence the marginal angle to a considerable extent. Thus, it was ascertained that the lead abietates are the most hydrophobic, while the abietates of aluminum, copper and iron are less hydrophobic and the abietates of calcium, magnesium and especially silver are the least hydrophobic agents.

The experimental definition of marginal angles of wetting in dispersion mediums was carried out according to the following formula:

$$\text{Cos } \Theta = 2.5 \frac{(\Delta 1)^2}{\tau} \frac{\eta}{\sigma} \frac{So}{\delta},$$

where:

Θ - marginal angle of wetting;

2.5 - empirical factor;

1 - path followed by the liquid during capillary impregnation, in cm;

τ - time in seconds;

TABLE 3

ANTICAPILLARY PRESSURE IN HYDROPHOBIC POWDERS

Kind of Material	Specific Surface (S_S m²/g)	Hydrophobizer	Cation	Anticapillary Pressure In Water Column (cm)	
				Experimental Data[1]	Evaluation Data Θ = 106 deg
	0.02	Naphtha Soap	Fe	7	12
Sand	0.02	Dimethyl-oxysilan	-	19	12
	0.02	Wood Tar	Cu	11	12
	0.02	Resin Soap	Cu	15	12
Clay	0.99	Resin Soap	Cu	125	400
Ash From the Heat and Power Plant Furnaces	0.40	Dimethyl-oxysilan	-	80	160
	0.40	Resin Soap	Cu	60	160
Sandy Loam	0.07	Fatty Soap	Fe	35	32
	0.07	Dimethyl-oxysilan	-	40	32
	0.30	Resin Soap	Cu	70	125
	0.30	Dimethyl-oxysilan	-	85	125
Loam	0.20	Resin Soap	Cu	50	88
	0.20	Dimethyl-oxysilan	-	60	88
	0.20	Naphtha Soap	Cu	36	88
	0.20	Naphtha Soap	Fe	30	88

[1] A slight increase of the anticapillary pressure shown in this column brings squirting of water through the pores.

η - viscosity in poises;

σ - surface tension of liquid in dynes;

S_o - specific surface in cm^2/cm^3 of the body;

δ - porosity $\dfrac{g-d}{g}$ (g - specific weight
d - volume weight)

Marginal angles of wetting (Θ) versus specific surface (S_s) values are shown in Figure 2.

As shown by the diagrams, in the process of the material passing from a massive piece to a coarsely ground state the marginal angle of wetting grows, then reaches its maximum and with the further grinding of the particles starts to minimize. The maximum angles of wetting in the above-mentioned experiments correspond to the specific surface of $2 \cdot 10^3$ cm^2/g. This relation is observed when the hydrophobic material is impregnated by petroleum. Consequently, the most favorable soils for hydrophobization are those the mechanical properties of which correspond to the specific surface of $(1-3) \cdot 10$ cm^2/g.

In connection with the change of the hydrocharacteristics of soil under the influence of hydrophobization, its thermal and electric characteristics are also changed.

Thus, according to the investigational data of Kolyasev and Levin (12) the heat conductivity factor of hydrophobic earths in air-dried condition is

$$0.17 - 0.36 \ \frac{K.\ cal}{m.\ hour.\ degrees} \ , \ i.e.$$

4 to 6 times lower than the heat conductivity of concrete and 3 to 4 times lower than the heat conductivity of brick, being approximately equal to the conductivity of wood.

The investigations of Kolyasev, Levin and Holodov prove that the specific electric resistance of hydrophobic earth in an air-dried state is $(5-9) \cdot 10^8$ to $(1.2-3) \cdot 10^9$ ohm/cm and approaches such insulating materials as asbestos and marble.

Consequently, hydrophobic earth may be used as a combined "hydro-thermo-electro" insulating material. In particular, the hydrophobic earth has been used by us for the electrically heated hot beds of the "screen grid type" and has proved itself to be a reliable hydro-thermo-electric insulator.

Experiments which we had conducted with the hydroinsulation of flat roofs on buildings proved the stability of hydrophobic earth against the variations of the atmospheric temperature and humidity regimes.
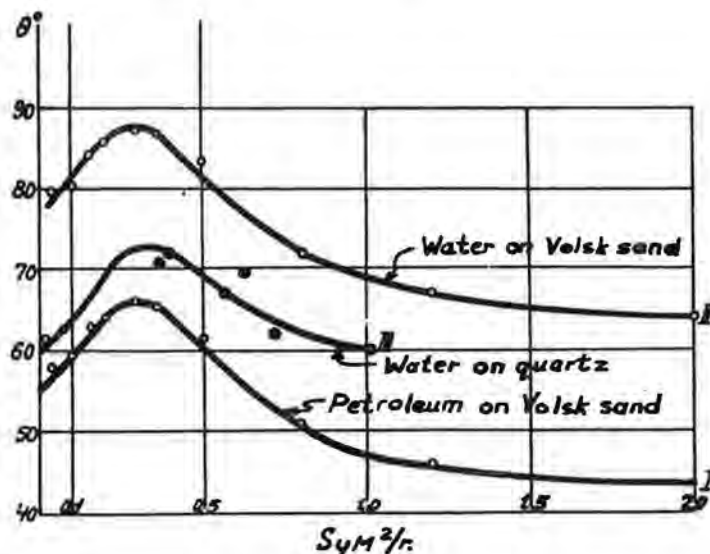

Figure 2. Alteration of Kinetic angle of wetting versus specific surface value.

The application of hydrophobic earth as an antifiltration barrier in irrigation channels has been successful (13).

The investigations of Selkyn (14) have shown that the use of a waterproof layer of hydrophobic earth, the formulae and technology of which had been worked out by the Agrophysical Institute (Kolyasev and others), minimizes the frost heaving of soil fourteen times as compared to the noninsulated soils.

The possibility of preparing hydrophobic earth as a building material out of unstable soils results in more economical construction. Thus, hydrophobic earth is employed to suppress the heaving of railway beds built under severe hydrological conditions (high ground water level, heaving ground), especially, if the use of coarse-grained material (sand, gravel, etc.) is connected with considerable expense.

SUMMARY

1. A brief survey is presented of possible mechanisms for providing and fixing hydrophobizers on the surface of minerals. The fundamental process of hydrophobization is considered as an adhesion process with the building up of an independent phase on the surface of the minerals.

2. For the purpose of hydrophobization any substances may be used with a sufficient degree of adhesion to the mineral, which are neither wetted by water nor soluble in the latter.

3. The main requirements for the hydrophobization are: a) the uniform distribution of reagent on the mineral surface; b) the building of a volume film resisting the hydrostatic pressures; c) the elimination of hydrate films from the mineral surface and from the hydrophobic covering.

4. The possibility is shown of using the hydrophobic earth as a combined thermo-hydro-electric insulator as well as a separate thermo- and hydro-insulating material.

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Flow of Water in Hardened
Portland Cement Paste

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Permeability of hydrated portland cement pastes was measured at four
temperatures. A theory based on viscous drag of fluid on particles,
taking into account the effect of adsorption on viscosity, was applied.
Particle size was estimated as $\phi^{1/4} \delta$ = 194Å or 201Å, first and second
approximations, where ϕ is the sphericity factor and δ the volume
diameter. The specific surface diameter, obtained from specific
surface of the solid phase as measured by water vapor adsorption, was
109Å or 95Å. This gave ϕ = 0.46 or 0.36, indicating sheets or fibers,
in agreement with electron-micrographs obtained in 1957.

● STUDIES of the permeability of hardened cement paste to liquid water were carried
on as one of several means of studying the colloidal structure of hydrated cement paste.
Carman's (1) successful adaptation of the Kozeny (2) analysis of fluid flow in granular
material indicated the possibility of the same kind of application to cement paste, which
was known to be composed principally of colloidal particles. First attempts to apply
the Carman-Kozeny approach were encouraging, but certain discrepancies were noted.
The discrepancies between theory and experimental results prove to be fundamentally
significant, and finally the Carman-Kozeny approach was set aside in favor of an anal-
ysis based on the Stokes concept of viscous drag as developed by Steinour (3). After
modification as required by the extreme smallness of the water-filled spaces in har-
dened cement paste, this analysis led to a measure of particle size in terms of "surface
diameter," and "sphericity factor." This value agreed with other information, particu-
larly specific surface as determined by water vapor adsorption and the Brunauer-
Emmett-Teller equation (4) and electron-micrographs obtained in 1957. The present
paper describes the experimental methods and results, gives the theoretical basis of
analysis, and shows the degree of fit between theory and experiment.

METHODS AND RESULTS

Preparation of Test Specimens

This paper is based on many experiments carried out over a period of about ten
years. Although precision of measurement was adequate, data obtained were generally
difficult to deal with because of differences between flow rates for supposedly identical
samples. Early attempts at theoretical analysis were only partly successful because
the data points were too scattered to settle crucial questions. Finally, it was dis-
covered that the principal cause of variations among similar samples was small differ-
ences in alkali content of the solution in the pores of the specimens. Only the final ex-
periments were used directly in this paper. They were made on specimens prepared
as follows:

A group of specimens was prepared from which nearly all the alkali was removed
by allowing it to diffuse into the curing water. Conditions were such that this required
more than 600 days. The permeability coefficients were measured from time to time
during the 600-day period, on companion samples. Gradual removal of alkali was
shown by a slow increase in coefficient of permeability, the final coefficient exceeding
the lowest by a factor of 5 or 6, and by chemical analysis at the end of the test. (Ver-
beck, in unpublished work, had previously shown that soluble materials reduced rate of
flow through specimens of paste much more than could be accounted for by the ordinary
effects of solutes on viscosity of water.)

These special specimens were made from an ultra-fine cement to obtain a final
product practically free from unhydrated cement, and so that a wide range of water-

cement ratios could be used without appreciable bleeding during the plastic stage. The special cement was prepared by passing 30 lb of a commercial type I product through a small air separator and discarding the coarser two-thirds. The resulting ultra-fine product had a specific surface of about 8,000 g per sq cm as measured by the Blaine meter. The hydration products from the ultra-fine cement showed about the same physical characteristics as those from a cement of ordinary fineness prepared from the same clinker.

Neat cement pastes were prepared and cast in glass tubes in the way described in a previous publication (5). Four different ratios of water to cement were used: 0.5, 0.6, 0.7 and 0.8. Specimens having still higher water cement ratios were prepared and tested, but results are not reported here because not all the alkali was removed from them before and during the test.
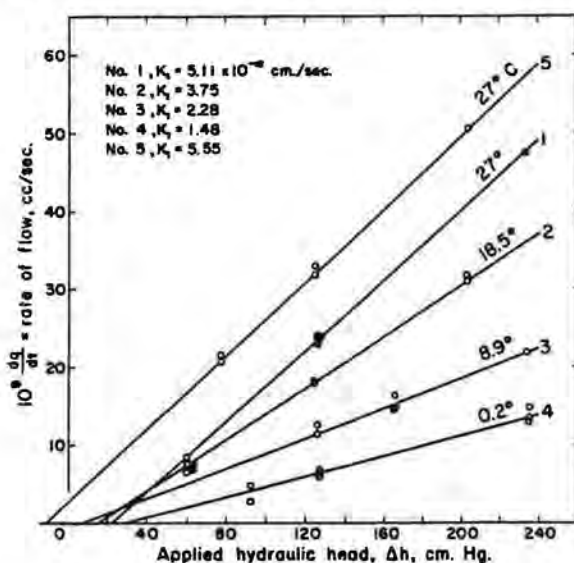

Figure 1. Rate of flow vs hydraulic head —W/C = 0.5, Specimen 4-13_b-B.
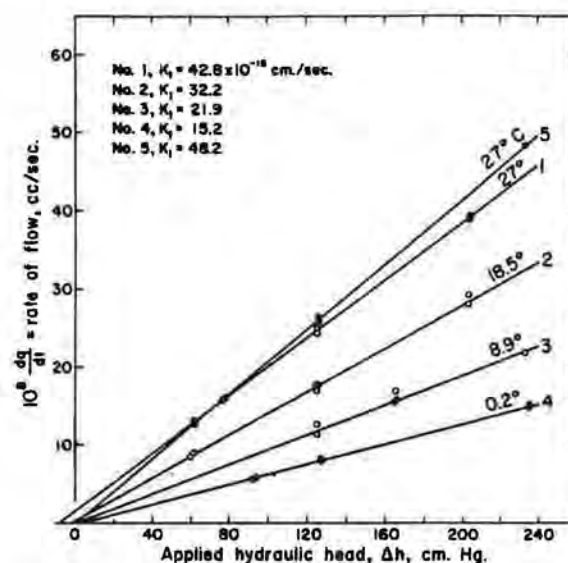
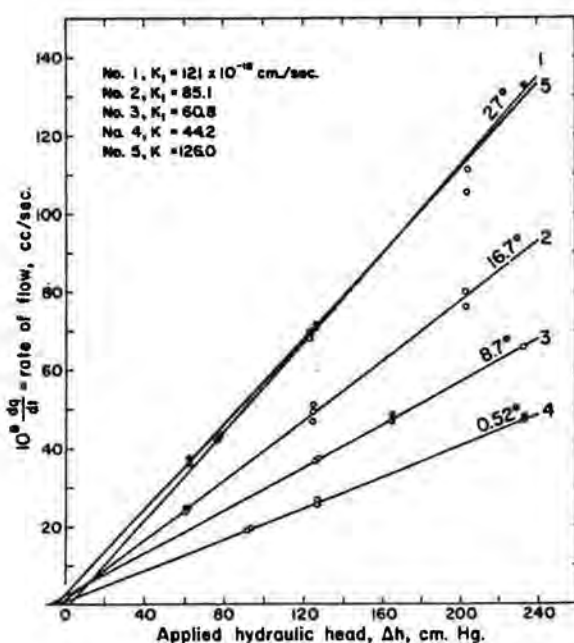Figure 2. Rate of flow vs hydraulic head —W/C = 0.5, Specimen 4-14_a-A.

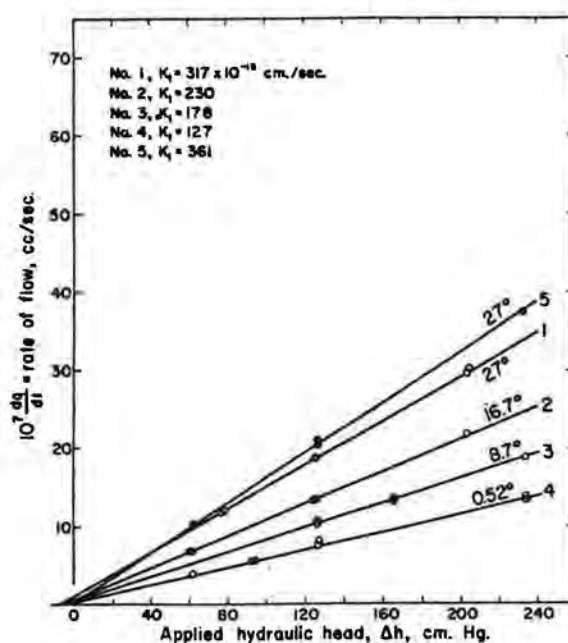Figure 3. Rate of flow vs hydraulic head —W/C = 0.7, Specimen 4-20_aC.

Figure 4. Rate of flow vs hydraulic head —W/C = 0.8, Specimen 4-28_bC.

The molds were not quite filled with paste, and immediately after placing the paste in the mold, 15 to 20 cc of water was added, and the mold was stoppered. The mold was then stored in a constant-temperature room (23 C) for about 20 months. During this time most of the alkali in the specimens diffused into the water at the top of the specimen (the "curing water"). Practically all the rest of it was removed while the specimen was under test, and before final rates of flow were established.

The mold was removed from the hardened cylinder of paste and one or more truncated cones for permeability tests were obtained by means of a lathe and a diamond saw, as previously described (5). After the permeability test was completed, each test specimen was analyzed for non-evaporable water content, evaporable water content, solid content, and alkali content. Cement and water were mixed under reduced pressure to obtain paste without air bubbles.

Permeability Tests

Coefficients of permeability were determined by means of the apparatus described before (5), with a modification. The modification consisted of equipping each of the two water baths with a cooling coil. This made it possible to measure the coefficient of permeability of each specimen at four different temperatures. At each temperature, rates of flow were measured at three different pressures, approximately 1, $1\frac{1}{2}$ and 3 atmospheres above ambient pressure. Sixty rates of flow were established, four at a time; two to five days being required to establish a rate at a given pressure.

The relationships between applied pressure and measured rate of flow are shown in Figures 1, 2, 3 and 4. Where two or three points for a given pressure are shown, they represent rates observed on successive days. A plot of such readings vs time shows that the differences are partly due to inaccuracy in measuring the exceedingly low rates of flow and partly due to small changes toward the final steady rate. The positions of the straight lines were established usually by the average of the last two or three readings at each pressure. Although some deviations may be seen, in general an increase in applied pressure produced a proportionate increase in rate of flow.

In most cases the best straight line for a given specimen and temperature does not pass through the origin. This is due to osmotic pressure, which in some cases aids the applied pressure and in other cases opposes it. During the course of an experiment it may vary in magnitude, and even may reverse direction, before final rates of flow are established. The development of osmotic pressure may be ascribed to electrolytes in the paste. The electrolytes tend to diffuse out of the specimen during a test and, because the volume of fluid exposed to the upstream face per unit of specimen area is not the same as that at the downstream face, and because of flow itself, small differences develop in concentrations of electrolyte. The test specimen functions as a semi-permeable membrane, thus osmotic pressure may be manifested. The principal electrolytes are sodium hydroxide, potassium hydroxide, and calcium hydroxide.

The specimens dealt with here were so nearly free from alkali that osmotic pressures were small, and in some cases nil. After the permeability tests were completed the specimens were tested for alkali content by means of the flame photometer (ASTM Designation C114). In each case the Na_2O content was too low to be detected and the K_2O was found to be, in order of ascending water cement ratios, 0.003, 0.003, 0.005 and 0.00 percent of cement weight. Osmotic pressure tends to change in the course of an experiment, but for this group of specimens the change was so slow under final conditions that the three flow-rates for a given temperature could be established before an appreciable change in osmotic pressure occurred.

The coefficient of permeability is directly proportional to the slope of a line such as one of those in Figure 1. The coefficient corresponding to each point in Figure 1 is tabulated in Table 1 along with other data to be discussed later. The method of calculation was the same as described before (5).

DISCUSSION OF DATA

Hardened cement paste is predominantly a gel; that is, an aggregation of colloidal particles. It has high capacity for evaporable water; upwards of 30 percent by volume

TABLE 1
OBSERVED COEFFICIENTS OF PERMEABILITY
c = solid content of specimen, cc per cc

Chronological Order	Temp., θ (deg C)	Temp., Abs., T	Permeability, $10^{15}K_i$ (cm/sec)	Log $10^{15}K_i$	$\frac{1,000}{T}$
Specimen 13$_b$-B; c = 0.586; $\frac{c}{1-c}$ = 1.415					
1	27.16	300.34	5.11	0.708	3.330
2	18.54	291.72	3.75	0.574	3.428
3	8.92	282.10	2.28	0.358	3.545
4	0.20	273.38	1.48	0.170	3.658
5	26.97	300.15	5.55	0.744	3.332
Specimen 14$_a$-A; c = 0.511; $\frac{c}{1-c}$ = 1.045					
1	27.16	300.34	42.8	1.631	3.330
2	18.54	291.72	32.2	1.508	3.428
3	8.92	282.10	21.9	1.340	3.545
4	0.20	273.38	15.1	1.179	3.658
5	26.97	300.15	48.2	1.683	3.332
Specimen 20$_a$-C; c = 0.471; $\frac{c}{1-c}$ = 0.890					
1	26.86	300.04	126	2.100	3.333
2	16.67	289.85	85.1	1.930	3.450
3	8.70	281.88	60.8	1.784	3.548
4	0.52	273.70	44.2	1.645	3.654
5	26.87	300.05	121	2.082	3.333
Specimen 28$_b$-C; c = 0.428; $\frac{c}{1-c}$ = 0.748					
1	26.86	300.04	317	2.501	3.333
2	16.67	289.85	230	2.362	3.450
3	8.70	281.88	178	2.250	3.548
4	0.52	273.70	127	2.104	3.654
5	26.87	300.05	361	2.558	3.333

as compared with 1 percent, more or less, for typical rocks. Yet the coefficient of permeability of paste is as low as that of most rocks (5). This is a manifestation of the paste's fineness of texture; the pores and particles are exceedingly small and numerous. A considerable fraction of, if not all, the water contained in these pores is adsorbed; that is, it is within the range of mutual attraction between water molecules and the solid surface. The question arises, therefore, as to whether all the water is mobile. Adsorbed water might have ice-like structure, and might show a "yield point," so that, at some threshold pressure, water immobile at a given pressure becomes mobile. If some of the water is immobile at a given pressure it is likely to be that in the first adsorbed layer, or that held in the densest portions of the structure, and in the wedge-shaped spaces where fibers cross each other. So far as flow is concerned, such immobile water would be part of the solid phase. All the particles would function as if they were larger than they are, and the total porosity would seem smaller than the total space occupied by evaporable water. There is also the possibility that water may enter the lattice of layered crystals, but not take part in flow.

Indications of the data to be presented hereafter are that flow through cement paste is not fundamentally different from flow through other porous bodies, even though flow is undoubtedly influenced by adsorption. As already mentioned, the data plotted in Figure 1 show conformity to Darcy's law. Many other data not included here confirm this aspect of the results. It may be concluded from that observation that if any of the water was immobile, it was immobile at all the pressures used in the experiments. Further analysis developed later herein leads to the conclusion that none of the water is immobile. There is no evidence that particles giving rise to viscous drag in the permeability test are larger than the particles of the solid phase; that is, there is no evidence supporting the supposition previously stated that some of the water held in the densest portions of the structure is immobile.

THEORY OF PERMEABILITY

Previous investigators have developed theories of flow through porous materials and granular beds. The subject has been dealt with mainly from two points of view. One view leads to considering the conduits in a granular bed to be analogous to a bundle of parallel capillaries, and applying the Poiseuille-Hagen law of capillary flow, using hydraulic radius (volume of water-filled space divided by the wetted boundary area of that space) as a measure of size of capillary. The Kozeny equation as used by Carman is the principal expression of this idea. The other point of view leads to considering the viscous drag of moving fluid on a particle. The drag may be developed by a particle falling through a fluid, or by flow through a granular bed where the particles are in fixed positions. This approach to the problem leads to a more general law than does the former.

The theory of permeability based on the concept of viscous drag can be approached by considering the drag on a single particle moving under gravitation through a large body of fluid. The driving force is the net weight of the particle multiplied by the gravitational constant:

$$F = (\rho_s - \rho_f)\ (\frac{\eta\delta^3}{6})\ g \tag{1}$$

in which   F = driving force;

ρ_S = density of the solid material;

ρ_f = density of the fluid;

g = gravitational constant (= 980 cm per sec per sec); and

δ = diameter of a sphere having the same volume as the actual particle.

The drag is a function of size and shape of particle, of velocity, and of viscosity of the fluid; that is (Stokes),

$$R = 3\pi\eta(\theta)\, V\, d_d \tag{2}$$

in which   R = resistance (drag);

$\eta(\theta)$ = viscosity of fluid at θ C, in poises;

V = velocity of fall, in cm per sec; and

d_d = drag diameter (that is, the diameter of a sphere having the same viscous drag as the actual particle) (6).

When force and drag are equal, the rate of fall is constant at "Stokes velocity," or

$$V_S = \frac{(\rho_S - \rho_f)\, g\, \delta^3}{18\eta(\theta)\, d_d} \tag{3}$$

Then, if

$$d_s{}^2 = \frac{\delta^3}{d_d} ,$$

$$V_S = \frac{(\rho_S - \rho_f)\, g\, d_s{}^2}{18\eta(\theta)} \tag{4}$$

which is "Stokes velocity" in terms of "Stokes diameter"; that is, Stokes Law for the fall of an isolated particle.

When there are many equal particles suspended in a fluid medium, the fall of the suspension is slower than that of an isolated particle of the same kind, and the rate is lower the higher the concentration of particles. Thus,

$$V(c, \theta) = V_S \phi_0(c) \tag{5}$$

in which $V(c, \theta)$ is the rate of fall of the suspension at temperature, θ, in which the volume of concentration of particles is c, and in which the particles are characterized by Stokes velocity, V_S; $\phi_0(c)$ is some function of the total volume of particles. The latter function operates as a reduction factor.

From theoretical and empirical considerations, Steinour (3) found, for isothermal conditions,

$$\phi_S(c) = (1 - c)^2 \exp(-kc) \tag{6}$$

where k_1 is a constant. (For spheres of tapioca and for microscopic glass spheres, he found $k_1 = 4.19$.)

From theoretical deductions by Vand (7), Hawksley (8) found

$$\phi_H(c) = (1 - c)^2 \exp - \left(\frac{k_2 c}{1 - Qc}\right) \tag{7}$$

Here k_2 is the same as the constant in Einstein's (9) equation for the effect of rigid particles in a fluid on the apparent viscosity of the fluid. Its theoretical value, 2.5 for spheres, has been confirmed experimentally for low values of c. Q is Vand's "hydrodynamic interaction" constant. Its theoretical value for spheres is about 0.6.

Mooney (10) also arrived at Eq. 7 with the same value for k_2, but with a different interpretation and evaluation of Q. From his point of view, Q is a "crowding factor" and depends on the range of particle sizes, if the system is polydisperse.

Eqs. 6 and 7 were compared by applying them to Steinour's data for tapioca suspended in oil. These data included a well-established rate of fall for an isolated particle, and values of c ranging up to about 0.5. Three assumptions were made:

$$\phi_S(c) = (1 - c)^2 \exp(-k_1 c) \quad \text{(Steinour)}$$

$$\phi_H(c) = (1 - c)^2 \exp \frac{-kc}{1 - 0.6c} \quad \text{(Hawksley)}$$

$$\phi_M(c) = (1 - c)^2 \exp \frac{-kc}{1 - Qc} \quad \text{(Mooney)}$$

These expressions were used in place of $\phi_0(c)$ in Eq. 5 and the constants not arbitrarily fixed were evaluated from the data by means of an electronic computer. The results were:

For $\phi_S(c)$, $V_S = 0.120 \pm 0.003$; $k_1 = 4.25 \pm 0.08$.

For $\phi_H(c)$, $V_S = 0.102 \pm 0.002$; $k = 2.87 \pm 0.05$; $Q = 0.6$ (arbitrary).

For $\phi_M(c)$, $V_S = 0.110 \pm 0.004$; $k = 3.51 \pm 0.27$; $Q = 0.31 \pm 0.11$.

The average of 150 tests of rate of fall of a single particle in a 1,000-ml oil-filled cylinder gave a velocity of 0.1120 ± 0.009 cm per sec. Correcting for wall effect increased this figure to 0.1194 ± 0.0095 cm per sec. Steinour's function apparently gives the most accurate prediction of the Stokes velocity.

Although the other functions do not fit the data quite as well as Steinour's, they might seem preferable because they include explicitly factors called for by analysis based on hydrodynamic considerations. However, they apparently are not valid expressions of theory, for not only do they give a relatively inaccurate prediction of Stokes velocity, but also they give incorrect values of k. The Einstein constant should have come out as 2.5 or perhaps slightly higher, because the tapioca particles were spherical, but it did not do so for either $\phi_H(c)$ or $\phi_M(c)$. On the whole, it seems that Steinour's simpler function takes into account adequately what the more explicit functions failed to do. As will be seen later, a still different function is required for the present case. At this point, the function will be left unspecified, except for the quantity $(1 - c)^2$; all agree on that, because it arises from fairly obvious considerations of the influence of presence of particles in the suspension on the buoyancy of a given particle, and on the upward velocity of water relative to a given particle. Hence, it may be assumed that

$$\phi(c) = (1 - c)^2 \exp\left(1 - \phi(c)\right) \tag{8}$$

for the specific case to which the ensuing discussion pertains.

The fall of a thick suspension of equal particles (monodisperse) or of a flocculated suspension of unequal particles (polydisperse) leaves an accumulation of clear fluid above the suspension. The velocity of fall, in cm per sec, is equal to the rate at which the clear fluid appears in the container above the suspension. Thus, using Eqs. 3 and 5, it is found that

$$V(c, \theta) = \frac{dq}{dt} \frac{1}{A} = \frac{(\rho_S - \rho_f) d_S^2 g}{18 \eta(\theta)} \phi_0(c) \tag{9}$$

in which q is the efflux from the suspension, in cc; t, is time, in seconds; and A is the area of the suspension, in sq cm.

By Darcy's law

$$\frac{dq}{dt} \frac{1}{A} = \frac{K_1 \Delta h}{L} \tag{10}$$

in which K_1 is the coefficient of permeability, in cm per sec, and $\frac{\Delta h}{L}$ is the hydraulic gradient in terms of hydraulic head.

In the suspension, the excess hydraulic gradient is due to the weight of the solids, minus the weight of the fluid they displace; that is,

$$d_f \frac{\Delta h}{L} = (\rho_S - \rho_f) c \tag{11}$$

$$K_1 = \frac{\rho f g d_s^2}{18\eta(\theta)} \frac{(1-c)^2}{c} \exp\left(-\phi(c)\right) \tag{12}$$

If Eq. 12 represents a thick polydisperse suspension in which all particles fall at the same rate, regardless of size, Stokes diameter, d_s, represents a "typical particle" which is not easy to define. In the present case, Stokes diameter will be replaced by a "surface diameter," as will be seen further on.

Hawksley pointed out that in using a formulation such as Eq. 12, the streamlines around each particle are assumed to be symmetrical with the general direction of flow, as in the fall of an isolated particle. In a thick, flocculated suspension, or in a granular bed, where the individual particles are not free to adjust themselves so as to equalize couples of forces acting on them, the patterns of flow deviate from the general direction. Citing arguments of Fowler and Hertel (11), he inserted an "orientation factor," ζ, which would appear in the first right-hand term of Eq. 12. This factor is essentially the "tortuosity factor" required by the Kozeny-Carman approach, which is practically constant (at least its product with the "shape factor" is constant) for a considerable range of c. Nevertheless, it is a function of c such that as c diminishes

$$\lim_{c \to 0} \zeta(c) = 1.0$$

For flocculated thick suspensions and for granular beds, $\zeta(c)$ may be assumed to be $\frac{2}{3}$. In terms of the foregoing development this means that if the streamlines around an isolated particle could be caused to deviate from the general direction of fall to the same extent that the streamlines in a bed of particles deviate from the general direction of flow, the average rate of fall of the isolated particle would be about $\frac{2}{3} V_S$. Thus, Eq. 12 should be written

$$K_1 = \frac{\rho f g d_s^2}{18\eta(\theta)} \zeta(c) \frac{(1-c)^2}{c} \exp\left(-\phi(c)\right) \tag{13}$$

in which $\zeta(c) = \frac{2}{3}$ for thick flocculated suspensions or granular beds. Using Steinour's data for uniform emery particles for both the dispersed and flocculated states, Hawksley (8) found $\zeta = 0.71$ for the flocculated state, which is considered satisfactory agreement with the theoretical value, $\frac{2}{3}$.

APPLICATION TO HARDENED PASTE

Hardened paste, composed of hydrated portland cement, is a porous solid and not an aggregation of discrete particles. Nevertheless, it is composed of particles, and the connections between particles apparently involve but a small fraction of the total surface of each particle. Therefore, to treat the material as an aggregation of discrete particles involves no conceptual difficulty. The particles in hard paste are exceedingly small, but smallness per se would not seem to preclude application of the theory as long as the particles are large relative to water molecules. A major difficulty does arise, however, from extreme smallness of interparticle spaces. Because of this, most of the fluid is in the force-field of the solid particles; that is, much of the water is adsorbed, as previously noted. Moreover, the force-field contains hydrated ions. The net effect is that the viscosity of the fluid cannot be treated as a constant at a given temperature; it is a function of the dimensions of interparticle space, and of the kinds and amounts of dissolved materials.

Adsorption forces probably cause the pattern of flow to be different from laminar flow in a uniform field. Nevertheless, experiment shows that for any given specimen of paste, the rate of flow is proportional to the pressure gradient (see Figs. 1 to 4). Therefore, in a given specimen, the coefficient of viscosity indicates the average rate of shear under unit stress. In other words, a coefficient of viscosity found in a given specimen of paste has the same significance that it ordinarily has. It differs from the ordinary coefficient in that it is not a property of the fluid alone.

Because some of the water in saturated hydrated cement paste, perhaps all of it, is subject to adsorption forces, viscosity should vary from point to point in the specimen,

and because the effects of adsorption are various, the average viscosity could be a function of the concentration of particles. Accordingly, $\eta(\theta)$ in Eq. 13 should be replaced by $\eta(\theta)\eta(c)$, the function $\eta(c)$ being a factor by which the normal viscosity is multiplied to obtain the actual average viscosity in the specimen. Making this substitution and taking logarithms

$$\ln K_1 = \ln B + \ln \frac{(1-c)^2}{c} - \ln\eta(\theta) -$$

$$\ln\eta(c) - \phi(c) \qquad (14)$$

in which

$$B = \frac{\zeta(c)\rho_f g d_S^2}{18}$$

$$= \frac{\rho_f g d_S^2}{27} \text{ for a granular solid}$$

$$(\zeta = \tfrac{2}{3}).$$

Empirical Relationship

Differentiation of Eq. 14 with respect to the reciprocal of temperature gives

$$\frac{d\ln K_1}{d\frac{1}{T}} = -\left[\frac{d\ln\eta(\theta)}{d\frac{1}{T}} + \frac{d\ln\eta(c)}{d\frac{1}{T}}\right] \qquad (15)$$

Figure 5. Permeability as a function of temperature: T = absolute temperature; K = permeability coefficient, in cm per sec; and $-$ slope $= 896 + 647 \left(\frac{c}{1-c}\right)$.

According to the theory of Eyring (12), this derivative of viscosity is a measure of the activation energy for flow. The first of the two derivatives in brackets would be the normal activation energy of the fluid; the second, the added activation energy required when the fluid is adsorbed. For non-associated liquids, activation energy, hence the first derivative on the right side, would be constant for a considerable range of temperature. However, for water it varies about 10 percent from the average for the range 0 to 30 C. The empirical plots in Figure 5 show, however, that it is nearly constant for water in paste; the variation of the derivative representing the effect of adsorption is apparently equal and opposite to the variation of that for free water over the temperature interval of these experiments. It is assumed, however, that the derivative of the part due to adsorption is a constant at a given particle concentration.

The effect of particle concentration on activation energy should depend on average distance between solid surfaces; here it is assumed to be proportional to the inverse of hydraulic radius, which is proportional to $\frac{c}{1-c}$. Thus,

$$\frac{d\ln\eta(c)}{d\frac{1}{T}} = a\left(\frac{c}{1-c}\right) \qquad (16)$$

in which a is an empirical constant. Integrated, this gives

$$\ln\eta(c) = \frac{a}{T}\left(\frac{c}{1-c}\right) + \text{constant} \qquad (17)$$

Since $\lim_{c\to 0} \eta(c) = 1.0$, the constant of integration is 0.

If it is assumed that $\phi(c)$ of Eq. 14 is proportional to the inverse of hydraulic radius, and is independent of temperature,
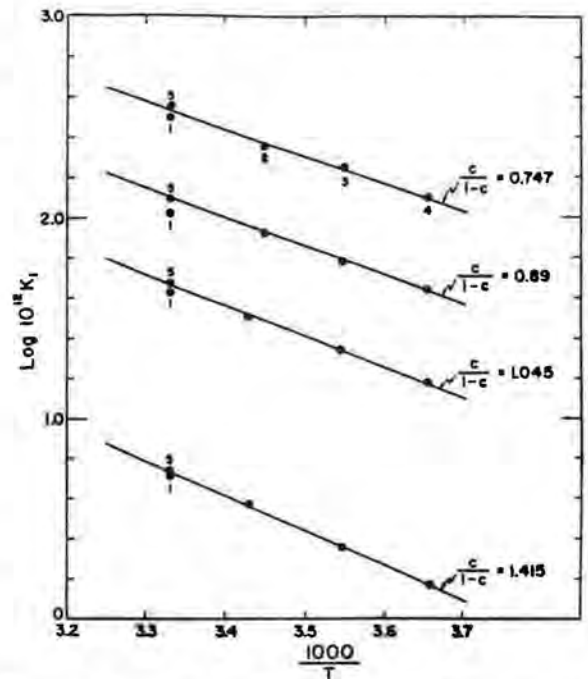
$$\phi(c) = \gamma\left(\frac{c}{1-c}\right) \qquad (18)$$

with γ being an empirical constant.

Substituting from Eqs. 17 and 18 into Eq. 14·gives

$$\ln \frac{K_1 c}{(1-c)^2} = \ln B - \ln \eta(\theta) - \left(\frac{a}{T} + \gamma\right) \frac{c}{1-c} \qquad (19)$$

This semi-empirical equation indicates that for data obtained at a given temperature, experimental values of the member on the left plotted against $\frac{c}{1-c}$ should produce straight lines, one for each temperature. Trial plots of the data in Table 1 (not reproduced here) show that the points conform very well to the expected relationship.

Fit of Data

The fit of the data in Table 1 to Eq. 19 was determined by the method of least squares. The first item of each group of four was omitted from calculations because of the following considerations:

TABLE 2
COMPARISON OF OBSERVED VALUES OF K_1 AND VALUES CALCULATED FROM EQ. 20

$B = 1.36 \times 10^{-10}$, $a = 1242$ and $\gamma = 0.7$

Temperature (deg C)	$10^{13} K_1$ Observed	$10^{13} K_1$ Calculated	Observed Minus Calculated
Specimen 13$_b$ - B			
18.54	3.75	3.43	0.32
8.92	2.28	2.16	0.12
0.20	1.48	1.35	0.13
26.97	5.55	4.95	0.60
Specimen 14$_a$ - A			
18.54	32.2	34.4	-2.2
8.92	21.9	22.8	-0.9
0.20	15.1	15.0	0.1
26.97	48.2	47.4	0.8
Specimen 20$_a$ - C			
16.67	85.1	87.7	-2.6
8.70	60.8	63.3	-2.5
0.52	44.2	43.5	0.7
26.87	121.0	126.9	-5.8
Specimen 28$_b$ - C			
16.67	230.0	229.0	1
8.70	178.0	168.0	10
0.52	127.0	118.0	9
26.87	361.0	324.0	37

The five points of each set were obtained in the sequence indicated in the first column. The first flow rate was established at 27 C, the second, third, and fourth at successively lower temperatures, and the fifth at the original temperature. The first test at 27 C gave a lower value of K_1 than did the last. This change was probably caused by loss of alkali from the specimen during the first test. The indications are that there was little or no further loss of alkali during the four subsequent tests. From the other 16 values, the least square calculation, done by electronic computer, gave the following values and standard deviations:

$$B = (1.36 \pm 0.1) \, 10^{-10}$$

$$a = 1242 \pm 133$$

$$\gamma = 0.7 \pm 0.5$$

Using these values the following empirical equation for the coefficient of permeability of the specimens represented in Table 1 is obtained:

$$K_1 = \frac{1.36 \times 10^{-10}}{\eta(\theta)} \frac{(1-c)^2}{c} \exp - \left[\left(\frac{1242}{T} + 0.7\right) \frac{c}{1-c}\right] \qquad (20)$$

Values of K_1 computed from Eq. 20 are compared with observed values in Table 2.

INDICATED PARTICLE SIZE

One object of this investigation was to determine what size of particle would be indicated by measurement of fluid flow, and to compare the result with indications from other kinds of measurement. Along with size there is also shape of particle to be considered. Studies by Åke Grudemo [1] during 1957 showed, by means of electron microscopy, that the particles in hardened paste have various shapes. The calcium silicate hydrates are (a) ribbon-like fibers, somewhat rolled up edgewise, and (b) sheets or foils aggregated as fluffy masses. The calcium aluminate hydrate and the calciumaluminoferrite hydrates occur as flat plates individually surrounded by calcium silicate hydrate. Something of size and shape can be expressed in terms of appropriate "equi-

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[1] During 1957, Åke Grudemo, of the Swedish Cement and Concrete Institute, was a guest scientist in the Portland Cement Association Laboratories, Skokie, Ill. His work is to be published.

valent spheres" and a "sphericity factor." Hawksley (6) summarizes the following hypothetical sphere diameters, three of which were previously defined:

δ = volume diameter: diameter of sphere having the same volume as the particle.

d_d = drag diameter: diameter of sphere having the same viscous drag as the particle in a fluid of the same viscosity and same velocity.

Δ = surface diameter: diameter of sphere having the same external surface area as the particle.

d_s = Stokes diameter: diameter of sphere having the same density and same free-falling speed as the particle in a given fluid.

d = specific-surface diameter: diameter of a sphere having the same ratio of external surface area to volume as the particle.

ϕ = sphericity factor: the ratio of surface area of a sphere having the same volume as the particle to the actual surface area of the particle.

$$d = \phi \delta \tag{21}$$

$$d = \phi^{3/4} d_s \tag{22}$$

$$d_s^2 = \frac{\delta}{\Delta} \tag{23}$$

$$\Delta = \frac{\delta}{\phi^{1/2}} \tag{24}$$

Owing to the smallness of interparticle spaces and to the force field within such spaces, streamlining of irregular particles probably does not occur. Viscous drag would seem to depend, therefore, on the extent of surface presented by the solid phase, and the average interparticle distance. The shape of the "typical particle" is probably not important in that respect. Accordingly, it is possible to identify the drag diameter with the surface diameter under the conditions of flow presumed, and thus, with reference to the relationship shown after Eq. 3:

$$\frac{\delta^3}{d_d} = \frac{\delta^3}{\Delta}$$

From Eq. 24

$$\frac{\delta^3}{\Delta} = \phi^{1/2} \delta^2$$

The definition of B given with Eq. 14 thus becomes

$$B = \frac{\rho g \phi^{1/2} \delta^2}{27}$$

where

$\rho_f = 1.0$ (assumed) and $g = 980$ cm per sec per sec.

Using the value of B given above,

$$\phi^{1/2} \delta^2 = \frac{1.36 \times 10^{-10}}{36.3} = 3.75 \times 10^{-12}$$

$$\phi^{1/4} \delta = 194 \text{Å}$$

From definitions previously given, the specific-surface diameter is $\phi \delta$. Hence, to evaluate ϕ the specific-surface diameter is needed.

Specific-Surface Diameter

In 1947, Powers and Brownyard (15) gave the specific-surface diameter of the particles in hardened cement paste as 140Å. This value has been revised downward because of the following considerations:

According to the BET theory,

$$\sigma = a \frac{N}{M} \frac{V_m}{c} \qquad (26)$$

in which

σ = specific surface area by BET method, in cm^{-1};

N = Avagadro's number, 6.023×10^{23};

M = molecular weight of water, 18 g per mol;

V_m = water required to cover the surface with a monomolecular layer, g; and

a = area covered by 1 molecule, in sq cm.

Powers and Brownyard let $a = 10.6 \text{ Å}^2$ per molecule, and their equation was

$$\sigma = (35.7 \times 10^6) \frac{V_m}{c} \qquad (27)$$

More recently, Brunauer (16) showed that $a = 11.4 \text{ Å}^2$ is a better value for these systems than is 10.6. On this basis the numerical coefficient becomes 38.5×10^6, which gives a specific-surface diameter about 7 percent smaller than that given by the first coefficient.

As described by Copeland and Hayes (14) in 1953, the method of drying samples of paste preparatory to adsorption measurement has been changed since the work reported by Powers and Brownyard was done, so that the non-evaporable water content is about 8 percent less than it was when determined by the original method. This change also increased V_m by about 13 percent; therefore, a present-day estimate of specific surface diameter from V_m would be further reduced. (There is reason to believe that the present method of drying gives more nearly the desired result than did the old.) A given sample treated by the 1953 method would give a higher value of σ than it would by the 1947 method, as follows:

$$\frac{\sigma_{53}}{\sigma_{47}} = \frac{38.5}{35.7} \times 1.13 = \frac{d_{47}}{d_{53}}$$

Hence if $d_{47} = 140 \text{ Å}$, $d = 114 \text{ Å}$.

This is a partial correction of the 1947 estimate. A further correction is based on the amount of unhydrated cement in the sample. The "typical paste" for which Powers and Brownyard calculated $d = 140 \text{ Å}$ probably contained about 5 percent of unhydrated cement in the form of relatively large particles of clinker. Therefore, the estimate, revised not only for new value of a and new method of drying (new value of V_m), but also for unhydrated cement, would be

$$d = 114 \times 0.95 = 108 \text{ Å}$$

which is the final corrected value corresponding to the original 140 Å.

For the specimens represented in Table 1, determinations of V_m were made by the 1953 method. The samples contained no unhydrated cement, and the cement was chemically the same as that to which the Powers and Brownyard value pertained. Therefore, the values obtained are directly comparable with the corrected Powers and Brownyard value. The results are given in Table 3.

These data indicate that

$$\sigma = (38.5 \times 10^6) \, 0.143 = 5.5 \times 10^6 \text{ cm}^{-1}$$

and

$$d = \frac{6}{\sigma} = 109 \text{ Å}$$

which is in good agreement with the corrected value of Powers and Brownyard.

Data in Table 3 show that the value of $\frac{V_m}{c}$, and hence of the specific surface of the solids, is the same in each of the four specimens regardless of differences in

TABLE 3

WATER VAPOR ADSORPTION

Ref. No.	$\frac{c}{1-c}$	$\frac{V_m}{c}$
13b - B	1.415	0.144
14a - A	1.045	0.143
20a - C	0.890	0.141
28b - C	0.748	0.143
Average		0.143

density. This means that the specific surface of the hydration products is independent of the original water/cement ratio of the paste. Various other data not given here support this indication that the hydration product of a given cement, hydrated at standard temperature, has a characteristic specific surface. Other data show that specific surface varies with chemical composition of the cement, but the variation is small.

Sphericity Factor

If it is assumed that values of d and $\phi^{1/4} \delta$ obtained in the foregoing pertain to the same particles, the value of ϕ can be computed. Since $d = \phi \delta$ (by definition) and $\phi^{1/4} \delta = 194$ Å (by experiment), it follows that $\phi^{3/4} = 109/194 = 0.56$, and $\phi = 0.46$. This value for sphericity factor may be compared with values in Table 4, cited by Hawksley (6).

The value $\phi = 0.46$ may be considered a first approximation. A second approximation may be obtained by considering the effect of calcium hydroxide crystals. Besides gel, the specimens contained crystalline calcium hydroxide, the crystals being much larger than gel particles and thus having a relatively low specific surface. Studies of related systems by Brunauer (17) indicate that the specific surface is not greater than 0.5×10^6 cm^{-1}. If is is assumed that σ_g = specific surface of gel particles, n_1 = their volume, and n_2 = the volume of calcium hydroxide,

$$\frac{n_1 \sigma_g + n(0.5 \times 10^6)}{n_1 + n_2} = \sigma = 5.5 \times 10^6$$

The weight of total solids in these specimens was about 1.234 g per g of original cement in the specimen, and the weight of calcium hydroxide was about 0.163 grams. Hence,

$$n_1 + n_2 = \frac{1.234W}{\rho_S}$$

$$n_1 = \frac{1.071W}{\rho_1}$$

$$n_2 = \frac{0.163W}{\rho_2}$$

in which

W = original weight of cement in the specimen; and
ρ_S, ρ_1, ρ_2 = density of total solids, gel, and calcium hydroxide, respectively.

For the present purpose, it will suffice to assume that $\rho_1 = \rho_2 = \rho_S$, which is not far from the truth. Then

$$\frac{n_1}{n_1 + n_2} = \frac{1.071}{1.234} = 0.868$$

$$\frac{n_2}{n_1 + n_2} = \frac{0.163}{1.234} = 0.132$$

$$\sigma_g = \frac{5.5 \times 10^6 - 0.666 \times 10^6}{0.868} = 6.26 \times 10^6,$$

say $\sigma_g = 6.3 \times 10^6$ cm^{-1}. This gives a revised specific-surface diameter of d = 95 Å.

It is now necessary to calculate a corresponding correction to the particle size indicated by the permeability measurement. Because crystals of calcium hydroxide are much larger than gel particles, they may be thought of as impermeable bodies embedded

TABLE 4

SPHERICITY FACTORS FOR VARIOUS PARTICLES

Kind of Particle	ϕ
Sphere	1.0 [a]
Portland cement	0.7 to 0.8
Emery	0.68 to 0.72
Ground glass	0.71 to 0.82
Fusain fibers	0.38
Mica flakes	0.28

[a] By definition.

in gel, reducing the fractional area through which flow may occur. If for the present purpose gel is defined as the porous substance occupying space not occupied by calcium hydroxide crystals, it follows that for a given gel (so defined) the coefficient of permeability is proportional to the gel content. In a hypothetical specimen containing no crystals of calcium hydroxide, the gel content is unity. In a real specimen the coefficient is smaller; that is,

$$\frac{K_g}{K_1} = \frac{1}{1 - \left(\frac{n_2}{n_1 + n_2}\right)c} = \frac{1}{1 - 0.132\,c}$$

where K_g is the coefficient of permeability of pure gel. It is apparent that the magnitude of the correction depends on c and is therefore different for each specimen. It will suffice to use the average c for the four specimens, which is 0.50. This value gives

$$K_g = 1.07\,K_1$$

Referring now to B as defined by Eqs. 14 and 15, B_g will be considered that parameter for pure gel. Then, with c constant,

$$\frac{K_g}{K_1} = \frac{B_g}{B} = \frac{\phi^{1/2}\delta_g^2}{\psi^{1/2}S^2} = 1.07$$

hence $\phi^{3/4} = \frac{95}{201} = 0.47$ and $\phi = 0.36$.

Indicated Size and Shape

On the basis of these values arrived, the "typical particle" in hydrated cement paste may be described as follows:

	First Approximation	Second Approximation
Sphericity factor, ϕ	0.46	0.36
Spec. surf. dia., d	109Å	95Å
Volume diameter, ϕ	237	264
Surface diameter, Δ	350	440
Stokes diameter, d_S	195	205

These values and Grudemo's electron-micrographs agree in that each indicates the particles in cement gel to be not spherical. From the electron-micrographs already mentioned, and electron diffraction patterns, it appears that paste is composed mostly of ribbon-like fibers, plates, and crumpled sheets, the substance being mostly amorphous or poorly crystallized. A value for specific surface estimated from measurements of micrographs indicates (but does not prove) that these are the very particles that adsorb water vapor.

The foregoing values rest on the assumption that water-vapor adsorption measures the same surfaces that are presented to flowing water. To test this assumption let it now be assumed that the particles are layered structures such that water vapor can penetrate and measure two "inside" surfaces for every two outside surfaces (edge areas can be neglected). If it is assumed that the outside surfaces are accessible to flowing water whereas the inside surfaces are not, the specific-surface diameter, d, of the particles as felt by flowing water is one-half that indicated by adsorption. On this basis the calculation of ϕ would be, using the second approximation of d,

$$\phi^{3/4} = \frac{2 \times 95}{194} = 0.98; \quad \phi = 0.97$$

This result indicates that the particles felt by flowing water are spheres, which is known to be false.

Let it now be assumed that interlayer water can measure only one internal surface;

that is, that only one layer of water molecules can be accommodated in the crystal lattice. In this case the specific surface of the particles felt by flowing water would be two-thirds that indicated by adsorption. The indicated sphericity factor would be

$$\phi^{3/4} = \frac{1.5 \times 95}{194} = 0.73; \quad \phi = 0.66$$

According to Table 4, such a sphericity factor is typical of shapes found in crushed brittle materials. This result also is contrary to evidence from electron-micrographs.

Alternatively, it could be assumed that water vapor measures only the outer surfaces of gel particles, and that the particles felt by flowing water are aggregations of those gel particles. This would mean approximately that the "permeability particle" is some multiple of the "adsorption particle." Any such assumption leads to sphericity factors exceeding unity if the number of particles per aggregation exceeds 2, and the result is therefore useless.

Thus, it seems that the original calculation, based on the assumption that adsorption measures the same particles that produce drag in the permeability test, is the only one that gives an acceptable result. Possibly, a paste contains some crystals so well developed as to admit interlayer adsorption, and possibly water could not flow through such crystals. However, these data indicate that if such crystals exist, and if they do exclude flowing water, they constitute a minor faction of the solids in the paste. If is seems absurd to suggest the possibility of flow through a crystal, it should be recalled that the flow under consideration is exceedingly slow, as shown in Figure 1. A typical average rate is 20×10^{-9} cm per sec, which is about $\frac{1}{4}$ in. per year. Since viscosity is not uniform, flow in some portions of the structure may be several orders of magnitude slower than the average rate. There seems to be no reason to suppose that physically adsorbed molecules would be immobile under a hydrostatic pressure gradient, whatever their situation might be.

GENERAL REMARKS

These data indicate that all the evaporable water (as defined by Copeland and Hayes (14)) is mobile under a hydrostatic pressure gradient, although some of it has high viscosity. If this is so, none of the evaporable water has a finite yield point under stress. Any change of stress in a concrete member, however small that change may be, should start a redistribution of evaporable water in the member, and such redistribution should be accompanied by shrinkage where the water content diminishes and swelling where it increases. This has long been recognized as a factor characterizing creep of concrete under sustained stress. It may be inferred that as far as this aspect of creep is concerned "seepage," the threshold stress for creep of concrete members, is zero, as indeed it seems to be in some experiments.

Of the two kinds of pores in hardened paste, gel pores and capillaries, the capillaries are continuous in some specimens, but not continuous in others. When they are not continuous, they are called capillary cavities, and are interconnected only by gel pores. Absence of continuous capillaries in the specimens used for this study is implied by the conclusion that adsorption measures the same surface area as that presented to flowing water. This conclusion is strengthened by data from other specimens not presented here showing unmistakable evidence of continuous capillaries in those specimens. This subject is to be dealt with in a separate paper.

If the volume diameter of a gel particle is about 260Å, as indicated by these data, the corresponding number of particles per unit volume of gel can be computed. The solid content of a unit volume of gel (exclusive of capillary cavities) is about 0.65. Hence, the quotient of 0.65 and volume per particle is the desired number. The volume per particle turns out to be 9×10^{-18} cc, or 0.6×10^{-18} cu in. Hence, the number of particles is about 7×10^{16} per cc, or 10^{18} per cu in. of gel.

A major component of the gel is probably a tricalcium disilicate trihydrate having a volume of about 140 cc per gram-molecular weight (16). This corresponds to about 2.3×10^{-22} cc per molecule. A gel particle having a volume of 9×10^{-18} cc would thus contain about 40,000 molecules. This indicates the degree to which the water-solid

relationship in cement gel approaches (and misses) that of a homogeneous solid solution.

CONCLUSIONS

1. The flow of water through a given specimen of hydrated cement paste complies with Darcy's law, but it is liable to be complicated by effects of osmotic pressure.

2. Within the range of paste porosity included in this report, part of the evaporable water, perhaps all of it, is adsorbed. Consequently, viscosity is higher than that of free water. (Also, viscosity is increased by the presence of solutes.)

3. Average viscosity of water in hydrated cement paste is a function of gel-particle concentration and temperature.

4. Temperature dependence of rate of flow in paste indicates a relatively high activation energy for flow, reflecting the effect of adsorption.

5. The theory of permeability based on the concept of viscous drag on particles as developed by Steinour, but modified to allow for variable viscosity, and modified by considerations advanced by Hawksley, gives a good fit to these data.

6. The particle size and shape indicated by permeability data, combined with adsorption data, are as follows: (second approximation) sphericity factor, 0.36; volume diameter, 264Å; surface diameter, 440Å; Stokes diameter, 205Å; specific surface diameter, 95Å. These data are compatible with electron-micrographs.

7. The sphericity factor obtained by combining permeability data with adsorption data indicate the particles to be sheets, or fibers, or both, in agreement with electron-micrographs.

8. All the evaporable water appears to be mobile.

9. The particles giving rise to viscous drag in the permeability test are apparently the same particles, which, when dry, adsorb water vapor.

10. In the specimens studied, there apparently were no continuous capillaries bypassing clusters of gel particles.

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

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● 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
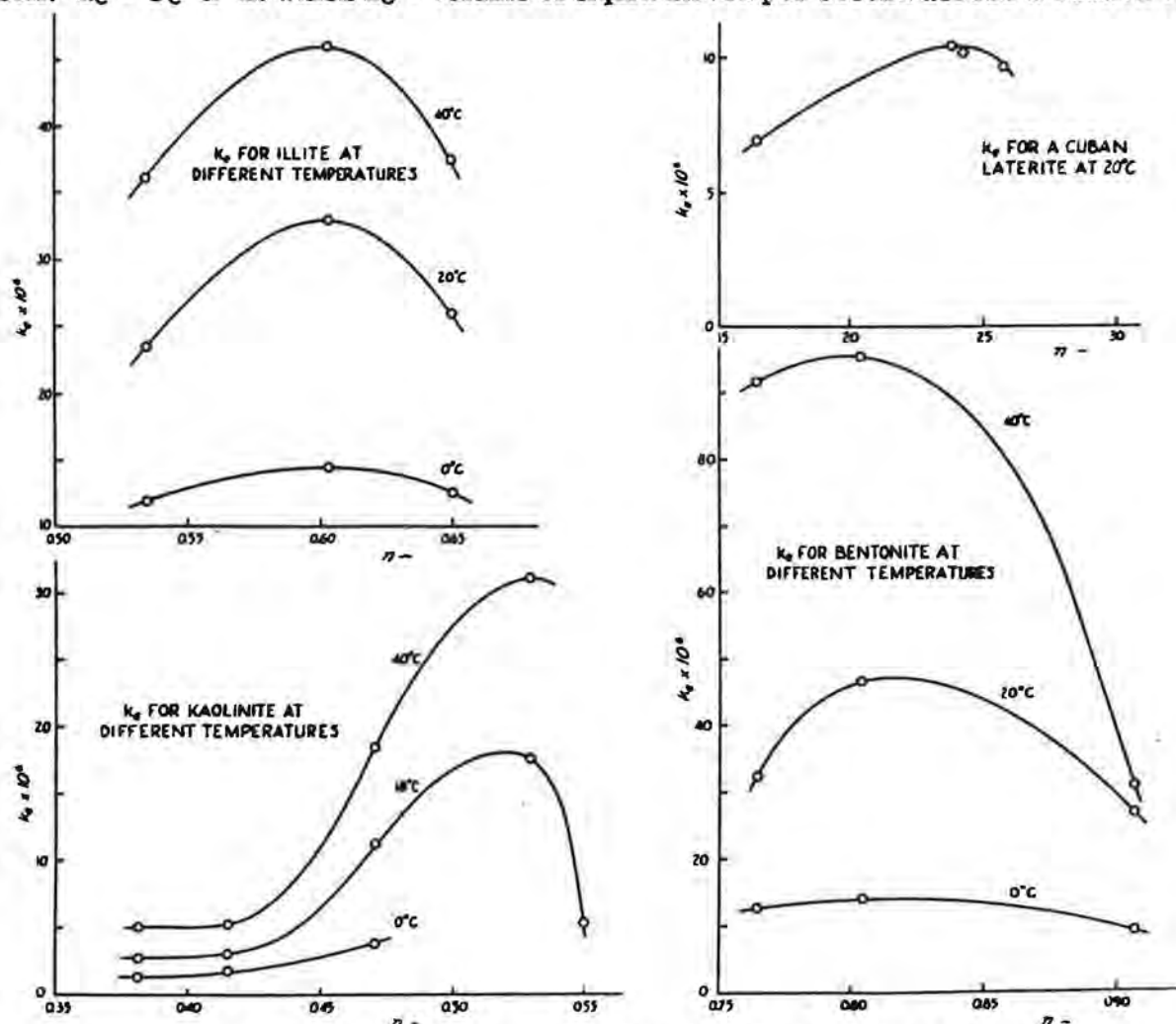

Figure 1. Electroosmotic transmission constants as functions of porosity.

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).
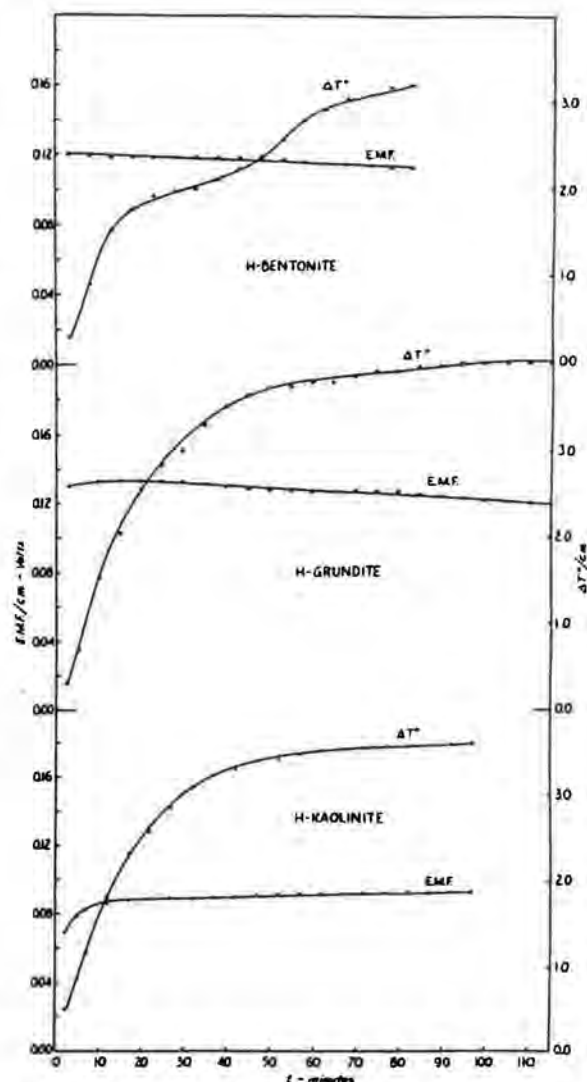

Figure 2. E.M.F. and temperature gradients developed in thermoosmosis experiments with clay minerals.

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 obstable 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).

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