

HIGHWAY RESEARCH BOARD

Bulletin 287

*Discussions on Water and
Its Conduction in Soils*

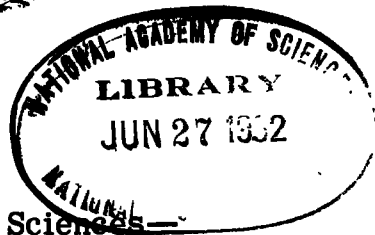
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***Discussions on Water and
Its Conduction in Soils***

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ACKNOWLEDGMENTS

The Chairman of the Highway Research Board Committee on Physico-Chemical Phenomena in Soils is sincerely grateful for the excellent cooperation given him by everyone concerned in the organization, presentation, and publishing of this Conference on Water and Its Conduction in Soils.

Thanks are due, first of all, to those who contributed the papers, reviews and discussions contained in this volume and to their respective institutions for permitting and aiding these efforts. Sincere appreciation is expressed to the Director and Staff of the Highway Research Board for their great interest and effective help in making this conference and its proceedings a reality and a success. The difficult and tedious job of reducing the sound record of the oral discussions of the conference to the printed word was started at the offices of the Highway Research Board, which produced the first rough transcript. This was checked against the sound track, and corrected where necessary, by Hans F. Winterkorn III. The corrected versions were then submitted to the original discussors for final checking and approval.

As in previous undertakings of this kind for the Highway Research Board, generous assistance was given by the Chairman of the Department of Civil Engineering and the Dean of the School of Engineering of Princeton University.

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

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Introductory Remarks

HANS F. WINTERKORN, Chairman, Committee on Physico-Chemical Phenomena in Soils, Princeton University

BECAUSE of the great impact made and interest created throughout the world by the International Symposium on Water and Its Conduction in Soils, presented at the 37th Annual Meeting of the Highway Research Board and published as Special Report 40, it was decided to have a follow-up session during the January 1960 Meetings of the Board. The stated purpose of this session was to study, digest, criticize, supplement, evaluate and, possibly, simplify for engineering use the information contained in the printed symposium volume. Invitations to participate in this endeavor were sent to contributors of papers to the International Symposium, members of the Committee on Physico-Chemical Phenomena in Soils, and other interested scientists and engineers in all parts of the globe. In order to facilitate contributions from non-English language areas, potential contributors were informed that papers and comments would be acceptable if written in French, German, Italian, Portuguese, or Spanish and that these would be translated into English by the Chairman.

The authors of papers for the original symposium were thus given a chance to supplement their papers, if new advances had been made since they were written, and were also invited to discuss other papers in the symposium.

Every interested and qualified scientist and engineer whose name was brought to the attention of the Chairman was invited to present supplemental information or constructive criticism and to point out especially interesting scientific aspects and practical applications.

The general discussion will be preceded by reports from the chairmen and members of three subcommittees established to digest and evaluate groups of symposium papers, additional reviews by committee members, supplementary statements by authors of symposium papers, and additional pertinent contributions.

Discussion and Review of Symposium Papers

This discussion contains reports from the chairmen and members of three subcommittees established to digest and evaluate groups of symposium papers, and from three additional members.

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In order that the maximum benefit might be derived from the papers published in Special Report 40 of the Highway Research Board, the Committee on Physico-Chemical Properties of Soils decided a special effort should be made to review all the papers and add any recent relevant research findings. The papers assigned to the discussor by Dr. Winterkorn were by Fukuda (1), Hutcheon (2), Czeratzki and Frese (3), Barbe (4), Croney et al (5) and Guinee (6).

Because the papers deal with related material, the writer has chosen to discuss them by subject matter to avoid repetition. Papers that contain a broad range of material may therefore be discussed under several different headings; others with a limited scope will be referred to in only one part of this review.

In reviewing these papers, no attempt has been made to cover all the material; further, the assumption is made that the reader is at least partially familiar with the subject matter in the original papers. Emphasis has been placed on those parts where new information has become available, either from the literature or through the research work of the National Research Council of Canada.

MOISTURE MOVEMENT

Thermally Activated Diffusion in Porous Media

Hutcheon's experimental findings on thermally activated diffusion in soil support the results of other research workers, particularly with regard to the observed rate of moisture flow. Bouyoucos (7), Winterkorn (8), and Taylor and Cavazza (9), among others, have reported the maximum experimental flow rate under temperature gradient to be from six to ten times the calculated rate based on vapor diffusion. Recently Woodside and Kuzmak (10) and Philip and DeVries (11) have independently reported an explanation for this anomaly. There is still disagreement, however, with regard to magnitude.

The experimental work by Woodside and Kuzmak involved measuring the temperature on the surface of spheres stacked in an open-pack arrangement, in a field of constant heat flow. The average temperature gradient across the pore was found to be six times the over-all temperature gradient, resulting in a vapor pressure gradient much greater than the one normally calculated. Philip and DeVries (11), using another approach, calculated the average temperature gradient across the pore to be twice the over-all gradient. It is also pointed out in these papers that in series (and perhaps also in parallel) with the vapor-filled pores are segments of liquid water which permit rapid moisture transfer. This fact, together with the steeper vapor pressure gradients, would appear to account for the accelerated flow rate normally observed.

Hutcheon (2) points out that the nonlinear temperature/vapor pressure relationship gives rise to a kind of surging flow and causes waves of higher moisture content through the material. He also accounts for the small net transfer of vapor in relatively dry soils (drier than the permanent wilting point). Here only a small change in moisture content brings about a disproportionate change in vapor pressure.

Hutcheon (2) shows, as did Croney et al (5) and Fukuda (1), that the direct temperature effect on the surface tension is small and does not account for the increased tra

er of moisture normally observed under temperature gradients. It is now generally believed that thermally activated diffusion results from a potential created by a temperature gradient across the vapor phase. This gives rise to vapor flow in the direction of decreasing vapor pressure gradients and may be combined with series flow in the liquid phase. In an open system the net flow is in the direction of decreasing vapor pressure gradients.

In closed systems, at relatively high moisture contents (3/10 atm), a dynamic equilibrium moisture content distribution condition can be reached, which is dynamic in the sense that vapor phase flow is from warm to cold and flow in the liquid phase is from the cold to the warm side. Salt added to such a system can accumulate at the hot end, as was shown by Gurr et al. (12).

Isothermal Flow in Porous Media

Moisture suction arises from the attraction between water molecules and the solid. At low moisture contents, the water may be held as a film on the solid surface. As saturation is approached, pores are filled in a manner similar to the rise of water in a capillary tube.

The technique of measuring suction or tension in the water is of great importance both for research and in practice. Fukuda (1) has theoretically analyzed the Richards pressure plate method of measuring suction and the influence of relative humidity external to the apparatus on the measured moisture-content/suction relationship. He concludes that, with the technique normally used, both relative humidity outside the chamber and the temperature are of limited importance.

Predicting the moisture content changes that occur when the soil is covered and evaporation is interfered with is of great interest for highway and airport construction. The British Road Research Institute has reported some measure of success, provided the surface covering was impermeable and semi-infinite in size. For the isothermal case, according to Cronney et al (5), the depth of the water table alone determines the ultimate pore water distribution. The moisture content distribution is calculated from the following equation:

$$u = s + \alpha P \quad (1)$$

in which

- u = pore water pressure when sample is loaded
- s = suction pressure with no loading
- P = overburden pressure
- α = compressibility factor

provided the water content as a function of s and the compressibility factor α are known.

This relationship has also been used to calculate moisture content distribution under grass cover and under bare soil from moisture tension values, measured as a function of depth. Variations in soil type with depth necessitated the use of several compressibility factors and moisture-content/suction relationships. Moisture contents calculated this way were compared with moisture contents determined by boring and sampling. Good agreement was obtained and this was taken as further substantiation of Eq. 1. Undoubtedly, this concept of predicting moisture contents has much merit. It is believed by Cronney and his co-workers that, together, suction and shrinkage results provide a valuable analytical method for estimating heave of structures resulting from either moisture changes when the surfaces are covered or a changed water table level. In the opinion of the writer this view warrants further consideration.

Guinnee (6) was concerned with determining moisture content changes and the source of the water in the soil under roads subsequent to construction. There is an obvious contrast between the approach used in the study by Guinnee and that of Cronney et al (5) previously discussed. Throughout the various investigations reported by Guinnee, the emphasis appears to have been on determining the path of surface runoff water and its point of entry in the roadway. Certainly, in some of the work reported, the main entry appears to have been past the edges of the pavement. The writer finds it difficult, however, to draw any general conclusions from the various studies reported; in fact Guinnee himself draws no conclusions but leaves this to the reader.



Figure 1. Uneven settlement of sidewalk caused by removal of soil moisture by large trees.



Figure 2. Ice lenses in marine clay.

(15) or Hardy (16). Ice crystallization rates have recently been determined on various molecular weight fractions of calcium lignosulfonate. A preliminary review of the results shows all fractions are probably about equally effective in reducing the ice crystallization rate in solution.

Further detailed research now nearing completion is concerned with the factors influencing rate of frost heaving. These investigations show a strong positive relationship between heaving rate and heat flow. This is also true for heaving rate and frost penetration rate.

Ground Movements

Barber's paper on ground movements (4) brings out many useful facts on the effect of water movement on soil for the practicing engineer. Currently under investigation at the Division of Building Research are ground settlements due to desiccation by trees and subsequent damage to buildings (17). In Ottawa, settlements of $1\frac{1}{2}$ in. due to shrinkage have been measured 20 ft from trees during a dry summer. Unfortunately, although some reswelling occurs in subsequent wet periods, a net settlement usually results. Artificial rewatering is sometimes partially successful. Figure 1 shows a picture of ground settlements around elm trees on an Ottawa street in a residential area

Frost-induced moisture flow is discussed here under isothermal flow, recognizing that some vapor movement frequently, but not necessarily, accompanies the process. Hutcheon (2) concludes that "frost induced pressure gradients within the liquid phase will not cause any appreciable flow of water when soil moisture conditions are dryer than those characteristic of moisture tensions in the vicinity of one atmosphere." Based on the work of the Division of Building Research, the limiting pF beneath the frost line is determined by the type of soil and density. However, in such freezing experiments the ice phase must be accommodated. In Hutcheon's experiments, no provision was made for frost heaving. This would presumably result in positive pressures being developed within the soil-ice system. Positive pressures on the soil-ice system have the same effect as moisture suctions in the liquid phase of the unfrozen layer, that is, an increase in either one will bring about a reduction in the maximum of the other (13).

Subsequent to the frost action research reported in 1958 by the Division of Building Research (13), the rate of ice crystallization has been studied in calcium lignosulfonate solutions as a means of investigating the retarding action it has on ice segregation in soils (14). Calcium lignosulfonate solutions, like some other organic solutions, cause a large reduction in ice crystallization rate depending both on concentration and on the degree of supercooling. This is an additional rather than an alternative mechanism to explain the reduction in frost heaving in soils treated with calcium lignosulfonate to those mentioned by Lam

These trees, 45 to 60 ft high, are growing on marine clay. It is thought that safe distances between structures and trees can be worked out for this soil. The distances will depend largely on the height and kind of tree and foundation depth.

The effect of rate of loading influences the amount of consolidation in a consolidation test, according to Barber. This general problem was studied by the Division in some detail with a view to a more accurate evaluation of the preconsolidation load (18). Contrary to the results reported by Barber, at least for the Ottawa marine clay, the size of the load increment had practically no effect on the shape of the pressure void ratio curve when the load application was continued to the same degree of secondary consolidation. Further, when loading was carried out at a constant rate of strain, the greater rates gave a slightly higher indicated preconsolidation pressure. This tended to shift the virgin compression of the curve over to the right. For these and other reasons, the generalizations by Barber (4), though they may be correct for some soils, should be viewed with caution.

The problem of avoiding frost heaving under cold storage structures is also briefly mentioned by Barber. Some general design considerations have recently been published by the Division of Building Research (15). This followed experience with a cold storage plant that had heaved more than 1 ft in the center of the building to the point where it was unserviceable. The structure was reclaimed by supplying warm air through an existing duct tile system under the building and thawing the frozen soil (20). The soil had been frozen to a depth of 9 ft. Equilibrium resettlement was obtained in about six months.

Soil Structures and Frost Action

The macro-structures developed in soils under freezing conditions are extremely well shown in the paper by Czeratzki and Frese (3). Comparing the structures developed and the disposition of the ice for different soils, the authors might well have included the contrasting ice lens formation in coarse-grained soils. In these soils the ice lenses are more flat and uniformly perpendicular to the direction of over-all heat flow.

Czeratzki and Frese show the vertical and horizontal ice forms as belonging to clay soils and the curved ice forms to loess soils. Ice lenses grown in marine clay containing 64 percent clay size and 36 percent silt show both forms possible in one specimen (Fig. 2). The sample was frozen at its natural moisture content of 60 percent. Water was also supplied at the bottom of the specimen. The "nutty" soil structure at the top is thought to result when water for the ice phase is available in the immediate vicinity of the freezing front involving a volumetric shrinkage of the soil. When the water content of the sample has been reduced so that the supply of water originates mainly from the groundwater table, the curved forms develop. The curious phenomenon is that the curved ice forms persist even when grown in a field of unidirectional heat flow as was the sample in Figure 2. This is, however, only one of the many problems in soils still to be explained.

Finally, the writer wishes to compliment all the authors on their very worthwhile contributions. The fact that some disagreement still exists between research workers merely points up areas where further work needs to be done and in no way detracts from the value of the papers.

REFERENCES

- Fukuda, H., "Mechanism of Soil Moisture Extraction from a Pressure Membrane Apparatus." HRB Special Report 40, 73-77 (1958).
 Hutcheon, W. L., "Moisture Flow Induced by Thermal Gradients Within Unsaturated Soils." HRB Special Report 40, 113-133 (1958).
 Czeratzki, W., and Frese, H., "Importance of Water in Formation of Soil Structure." HRB Special Report 40, 200-211 (1958).
 Barber, E. S., "Effect of Water Movement on Soil." HRB Special Report 40, 212-225 (1958).

5. Croney, D., Coleman, J.D., and Black, W.P.M., "Movement and Distribution of Water in Soil in Relation to Highway Design and Performance." HRB Special Report 40, 226-252 (1958).
6. Guinnee, J.W., "Field Studies of Subgrade Moisture Conditions." HRB Special Report 40, 254-267 (1958).
7. Bouyoucos, G. J., "Effect of Temperature on the Movement of Water Vapor and Capillary Moisture in Soils." Jour. Agric. Res., 5:141-172 (1915).
8. Winterkorn, H. F., "Fundamental Similarities Between Electro-Osmotic and Thermo-Osmotic Phenomena." HRB Proc., 27:443-454 (1947).
9. Taylor, S.A., and Cavazza, L., "The Movement of Soil Moisture in Response to Temperature Gradients." Proc., Soil Science Society of America, 18:351-358 (1954).
10. Woodside, W., and Kuzmak, J.M., "Effect of Temperature Distribution on Moisture Flow in Porous Materials." Trans., Amer. Geophys. Union, 39:676-680 (1958).
11. Philip, J.R., and DeVries, D.A., "Moisture Movement in Porous Material Under Temperature Gradients." Trans., Amer. Geophys. Union, 38:222-232 (1957).
12. Gurr, C.G., Marshal, T.J., and Hutton, J.T., "Movement of Water in Soil Due to a Temperature Gradient." Soil Science, 74:335-345 (1952).
13. Penner, E., "Pressures Developed in a Porous Granular System as a Result of Ice Segregation." HRB Special Report 40, 191-199 (1958).
14. Penner, E., and Robillard, P., "The Use of Waste Sulphite Liquor to Reduce Frost Heaving in Soils." (In print.)
15. Lambe, T.W., "Modification of Frost Heaving of Soils with Additives." HRB Bull. 135, 1-23 (1955).
16. Hardy, R.M., "Prevention of Frost Heaving by Injection of Spent Sulfite Liquor." Proc., 3rd Internat. Conf. on Soil Mechanics and Foundation Engineering, 2:103-106 (1953).
17. Bozozuk, M., "Ground Movements near Trees." Division of Building Research, Project Note 30 (April 1, 1959).
18. Hamilton, J.J., and Crawford, C.B., "Improved Determination of Preconsolidation Pressure of a Sensitive Clay." Paper presented to ASTM (June 1959).
19. Pearce, D.C., and Hutcheon, N.B., "Frost Action Under Cold Storage Plants." Refrigerating Engineering, 66:33-35, 74-76 (Oct. 1958).
20. Hamilton, J.J., Pearce, D.C., and Hutcheon, N.B., "What Frost Action Did to a Cold Storage Plant." Jour. Amer. Soc. of Heating and Air-Condition. Engineers, 1:54-58 (1959).

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The subcommittee was assigned the review of ten papers. Inasmuch as some of the reports did not come in, only five of these papers will be reviewed: "Water Structure and Bioenergetics" by Szent-Györgyi (1), "Mechanism of Moisture Equilibrium and Migration in Soils" by Derjaguin and Melnikova (2), "Movement and Equilibrium of Water in Soil Systems as Affected by Soil-Water Forces" by Low (3), "Influence of Surface Forces on Flow of Fluids Through Capillary Systems" by Flood (4), and "Flow of Water in Hardened Portland Cement Paste" by Powers, Mann, and Copeland (5). These papers will be considered separately, presenting highlights and pointing out some of the major concepts employed, and then collectively.

Referring to the papers by Derjaguin and Melnikova (2) and Low (3), the major concepts, relative to the flow of water, are that water moves not only under a pressure gradient but also under other gradients. Some of these other gradients are temperature, salt and ion concentration, electrical potential, and the potential energy gradients.

Concerning the temperature gradient, Mr. Penner just reported that water moves as a result of temperature gradients. Apparently there is some disagreement on how it moves or why it moves. Some people seem to think it moves as a result of the change in surface tension of the water. Others seem to think it moves in the liquid phase. Still others think that it moves in the vapor phase. In any event, Derjaguin and Melnikova in their paper and Low in his paper point out that water should move, and it appears from the discussions that they believe it moves in the liquid phase in response to a temperature gradient, though these authors would probably agree that water will also move in response to a vapor pressure gradient, which can be set up by a temperature difference. This can be of extreme importance to people in engineering.

Water can also move in response to a salt concentration gradient. To cite a familiar experiment in the biological laboratory, when a prune or raisin is immersed in water, the prune or raisin will swell; it swells by osmosis. Water moves into the region of higher solute concentration—in this case, the sugar solution. The sugar has to be restrained, though, from moving, from diffusing itself, and that restraint is imposed on it by the prune skin or the raisin skin; in other words, by a semipermeable membrane. In the case of clay, at the surfaces of the clay particles there are high ion concentrations because of the electrical attraction between the particle itself and the exchangeable cations. The restraint imposed on the ions is an electrical restraint. They have a certain freedom to diffuse away from the surface of the colloid particle*. Consequently, there is the possibility of water moving toward the particle surface in response to a solute concentration gradient. The following effect is therefore set up in the soil. If, in one region, there is a heavy clay with a high base exchange capacity and a large concentration of cations in the region of the clay mineral surfaces and in another portion of the soil a region where the particles are of silt or sand size or of a lesser base exchange capacity than the heavy clay, then there is an ion concentration gradient and the water will move to the regions of higher ionic concentrations, causing the clay to swell. The consequences are apparent; there is the breaking up of slab foundations in houses, the heaving in of basement walls, the heaving of foundations.

Water also moves along an electric potential gradient. This, of course, is well known to engineers, inasmuch as it is the basis of their methods of electro-osmotic drainage and electrochemical soil stabilization. Such water movement is again caused and conditioned by the movable exchange ions and the fixed countercharges on the surface of the soil minerals.

The one type of gradient not as well known, in soils at least, is the potential energy gradient imposed on the water. From a macroscopic standpoint, the movement of water along a potential energy gradient is quite familiar. The water running down a hill is the

Chairman's note: See "Studies on the Surface Behavior of Bentonites and Clays." Soil Science, 41: No. 1 (1936).

movement of water along a potential energy gradient. Here there is water in the gravitational field of the earth and the water running down the hill to a lower potential energy level. In trying to apply this in the soil, the gravitational term for water flow in soil rightly comes to mind. However, there is another potential energy term that should be considered. These clay mineral surfaces have their own force fields which attract the water to them. These are analogous to the gravitational field, in that water in the more intense fields of the clay particle surfaces has a lower potential energy than water in the less intense fields. Therefore, water can move into regions where the field in the vicinity of the particle surfaces is strong. This again results in swelling and its undesirable engineering consequences.

As far as water movement is concerned, the major concept one obtains from the papers by Derjaguin and Melnikova and by Low is that water moves in response to other gradients in addition to the pressure gradient.

In all five papers reviewed there occurs again and again the concept that adsorbed water on solid surfaces is sufficiently extensive to affect the movement of water past these surfaces, especially in porous solids where there is an extensive surface area. Each paper points to this concept.

Szent-Györgyi (1), believes that in water itself there is a delicate balance between the tendency for the water molecules to be dispersed by heat agitation and the tendency for the water molecules to come together in an ice-like structure in response to mutual forces of attraction. There is a very delicate balance between these two tendencies. If a colloidal surface is put into water, this surface attracts the water molecules and stabilizes water molecules in the vicinity of this surface. This stabilization of a region of water molecules tips the delicate balance in favor of the more coherent rigid water structure. It minimizes the effect of thermal agitation and enhances the effect of mutual cohesion of the water molecules, which seems reasonable. Using this idea, he proposes a very interesting hypothesis—the contraction and expansion of a muscle fiber is governed by the buildup and the breakdown of the water structure on that muscle fiber. When a very small amount of adenosine triphosphate is injected into this water there is a breakdown of the water structure and the muscle contracts. Then there is again a gradual buildup of the water structure and the muscle expands. Here, then is a theory from biology of the flexing of muscles as a result of the water structure on the muscle fibers. Szent-Györgyi proposes another interesting postulate—one that is extremely pertinent to people in agriculture: the semipermeability of the membranes of root cells is governed by the water structure on the pores of these membranes. Further it is known that ions are surrounded by an adsorbed water layer, the hydration shell of the ion. If the hydration shell of the ion is compatible with the water structure in the membrane pores, the two structures will fuse and the ion will pass through the membrane into the plant. On the other hand, if the hydration shell around the ion is incompatible with the water structure on the pores of the membrane, that ion cannot penetrate the membrane.

Derjaguin and Melnikova (2) also postulate some type of adsorbed water layer on the surface of solid particles which affects water movement. They took rigid ceramic and carbon filters and coated the pores of these filters with oleic acid. Oleic acid is a hydrophobic material. When the pores of these filters were coated with this hydrophobic material, the permeability of the filters was increased a great deal over the permeability of the filters when there was no oleic acid present on their surfaces. This is part of their evidence that some type of adsorbed water layer that impedes the movement of water through the pores of these filters exists. In the discussor's work, there is a specific volume of water on the surface of colloidal particles that is greater than the specific volume of normal water, indicating a structural rearrangement in the water as compared to normal water. There is other evidence of this kind that has also been obtained.

In the discussor's paper (3), there is additional evidence for a water structure, an adsorbed water layer. Recently the viscosity of water in the pores of clay pastes was studied, and the indications are that the viscosity of water in these pores is higher than that of normal water.

In the work by Flood (4), a porous carbon rod was exposed to water vapor of different pressure at each end of the carbon rod and the absolute pressure on either end was

aised, but the vapor pressure gradient was kept constant. The interesting thing he observed was that the flow rate of the water through the carbon rod also increased as the mean relative humidity of the air increased, the mean relative humidity being the average of the vapor pressures at the two ends of the carbon rod divided by the vapor pressures of water (saturated water vapor). This presents an interesting problem. If the movement of the water through this carbon rod was in the vapor phase, as the mean relative humidity increases, the layer of adsorbed water on the pore walls would be expected to get thicker and the void volume to get smaller; hence, the volume available for vapor diffusion would decrease and vapor transfer should go down. The reverse was the case; as the relative humidity increased, transfer of water through the carbon rod went up. Flood therefore concluded that the transfer of water through the carbon rod under the vapor pressure gradient was in the liquid state in the form of films on the surface of the carbon rod. It is readily apparent that what he states has a direct bearing on what Mr. Penner just reported. The conclusion from those papers was that water moved in response to a thermal gradient in the vapor phase and as a result of the vapor pressure gradient induced by the temperature difference. Here therefore is a man imposing a vapor pressure gradient directly, not by changing the temperature between the ends of the rod but by adjusting his vapor pressure, with evidence that the water was moving through the carbon rod in the liquid state. There is apparently some difference of opinion here.

Powers, Mann, and Copeland (5), in studying the movement of water through hardened portland cement paste, determined the temperature coefficient of the viscosity and by that means the activation energy for water to flow through the hardened cement paste. The activation energy is supposed to be the energy required for the water molecules to change positions as they move. The authors found an activation energy of 800 calories per mole for the movement of water through this hardened cement paste. Because the activation energy for the movement of pure water is only about 3,900 calories per mole, they conclude that the viscosity of the water in the hardened portland cement paste is much higher than the viscosity of normal water.

Although the paper of Szent-Györgyi refers only to biological materials, which are somewhat foreign to the engineer, it is especially stimulating. The main point that he makes is that in biological materials water has greater order and rigidity than it has in the free state. This order derives from the delicate balance between the tendency for water molecules to unite in a solid structure and the tendency for them to disperse because of heat agitation being disturbed when a layer of water is immobilized at a surface. The immobilized layer protects adjacent layers from heat agitation by a cooperative action. Szent-Györgyi's ideas can be applied equally well to other colloids, such as clays.

The paper by Derjaguin and Melnikova presents the concept of a disjoining pressure exerted by a liquid layer on the surfaces bounding it, tending to move them apart. This disjoining pressure is attributed to the overlapping of ion atmospheres extending from the bounding surfaces. To calculate the disjoining pressure, the authors invoke the Laplace formula for the pressure drop across curved surfaces. The disjoining pressure is supposed to equal the calculated pressure drop from gas to liquid in the particle contact zone minus the calculated pressure drop from gas to liquid in the intervening moisture-film zone. However, in arriving at this method of determining the disjoining pressure, the assumption was made that, at equilibrium, the pressure in the contact zone of moisture is the same as the pressure in the film moisture. This assumption is not valid because water in the thin moisture films is under the influence of adsorptive forces, and therefore, has a lower potential energy and higher pressure than water in the contact zones. The situation is analogous to that existing in the earth's atmosphere. As the earth's surface is approached, the potential energy of the gas molecules in the gravitational field increases but the gas pressure increases. Yet mechanical equilibrium exists.

In the latter part of their paper, Derjaguin and Melnikova discuss the different factors causing the migration of moisture through soils. In addition to pressure gradients they recognize the contributions of electric potential, temperature, and solute concentration gradients. They point out that the flow equation has the same form for each gradient causing movement of water.

The paper by the discussor illustrates the application of classical thermodynamics to a nonequilibrium process, namely, the flow of water in soils. The gradients in Eq. 5 of the paper are the same as the gradients mentioned in the preceding paper except that one additional gradient is included, that is, the potential energy gradient. From Eq. 5 the precise nature of the coefficients in Eq. 15 of the paper by Derjaguin and Melnikova can be determined.

In the discussor's paper, evidence is presented for the concept that attractive clay water forces exist at clay surfaces. This evidence is taken to mean that the potential energy of water is lower in the vicinity of these surfaces than it is farther away and that, for this reason, the potential energy of the water is a factor governing water movement and equilibrium.

Flood uses in his paper the thermodynamic concept that at equilibrium the chemical potential of water is the same in all volume elements of a capillary system and that for maintenance of equilibrium during any process the change in the chemical potential of the water must be the same in each volume element. The reviewer subscribes to this concept but does not agree with the author's use of v in the equation

$$du = -S dT + v dp$$

Here, v is an intensive property, being the volume per mole (or per gram) of the water. Yet the author uses it as an extensive property in his equations. For example, in the above equation he replaces v by δv , where δv is regarded as an element of volume. This cannot be done legitimately.

Flood states, "Since surface forces may easily increase fluid densities by factors 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." This statement receives qualitative support from his data for moisture movement in a carbon rod. The flow rate increased as the mean relative humidity in the rod increased, indicating liquid transfer in the adsorbed state rather than vapor transfer. The author cites evidence that the viscosity of the adsorbed water is greater than that of ordinary water.

Powers, Mann, and Copeland (5) present a derivation of the flow equation that is stimulating because it is unconventional and logical. However, the theoretical validity of separating the viscosity into two components, as is done in Eqs. 14 and 15, is questionable.

There is one recurrent concept in all of the papers discussed. This is that adsorbed water extends a significant distance from the surfaces of colloidal or porous material and has properties different from those of normal water. In particular, this water is more viscous than normal water and, therefore, flows less readily*.

REFERENCES

1. Szent-Györgyi, A., "Water Structure and Bioenergetics." HRB Special Report 40, 14-16 (1958).
2. Derjaguin, B.V., and Melnikova, N.V., "Mechanism of Moisture Equilibrium and Migration in Soils." HRB Special Report 40, 43-54 (1958).
3. Low, P.F., "Movement and Equilibrium of Water in Soil Systems as Affected by Surface Forces." HRB Special Report 40, 55-64 (1958).
4. Flood, E.A., "Influence of Surface Forces on Flow of Fluids Through Capillary Systems." HRB Special Report 40, 65-72 (1958).
5. Powers, T.C., Mann, H.M., and Copeland, L.E., "Flow of Water in Hardened Portland Cement Paste." HRB Special Report 40, 308-323 (1958).

* Chairman's note: For a fine presentation of this, see Philip F. Low, "Physical Chemistry of Clay-Water Interaction." *Advances in Agronomy*, 13:269-327 (1961).

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The authors and subjects included in this report are W. H. Rodebush and A. M. Buswell, "Properties of Water Substance" (1); R. E. Grim, "Organization of Water on Clay Mineral Surfaces and Its Implications for the Properties of Clay-Water Systems" (2); W. C. Waidelich, "Influence of Liquid and Clay Mineral Type on Consolidation of Clay-Liquid Systems" (3); F. E. Kolyasev and A. G. Holodov, "Hydrophobic Earth as a Means of Moisture-, Thermal-, and Electric-Insulation" (4); W. E. Schmid, "Water Movement in Soils Under Pressure Potentials" (5); F. L. D. Woollorton, "Moisture Content and CBR Method of Design" (6); H. F. Winterkorn, "Mass Transport Phenomena in Moist Porous Systems as Viewed from the Thermodynamics of Irreversible Processes" (7); and A. R. Jumikis, "Some Concepts Pertaining to the Freezing of Soil Systems" (8).

The determination of the exact composition and properties of water has engaged the attention of numerous investigators since Cavendish (about 1781) showed that hydrogen and oxygen burn with the formation of water and that this union takes place in approximately the proportion of two volumes of hydrogen to one of oxygen. Before this discovery by Cavendish, water was considered as a simple, elementary substance. As with the discovery of any basic physical, chemical, or mathematical relationship, scientific man's mind becomes further saturated with knowledge and ideas and his life becomes more complicated, for studies since Cavendish's discovery have shown water to be an extremely complex substance.

Rodebush and Buswell (1) have shown the hydrogen atom of water to be ambivalent even though it is capable of forming but one primary valence bond with oxygen. This bonding action causes an apparent reversal of the charges of the hydrogen from negative to positive, whereby the hydrogen is capable of attracting an oxygen atom from another molecule and forming the so-called hydrogen bond, a relatively weak bond when compared with the primary valence bond. Because of the hydrogen bonding between water molecules, it can be assumed that the molecules of liquid water are highly associated with practically no unassociated molecules present. This is supported by infrared absorption data of liquid water and by energy considerations. Thus, the molecules are not free to rotate. This leads to the concept that the whole mass of liquid water constitutes the molecule.

The best clue to the structure of water comes through consideration of the structure of ice, which is reasonably well understood; the only marked differences between ice and water being the density, viscosity, and related properties. Ice forms hexagonal crystals, generally of microscopic size and similar to the hexagonal symmetry of the snowflake. 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 inferred. Ice might be expected to crystallize in the cubic systems but, due to a strain of the bond angles of the water molecule, a hexagonal crystal is formed. Each water molecule is surrounded by four neighbors forming a tetrahedron with one molecule at the center and the other four at the apices of the tetrahedron, the jointing being due to hydrogen bonding. Because each molecule is surrounded by only four others, the packing is not very close. Thus, ice is not a very dense crystal.

When ice melts to liquid water, the hydrogen bonds are stretched and the molecules move farther apart. If it were not for a crowding together of additional molecules, the effect of this stretching would be to decrease the density and produce a large absorption energy. However, the regular structure disappears and each molecule is surrounded by five or more neighbors, rather than four as in ice, causing an arrangement that is constantly shifting, resulting in a closer packing and an increase in density.

The subcommittee included G.C. Blomquist, Chairman; D.T. Davidson, Iowa State University; J.H. Havens, Kentucky State Highway Department; and E.B. Kinter, Bureau of Public Roads.

In an unassociated liquid such as benzene the molecules move around and slide past each other, thus encountering a certain amount of resistance. In liquid water the molecules are attached by hydrogen bonds and at least one must be broken before any flow can occur, resulting in a rolling rather than a sliding motion. The viscosity of water is much less than might be expected from a consideration of the amount of bonding between molecules because it is unnecessary to break both bonds between the hydrogen of one molecule and the oxygens of two other molecules at once. The greater viscosity of ice is due to each hydrogen being firmly bonded to a single oxygen atom from another molecule. This bond must be broken completely before movement can occur.

The heat capacity of liquid water is 18 calories per mole and is quite constant from the melting to boiling points, whereas the heat capacity of ice is less than half this quantity. This high heat capacity indicates the atoms of liquid water must be more loosely bound than in the rigid structure of ice and gives support to the assumption that there is an increase in ionic character for the atoms in liquid water.

Water is an excellent solvent for electrolytes due to its associated structure of high dielectric constant, but it has extremely small electrical conductivity itself, which accounts for the water molecule having little tendency to dissociate into free ions. Electrolytic molecules, such as sodium chloride, are easily dissolved in water due to their being ionic compounds. When this occurs, the structure of the liquid water is broken down and undergoes some modification. However, there is another class of substances that have little solubility in water but that actually have the effect of augmenting the structure of water; that is, nonpolar compounds. There are also compounds that are intermediate between ionic and nonpolar compounds in that the molecule includes both ions and nonpolar parts. An example of the latter are protein molecules, which may be likened to plastics and for which water may be regarded as a plasticizer.

Although water is primarily regarded as a solvent for electrolytes, Rodebush and Buswell feel that considerable knowledge about water can be gained by an analysis of solutions of nonpolar molecules. They illustrate the structure situation by showing the existence of solid hydrates, in these solutions, that separate at temperatures well above the freezing point when ever the partial pressure of the gas above the solution is sufficiently high. These hydrates came to their attention when natural gas lines became clogged with a solid precipitate at temperatures as high as 20 C. The cause for these compounds was reported as a lack of attraction between the water and gas molecules, with the water forming a cage around the gas molecules one layer thick. The strain, which in the case of ice prevents the formation of a cubic crystal, does not build up here.

When the gas molecules in solution reach a certain concentration, the cages unite, forming a cubic lattice that is stable even above the melting point of ice, though the stability is lost if the gas escapes from the solution. Thus, in water, a hydrate can form when there is an electrically neutral molecule of the right size for the water molecules to collect around it in a cage. The cage can grow to a larger crystal.

Only small cations are strongly hydrated. If the size of the cation is such that the volume when combined with two water molecules is about that of methane, a situation exists similar to the gas hydrates. The ultimate size may be very large. Anions may attach several water molecules by hydrogen bonding, but a shell does not form. Thus the ionic mobility depends on the degree of hydration of the ion and not on the individual ionic size. In the case of hydrogen and hydroxyl ions having mobilities higher than all other ions, a mechanism termed "proton transfer" is given. This transfer can be visualized as the continuous formation of new cages as these ions move.

Grim (2) presented evidence that some definite geometric organization of the water held on the surfaces of clay particles exists. He further presented some implications of such water characteristics on the properties of clay-water systems.

There is sufficient evidence in the literature to indicate that the water held on clay mineral surfaces is not in the state of liquid water but has some geometric organization. This organization has been pictured best as an extended net of hexagonal groups of water molecules. The net of nonliquid water fits into the organization of oxygen atoms on basal surfaces of clay minerals or between the clay mineral surface. Another nonliquid water net is included by hydrogen bonding.

The degree and kind of water organization is influenced by several factors, some of which are in the clay mineral itself. Some of the flat surfaces of clay minerals are composed of oxygen atoms and others are composed of hydroxyls. The variance in the ease of cleavage that exists among the clay minerals results in the variations of availability of flat surface and, hence, a difference in the amount of oriented water developed.

Other factors influencing water organization are found in the adsorbed components on the surface of clay particles. These adsorbed cations 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. The adsorbed cations determine the thickness of the oriented water layers by the manner in which these adsorbed cations fit into the geometry of the water net. On the whole, they may retard or enhance the formation of the water net and may actually determine the geometry of the water net. For example, the sodium ion favors the development of thick layers of water if water is available. Potassium, hydrogen, aluminum, and ferric ions have very small potential for the growth of thick layers.

On the basis of the consideration that the bonding force between clay particles is directly influenced by oriented water molecules and indirectly by the adsorbed components on the clay surfaces, the following statements seem warranted:

1. Materials with very high moisture contents could possess considerable strength.
2. A material can exhibit tremendous difference in strength with a slight change in moisture content.
3. A slight change in the adsorbed cation composition might well cause a destruction of the orientation of some water molecules inasmuch as the replacing cation would not permit the same maximum amount of oriented water as the replaced cation.
4. Soils and clays can experience a reduction in volume apart from association with surface drying and without the application of an external force.
5. The development of the properties of clay-water systems is influenced by time, because the development of oriented water is a crystal growth requiring considerable time.
6. Materials whose properties would be most influenced by oriented water considerations would likely be those with high limits and high sensitivity.

The compressibility of clays and clayey soil materials is a problem haunting any engineer concerned with an earthen embankment or foundation design due to the extreme variability and highly complex nature of the soil-liquid systems that may be encountered. As surface water enters a soil profile, it becomes intimately mixed with a mass of constantly decomposing mineral materials and organic matter and becomes a dynamic and fluctuating solution containing traces of every element present. Some of the water, as well as the dissolved cations, is absorbed by the clay and colloidal solids, while the remainder of the solution is still in a state of free movement. Often, this solution is regarded by engineers simply as "water," a liquid free of any impurities and with a pH of 7.00. In order to comprehend the complexities of consolidation of a soil material under load, it is necessary for the soil engineer to understand the material he is dealing with; that is, soil and water, whether separate or in combination. Clays, with their unique absorbing powers, are the predominant active fraction of a soil material and water is in itself a complex liquid. Waidlich (3) undertook in his study to define the role of water in the consolidation process by comparing consolidation data of three different well-defined clays and seven different liquids with each clay. The clays consisted of two non-expanding materials: (a) Georgia acid kaolinite, (b) Goose Lake white clay—predominantly halloysite and one expanding-type lattice, (c) Na-Bentonite, a montmorillonitic clay mineral. The liquids used were water and six organic liquids differing in molecular structures, dipole moments, and dielectric constants; that is, methanol, ethanol, propanol, butanol, aniline and nitrobenzene, in the order of increasing molecular weight.

Experiments performed for the investigation included the following:

1. Standard consolidation tests, with proper preventions against evaporation of the more volatile liquids.

2. Specific gravity, with some modifications due to the harmful vapors of several of the organic liquids.

3. Standard Atterberg limits, though grooves were cut in the liquid limit dish to prevent the white clay from slipping along the surface of the dish rather than flowing independent of the dish.

The data of the study were tabulated, graphed, and correlated with the dipole moment, dielectric constant, and molecular weights of the various liquids used. The compression and expansion indices of each clay-liquid complex were obtained from the slopes of the void ratio/log pressure consolidation curves.

The dominant influence of the liquids on the compression index of the nonexpanding lattice clays appeared to be the dipole moment. In general, the larger the dipole moment of the liquid used, the larger was the index for the kaolinite, whereas the larger liquid moments caused increasingly smaller compression indices of the white clay. Exceptions were noted with the liquids aniline and water that could not be fully explained on the basis of this study. The compression indices of the expanding lattice clay, montmorillonite, appeared to be affected to a greater degree by the dielectric constant than by the dipole moment of the various liquids; that is, generally decreasing compression indices with corresponding decreases in dielectric constants of the liquid. This was apparently due to the absorption effects between nonexpansive and expansive clay lattices and also to the definitive differences between dipole moments and dielectric constants.

Considerably less correlation is apparent between the expansion indices and the dipole moments and dielectric constants. Several factors having an effect on the expansion index are (a) the dipole moment, (b) the dielectric constant, (c) the effect of the sorbed liquid on the elastic rebound properties of the soil, and (d) size and structure of the liquid molecules.

Other factors that may be affecting the state of the soil-liquid complex while under compression and rebound are (a) the exchange properties of the liquid, (b) the exchange capacity of the clay minerals, (c) the pH of the soil-liquid complex, (d) the size of the clay particle, and (e) changes of a liquid's viscosity due to changes in temperature. Though there may be still other influences on the systems, it must be made clear these factors do exist but are not conclusively accounted for.

Of particular interest is the curious effect of viscosity of the liquids on the determined qualitative values of permeability from the consolidation tests. Permeability is generally assumed to vary inversely with the viscosity of the permeating liquid. Of the soil-liquid complexes containing the several liquids having viscosities higher than that of water, the permeability under load was also higher. The two most plausible causes for this effect are (a) the effect of liquid on the structural arrangement of the solids, making larger individual pores, and (b) the different thicknesses of the absorbed or "restrained" liquid layers.

The specific gravity of the nonexpanding and expanding clays are noticeably affected by the dipole moments and dielectric constants, respectively. However, the size and structure of the liquid molecule shows a correlation with specific gravity of the clays corresponding to the correlation of the dipole moments and dielectric constants with compression and expansion indices.

Kolyasev and Holodov (4) state that immense construction works of all sorts are under way all over Russia and that the natural foundation of these works, the soil, is subject to the action of water, temperature, electricity, and pressure, which affect the life of the construction and the suitability of the soil. Measures have been taken to increase the resistance of soils to these influences by decreasing properties such as water absorption, filtration, swelling, and wetting. For this purpose a new branch of physical chemistry has developed that makes use of hydrophobization, or waterproofing, methods. Before this time, methods for waterproofing have involved treatment of the soil with surface active agents, bitumen, copper abietate, paraffin and resin vapors, vapors of organic silicon compounds, siliconates of heavy metals, and metallic salts of fatty acids.

Fundamentally, these treatments attempt to cover water-attracting surfaces with water-repellent material. Obviously, for success, the covering material must be pro-

erly applied to the soil, which, in turn, must retain the reagent. Of the several properties enabling the soil to retain added agents, four are applicable to waterproofing problems: (a) chemical absorption, (b) chemisorption, (c) physical adsorption, and (d) physico-chemical or reversible adsorption.

In chemical absorption, added anions produce with cations of the soil solution insoluble salts that precipitate among the soil particles, forming a mechanical mixture. Chemisorption involves the reaction of anions or cations in the dispersion medium (that is, the soil water) with ions that are a part of the mineral particles themselves, forming water repellent compounds.

Physical adsorption involves a reduction in the free surface energy of the dispersion medium. This may result from (a) an increased concentration of the dissolved matter in the first layer of water on the solid particles or (b) the coagulation of colloidal particles into aggregates.

Physico-chemical adsorption is the familiar cation exchange process in which cations of the solid phase interchange reversibly with cations of the liquid phase.

It has been the general assumption that the power fixing a waterproofing agent to the surface of soil particles represents chemisorption, in which polar groups of applied organic substances link with either positively or negatively charged areas that exist on soil mineral surfaces as a result of fragmentation of the soil particles. However, preference has been shown for the physico-chemical, or cation exchange, explanation because clay mineral surfaces contain negatively charged sites (oxygen and hydroxyl ions) that require cations (positive charges) for neutralization. Literature is cited showing that charged sites do not occupy more than 10 percent of the mineral particle surfaces and that such a small proportion of active surface is not sufficient for successful waterproofing. Further, 90 percent or more of a waterproofer attached to mineral surfaces by this type of property is removable by organic solvents, and thus cation exchange cannot be considered as satisfactory.

Waterproofing by surface active agents has been investigated intensively at the Soil Physics Laboratory at Leningrad—especially with sodium salts of organic acids, the organic radical being the water-repellent agent. For effective waterproofing the soil particles should be completely covered. This is accomplished by mechanically mixing to obtain homogeneity. Mixing is thus a second technological necessity.

During the mixing the soap is alleged to be adsorbed molecularly on the soil surfaces. The material is then dried to remove water films so that particles of soap and soil will approach each other more closely and prevent rewetting of the soil particles. Thorough drying is thus a third technological requirement*.

The waterproofing agent is considered simply as a layer of material over a certain amount of mineral surface. To form an effective layer the agent must (a) not be wettable or water soluble, (b) adhere well to the mineral surface, and (c) distribute well and easily in the soil mass.

Important effects of waterproofing are the reduction of water-holding capacity, increase of drying rate, and decrease in hygroscopic moisture, the latter by as much as 80 percent. Waterproofed soil is an unusual material, being unwettable, friable and quite porous, with interconnected capillaries. Capillary rise is slow, and the soil withstands various hydrostatic pressures. It is thus useful for protecting structures from the influence of water.

Hydrostatic pressures withstood by soap-treated soils have been determined experimentally by means of soil packed in paraffined glass tubes, with measured values as high as 125 cm of water. This resistance to water pressure is influenced by the marginal angle of wetting, which increases upon waterproofing. This angle also varies with surface area; soils in the range of surface area from 1 to 3×10^3 sq m per g are most susceptible to waterproofing treatments.

Waterproofing also changes thermal and electrical characteristics, the heat conductivity of waterproofed soils being 4 to 6 times lower than that of concrete, 3 to 4 times lower than that of brick, and about equal to that of wood. Electric resistance approaches that of asbestos and marble. Consequently, waterproofed soil may be used as a com-

* Compare with similar methodology and results described in "Oiling Earth Roads," Ind. and Eng. Chem., 26:815 (1934).

bined heat and electrical insulator, and has been so used by the authors in electrically-heated hot beds. Kolyasev and Holodov state that they have experimental evidence proving its usefulness for flat roofs on buildings. References are made to successful use as a lining in irrigation channels, for minimizing frost heave, and to suppress heaving of railway beds due to a high water table.

Schmid (5) recapitulated the development of the rational hydraulic theory and its application to the flow of water through soils and recognized the absorbed or fixed water layers in clays and their apparent manifestation as a departure from elementary theory. Thus, for clay-type soils, it has become necessary to introduce the concepts of equivalent or effective capillary diameters and porosities to obtain agreement between theory and observed permeabilities.

Permeability might be regarded, therefore, as a tangible parameter that is useful not only in estimating volume or rate of water movement but also in gaining significant inferences as to the structural and physico-chemical nature of the soil.

Wooltorton (6) presented a concise literature review and discussion of the CBR method of test and its application to pavement design. Different methods of laboratory compaction (static loading, impact, and kneading) are compared with field compaction procedures. Such comparison shows that kneading action more nearly simulates the compacted soil structure as obtained in the field. The dangers of overcompaction, of plastic soils, are emphasized. Such soils tend, with time, to revert to their natural density, a value close to that obtained by the standard Proctor test.

The most important problem connected with the CBR design method is the proper estimation of the ultimate moisture content that the compacted material will reach in the field and to design the structure accordingly. Methods of predicting this value under particular conditions are discussed with emphasis on the "suction-pressure" method proposed by Croney. Referring to this method, Wooltorton states that the principles involved and conclusions reached are not clear at all and indicates that some are questionable. He then lists more logical, empirical methods for estimating ultimate moisture contents. These estimations provide a wide range of values, however.

Although no formal conclusions are offered in this paper, the following statements are made in the text:

1. Ultimate, in-place CBR or stability depends on (a) method of compaction, (b) ultimate density obtained, (c) equilibrium moisture, and (d) any structural strength developed in the soil with time.
2. When designing to a specific density, the value must (a) be sufficient to eliminate the possibility of appreciable consolidation; (b) be high enough to provide an economic value to the increased stability; (c) give in conjunction with its moisture content a condition of minimum volume change; and (d) not be so high as to cause loss of stability and future densification by traffic or by overcompaction during construction.
3. In cases where there is a possibility of overcompaction (as in soils of higher plasticity) it is advisable that they be compacted at a moisture content slightly below optimum.
4. Ultimate moisture content to be expected in the field is quite variable and dependent on climate, water table elevation, soil structure, soil density, and the chemical composition of the soil.
5. Types of granular materials used for base construction can affect the required base thickness by as much as 60 percent.
6. Maximum density and stability of fine-grained soils depend on the clay minerals present and on homoionic variations of these minerals. The manner in which these variations occur is not known but their effect may be considerable.
7. The CBR test is a satisfactory design method if the ultimate moisture content to be reached in the field is known. At present, there exist only approximate methods of estimating this ultimate moisture content.

Wooltorton's recent work indicates that there is a suspicion that standard CBR test is unsuitable for some of the subgrade materials encountered in Kenya and that modifications in the specifications for that test may become necessary.

Certain soils were found to be usefully classified only in a system that introduced maximum density and optimum moisture content ranges to establish a design philosophy suitable to Kenya.

The most recent work is concerned with red and red-brown soils of Kenya, their clay mineral composition, and its influence on standard design criteria.

There are indications that the more alkaline-reacting soils should be compacted at a moisture content below Proctor optimum to diminish the chance of maximum moisture contents in excess of the plastic limit. Another recommendation is for in-situ CBR testing to eliminate possibilities of producing appreciable CBR values within a moisture content range eventually productive of plastic yield and surface distortion.

In any system or process encompassing soil-water systems and the movement of water therein, the system will respond in such a way as to relieve any unbalanced pressures or strains. Thus, an applied pressure, whether it be mechanical, gravitational, electrical, thermal, or combinations thereof, is, in effect, an unbalanced force acting on the system. By analogy, then, these unbalanced forces are manifested as acceleration or deceleration where the system is assumed to pass from one state of dynamic equilibrium to another and as work where the system is assumed to be changed from one level of static equilibrium to another. In simpler terms, these are "cause" and "effect" situations; and quantitatively the cause must equal the effect. This, of course, is in line with the conservation of energy.

In further regard to quantitative treatments of "cause" and "effect," an energy-balancing equation may be written to describe the process. Likewise, and paralleling the energy balance equation, there may be written a materials-balancing equation, assuming, of course, that there is no attendant transformation of matter into energy—a practical assumption in the problem at hand.

Agreement between the summation of energies involved in any complexity of transient or concurrent mechanisms transpiring between and directly related to "cause" and "effect" and the net energy change of the system, as determined by experiment, provides sufficient evidence that all the mechanisms have been taken into account and are understood. Disparities, in this respect, would, of course, provide convincing evidence that hidden mechanisms were involved and that the process has not been successfully analyzed.

In dealing with the movement of moisture through soils, there is always some conflict between rationality and irrationality. This, of course, usually stems from a misunderstanding of the mechanisms involved and emphasizes the necessity for preserving rationality by frequent recourse to the general theory.

Because of the national importance of the soil freezing problem in the United States and elsewhere, attempts have been made to learn and understand the basic phenomenon relative to frost action in soils. Work on freezing soil systems has been found to be very difficult and complex because of the many independently or mutually reacting processes induced by various factors when soil is subjected to thermal potentials.

The knowledge of the performance of a soil system, under freezing conditions, is necessary in designing and constructing highways, airports, and other earthworks.

Jumikis (8) presents various basic physical concepts such as the process, the system, primary and induced potentials and modes of possible soil transport used in a soil freezing experiment, and attempts to detect the final result on soil caused by a freezing thermal potential as the driving energy for the upward transfer of soil moisture from the ground water to the freezing ice lenses.

The energy concept makes possible the study of the freezing soil system in its entirety. In this concept, "potential" or "potential difference" between two points of a freezing system is the energy measured by work done 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. Because the tension of the soil moisture is not of the hydraulic type but an intrinsic property of the soil system that depends on the mutual affinity of the water to the surfaces of the solid soil particles, the soil moisture tension would quantitatively manifest the total joint and net action of all the system's internal forces in displacing an elementary or differential value of soil moisture.

The various potentials that might occur under varying conditions in the freezing soil systems may be broadly classified as (a) primary potentials and (b) secondary or induced potentials. Primary potentials are those applied externally to the system and may be thermal, electrical, gravity or other possible potential. A secondary potential may be

heat, electric, or concentration potential, but not gravity potential. Induced potentials may act and contribute to moisture flow in the same direction as the flow caused by a primary potential, or it may act in the opposite direction, depending on the properties of the porous material or membrane; hence, the net amount of the upward moisture transport in a soil system upon freezing is an algebraic one.

Soil moisture can be transported upward through the porous medium of soil upon freezing (a) as a liquid (film transport), (b) as a vapor (vapor transport), or (c) as a liquid and vapor (film-capillary transport). A combination of all three may take place depending on changing temperature and vapor pressure conditions, type of electrolyte, the freezing soil, and the distribution of the variously sized voids. However, the clue as to which mode of transport is most likely to take place is provided by the degree of density and the continuity or discontinuity of moisture in the liquid form in the voids.

Vapor transport occurs 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 driving pressure is the difference between the two partial vapor pressures at the warmer end and the upper or freezing region. Vapor transport cannot take place in fully saturated soil or in very densely packed soil.

Film-capillary transport occurs if the soil is so packed that soil moisture can occur in the voids absolutely. The driving pressure is the vapor pressure difference, as above plus a flow pressure caused by the molecular motion of warmer water particles toward the cold front.

Film transport occurs in very dense, closely packed soil where the moisture around and between the soil particles forms uninterrupted liquid films through the entire soil system down to the ground water supply. The driving pressure is the pressure difference between two points under consideration by thermoviscous flow of film moisture plus other possible potentials. The amount of moisture transferred depends on the specific area of the soil particles in a unit volume; that is, the greater the density, the more moisture films.

The amount of segregated ice in a frozen soil system depends very much on the intensity and rate of freezing. Quick freezing resulted in a rise in moisture content at the ends of the soil cylinder tested, but no ice layers were visible. Slow freezing brings clearly visible ice layers of various thicknesses. Ice segregation takes place also under cyclic freezing and thawing conditions.

REFERENCES

1. Rodebush, W. H., and Buswell, A. M., "Properties of Water Substance." HRB Special Report 40, 5-13 (1958).
2. Grim, R. E., "Organization of Water on Clay Mineral Surfaces and Its Implications for the Properties of Clay-Water Systems." HRB Special Report 40, 17-23 (1958).
3. Waidelich, W. C., "Influence of Liquid and Clay Mineral Type on Consolidation of Clay-Liquid Systems." HRB Special Report 40, 24-42 (1958).
4. Kolyasev, F. E., and Holodov, A. G., "Hydrophobic Earth as a Means of Moisture Thermal-, and Electric-Insulation." HRB Special Report 40, 298-307 (1958).
5. Schmid, W. E., "Water Movement in Soils Under Pressure Potentials." HRB Special Report 40, 164-177 (1958).
6. Wooltorton, F. L. D., "Moisture Content and CBR Method of Design." HRB Special Report 40, 268-297 (1958).
7. Winterkorn, H. F., "Mass Transport Phenomena in Moist Porous Systems as Viewed from the Thermodynamics of Irreversible Processes." HRB Special Report 40, 324-338 (1958).
8. Jumikis, A. R., "Some Concepts Pertaining to the Freezing of Soil Systems." HRB Special Report 40, 178-190 (1958).

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The paper on "Importance of Water in Formation of Soil Structure," by W. Czeratzki and H. Frese, is essentially a translation with occasional interpretation of two pamphlets that accompany two films made at the Institute for Soil Technology at Braunschweig-Völkenrode, West Germany, in 1956-57. The last part of this translation is taken from another work done by the major author. The films are silent, but have subtitles in German; together they run about 25 min. The price for both films is around \$60, and they may be obtained from the Institut für den wissenschaftlichen Film, Göttingen, or from the Institut für Bodenbearbeitung, Braunschweig-Völkenrode.

The amount of precipitation and evaporation of water and its physical state as influenced by temperature greatly affect aggregate formation and thus soil structure. Such processes may be dynamic, but are relatively slow. Therefore, time-lapse cine-photography was employed to catch those fleeting moments in the formation of soil structures.

Wetting and Drying

The soil chosen was presumably a humic glei that had developed on Opalinus clay in the province of Württemberg, southern Germany. (The Opalinus clay is the lower part of the Jurassic formation and is characterized by the predominance of weathered fossil remains of *Leioceras opalinum*.) Approximately 50 percent of the soil is smaller than μ in size. A sample was dispersed in water and a brick formed. Wetting was accomplished by a fine spray of water; drying, at 30 to 40 C under a heat lamp.

As viewed from above the first wetting caused a roughening of the surface with formation of small air blisters as the water replaced the entrapped air. Subsequent drying resulted in very fine fissures indicating that the water had penetrated to a considerable depth. In addition it might be reasoned that the location of the fissures was random in nature because the sample had been mixed homogeneously and little translocation of soil particles had occurred during the first wetting.

During the second wetting the soil absorbed more water because of the opened fissures and the roughened surface. The fissures closed and the edges swelled, and there was some particle movement. Upon drying, cracks formed quickly at first and then more slowly—often with a "jerking" movement. Only part of the fissures initially formed resulted in these cracks.

Because the picture obtained by these experiments presents only a two-dimensional view, the time-lapse camera was set up so that the soil could be seen from a side. The soil here was a fine-textured soil developed on alluvium, and a brick was prepared as already described. Wetting of the sample again resulted in a roughening of the surface and formation of air blisters. Some cracks were formed upon drying; however, they do not penetrate deeply into the soil. Subsequent wetting of the soil specimen occurred at separated intervals to avoid flooding or erosion. Water movement in the soil is primarily via the fissures and cracks formed upon drying. The drying fissures at first were zigzag in nature and often horizontal. Drying began on the walls of the vertical cracks with their resultant widening. At the same time a zone of horizontal cracks formed which progressed downward, though not as far as the vertical cracks. Vertical cracking of the soil upon drying penetrated deeper than the horizontal cracking, the latter being restricted primarily to the surface.

Freezing and Thawing

Essentially two phenomena occur when a soil is saturated with water and then frozen:

1. The movement of the weakly bound capillary water to the freezing zone.
2. The incorporation of this water as ice in the intermittent soil layers.

If frost penetrates the soil from one direction, its effect on such ice segregation may be "homogeneous," if there is no macroscopic change as compared to the unfrozen soil; "heterogeneous," if various frost forms occur as influenced by soil type, rate of freezing, and water supply to the freezing zone. Generally, it can be said that frost causes a horizontal layering in fine sand and silty soils; a polygonal type of structure in clayey soils due to a removal of water and subsequent shrinkage of the clay. If the water content drops below a certain limit for a certain soil, it will freeze homogeneously. An increase in moisture content may cause heterogeneous freezing.

Experimentally, the samples were passed through a 2 mm sieve and pressed into a cylindrical form 10 cm high and 12 cm in diameter; one side was then cut flat for photographic purposes. Provision was made that the frost could penetrate only from above and that the bottom of the sample was in constant contact with an artificial ground water table. The temperature at the soil surface was kept at -1 to -1.5 C.

Diluvial Sand.—Mechanical analysis indicated the soil to have about 77 percent diluvial sand between 0.02 and 2.00 mm. Because of the large particle size the frost did not form any layering of ice but rather a homogenous freezing. In the film this was seen as a downward moving shadow, this being caused by the freezing zone.

In the following three soils an understandable, nevertheless pedologic, error was made in the translation of the names of the soils. The following corrections should be made in the report:

Original German	Literal Translation	Correct Translation
Schwarzerde	Black earth	Chernozem
Para-Braunerde	Para-brown earth	Gray-brown Podzolic soil
Boden aus Kreide Ton	Soil on chalk clay	Humic glei

A-Horizon of a Chernozem on Loess.—Horizontally oriented ice lenses were formed from the top down. The edges of some layers curved upwards and joined others thus forming a net-like frost structure. The ice lenses formed very quickly at first, then formation slowed down but continued to thicken even after the ice front had passed.

A₃-Horizon of a Gray-Brown Podzolic Soil on Loess.—Frost structures formed are much the same as in the Chernozem just mentioned. Such structures are seldom observed in nature; this is supposed to be due to the slow freezing rate and good water supply in this experiment.

Humic-Glei Soil.—Because of the restriction on water movement in this sample due to the high clay content (about 25 percent less than 2μ), the soil specimen was made up with a sufficient amount of water in the beginning. In addition to this, freezing caused a removal of water immediately next to the freezing zone and resulted in contraction cracks. These cracks were then filled with ice. Initial frost forms were at first parallel, needle-like vertical ice layers that later were connected by horizontal lenses. The polygonal frost structures that resulted continued to thicken throughout the experiment.

Form of Frost Aggregates in Clay

In this case, soil specimens were frozen and then cut so as to give a vertical and horizontal picture.

A Ca-montmorillonite showed pronounced vertical ice lenses with the horizontal lenses being thinner and less definite. The predominance of the vertical forms was due to their formation in advance of the freezing front; initial vertical fissures providing stress-free spaces into which water may crystallize to ice. Increasing capillary-gravity tension of the water resulted in less well-developed horizontal ice layering. Polygonal frost forms were developed normal to the surface, as is also the case in dried mud flows, basalt flows, etc.

Frost forms in a Na-montmorillonite were similar to those in its calcium counterpart. Here, however, the size is smaller and less regular due to variations in swelling capacity and water absorption.

A calcium and a sodium sandy-clayey loam were also observed. Again the sodium variation showed less regularity in formation of frost structures than the calcium counterpart.

Weathering and Erosion

A second paper on "Effect of Water Movement on Soil," by E. S. Barber, shows that the effects of water movement on soil may be external or internal. Externally, sheet erosion and gulying are well known. Often certain soils (for example, loess) exhibit natural cementation and thus are relatively resistant to surface erosion. If this natural cohesion is destroyed by reworking the soil, severe erosion may result.

Internal erosion includes chemical and physical processes. Leaching of soils and formation of clay minerals and subsequent translocation thereof are found in many soils. Physical internal erosion may be responsible for drainage pipe collapse as well as degradation of subdrains due to silting. Soil-water pumping under concrete slabs is a type of internal erosion.

Consolidation and Swell

When a confined specimen of a clay soil is subjected to a load, slipping and bending of the individual clay platelets causes a volume decrease. If the load is released, the plates unbend and there is a volume increase. Reapplying the load causes hysteresis due to less and less slippage. Similar effects are caused by wetting and drying, the effects of surface tension replacing the mechanical load. The amount and rate of consolidation is dependent on water movement in the soil and/or its structure.

Wetting of soils rich in clay causes swelling due to the absorption of water. Often the vigorous escape of air may disrupt the sample when slaked. Movement of water in soil as influenced by temperature gradients may be controlled in part by the use of effective insulation.

Seepage Forces

Because soil is buoyed up in proportion to the amount of water it displaces, settlement of the surface occurs if the water table is lowered. In Mexico City well pumping has caused an average annual settlement of about 13 in.

The lateral flow of water is important in landslides, particularly if clay layers are exposed by cuts. Upward flow of water may be caused by too rapid excavation in clay or sand, if bulkhead sheeting is used where the water table is uneven, or if a "quick" condition is caused by a vibratory load applied on loose saturated sand; for example, between wiggling toes on a beach.

Compaction

The optimum moisture for compaction is reached when

1. The surface tension is reduced sufficiently to permit a denser arrangement of particles.
2. The internal friction is at a maximum due to less pore space water.
3. The least amount of pore space water will re-expand after the impact load is eased.

Continued compaction beyond optimum causes weakening due to formation of shear surfaces. Even distribution of moisture and the addition of certain chemicals aid in increasing the density.

Capillary Flow

Capillary movement of water in soil depends greatly on particle size and/or surface area. A no-flow layer, such as a sand layer between silts, may cause road failure be-

cause moisture tends to increase toward the no-flow condition. The upward flow of capillary water may bring soluble soil stabilizers to the surface where they may either be washed away or cause "case-hardening" at the surface; that is, blooming of carbonate on cut loess surfaces.

Temperature and Electricity

Temperature as well as the amount of air in water influence the amount of pressure and/or volume change of soil water. Electrical current has been used in direct work with soil settlement and also in various types of prospecting.

Movement and Distribution of Water

A third paper on "Movement and Distribution of Water in Soil in Relation to Highway Design and Performance," by D. Croney, J. D. Coleman, and W. P. M. Black, shows that the simplest method of determining the water content of a soil is on a weight basis. The resultant value does not, however, take into account the previous water history of the soil, moisture gradients, and similar energy relationships. Movement of water in a soil mass is due to a potential gradient, which in turn is caused by hydrostatic pressure, vapor pressure, or a combination of both.

In nature, a particular soil sample is subjected to a stress by the surrounding soil. Therefore, the pore-water pressure may be regarded as an algebraic sum of two components; that is, the suction and the effect on the suction of applied stress. Hence,

$$u = s + \alpha P$$

in which

u = pore-water pressure

s = suction in the sample when free from external load

P = applied pressure

The limits of α are therefore 0 and 1.

Moisture movement within a soil may also cause a volume change. A new optical projection method as devised by the Road Research Laboratory of the United Kingdom is described. From measurements of height and diameter the volume is computed.

Work done has shown water vapor movement to be greatest in the least saturated soils. In temperate climates the relation between heat and moisture transfer tends to be linear; whereas in extreme climates the relation is nonlinear and a net upward moisture flow is expected. The extent to which water will move into a frozen zone causing frost-heave depends largely on the suction of the unfrozen soil as well as the frozen soil.

The Road Research Laboratory has modified the apparatus used with the suction plate, pressure membrane, and sorption balance methods in determining soil moisture. The results of such modifications show, for example, that for most natural conditions over-consolidated clays increase in suction on shearing and normally-consolidated clays tend to decrease in suction on shearing.

Equations are derived that are useful in describing the pore-water/suction energy relationships. Additional work has been done on the close relationship between suction and the bearing ratio of the soil. At the Road Research Laboratory, it has been the practice in designing flexible road pavements to estimate first the equilibrium moisture content of the subgrade using the method outlined in the original article. The CBR test is then carried out at the moisture content and density most likely to be achieved in the field.

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Water that enters soil either remains within soil pores or moves to other regions and the character of the soil and of the void spaces within the soil determines to a considerable extent the deposition of the infiltrated water. Because highway engineering design and highway operation procedures depend on the performance of soils, which in turn depends a great deal on moisture content and movement, it is important to the engineer that he be able to characterize the mechanism of soil moisture retention and accurately determine equilibrium points that express differences in the water relations of soils.

Anyone can reason that water will flow from a wet to a dry region, but a quantitative description of the driving forces for flow is not as obvious. One of these forces can be measured by capillary potential or tension. Capillary potential is a quantity that expresses the attraction of the soil at any given point for water and is defined as the work required to pull a unit mass of water away from a unit mass of soil. It is numerically equal to tension but is opposite in sign, is always a negative quantity, and can never be greater than zero. Capillary potential is a true potential and therefore any flow of water will occur from a high to a low value. Table 1 illustrates the relationship between tension and capillary potential.

H. Fukuda has answered in his paper, "Mechanism of Soil Moisture Extraction from a Pressure-Membrane Apparatus," several questions concerning the integrity of the pressure-membrane extraction apparatus developed by Richards. The effects of temperature and humidity in the atmosphere surrounding the apparatus are important questions because these conditions represent outside forces that influence the results obtained. Fukuda has conclusively shown, theoretically and experimentally, that the effects of air humidity

and room temperature are minor and can be neglected in this case. These results then preclude the necessity of elaborate precautions to prevent adverse effects of humidity and temperature in the normal determination of soil moisture tension.

Soil tension data are not used by engineers to any great degree. Further research on the correlation of soil moisture data with soil moisture tension needs to be done to enable engineers to use this accurate tool for characterizing soil moisture. A step in this direction has been taken by R. L. Rollins and D. T. Davidson* in which they report correlation of liquid limits and plastic limits with soil moisture tension.

TABLE 1

Moisture Condition of the Soil	Tension	Capillary Potential
Dry	High (x)	Low (-x)
Wet	5	-5
Saturated	Low 0	High 0

*Unpublished paper presented at the 58th Annual Meeting of the ASTM, 1955.

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Recent research on the movement of soil moisture due to a thermal gradient has had for its primary goal the determination of the mechanism of flow. Various techniques have been used to differentiate between liquid and vapor flow and to determine which method of transfer predominates in a given system. Many investigators, such as Hutcheon (1), have concluded that the moisture transfer was several times that calculated by the simple molecular diffusion theory. Research results also indicate that there exists a critical soil moisture content at which maximum net moisture transfer occurs.

Philip (2) in his paper, "Physics of Water Movement in Porous Solids," briefly outlines a theoretical concept relative to the movement of moisture due to a thermal gradient. This concept explains many of the heretofore unexplained factors in this area of research. Although additional experimental verification and refinement of theory are necessary, it is believed that the concept proposed by Philip opens the way for a more complete understanding of this problem.

Inasmuch as this phase of moisture transfer was, of necessity, limited in Philip's general discussion of moisture movement in soils, it seems appropriate at this time to discuss his theory in more detail and to present some additional experimental evidence that substantiates the concept.

The concept proposed by Philip and De Vries (3) is based on the following two propositions:

1. In a three-phase soil, water, and air system subjected to a thermal gradient, the temperature gradient across the pores of the system are several times the average temperature gradient of the system.

2. In a relatively dry soil, water wedges at the contact points of the soil particles restrict vapor diffusion to a pore dimension and provide a capillary flow path of low resistance between soil pores.

On the basis of the first proposition, Philip and De Vries compute the temperature gradient across the pores in a soil water system as a function of the volumetric moisture content, the sum of the air-filled voids and volumetric moisture content, and the temperature. These considerations lead to the following equation:

$$\eta = \frac{A + \theta}{A_a} \frac{(\nabla T_a)}{(\nabla T)} \quad (1)$$

in which

A = volume of air-filled voids

θ = volumetric moisture content

a = tortuosity factor used in simple theory of gaseous diffusion in soils

$\frac{\nabla T_a}{\nabla T}$ = ratio of temperature gradient across pores to average gradient over system

η = ratio of moisture flow predicted by proposed theory to that predicted by the simple diffusion theory

The authors of the theory postulate that it will be invalid when either of the following situations arise:

1. When the moisture content θ exceeds some value θ_k , where θ_k refers to that moisture content at which the capillary conductivity is some arbitrary fraction of the capillary conductivity at saturation.

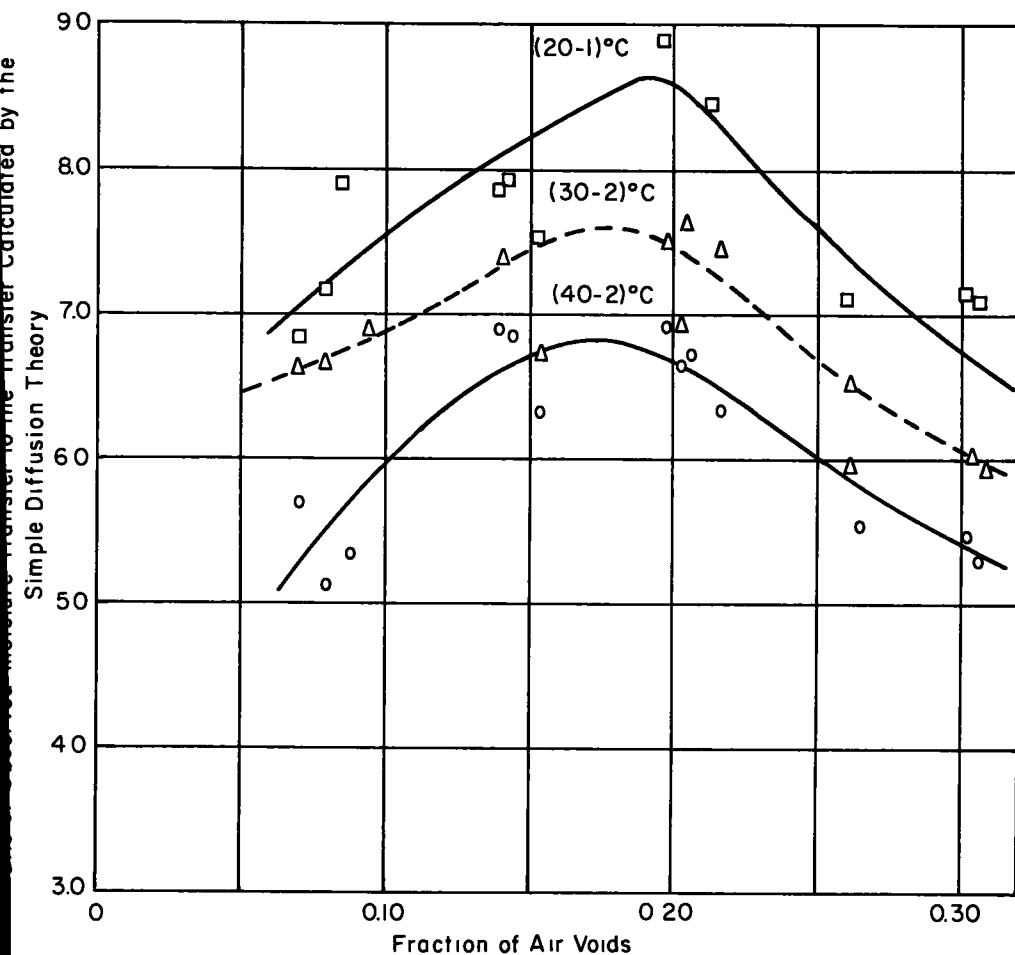


Figure 1. The relationship between ratio of the observed moisture transfer to calculated transfer and the fraction of air-filled voids.

2. When the moisture content is less than θ_k but the density of the soil mass is such that $A < A_k$ where A_k is the volume of air-filled voids corresponding to θ_k .

If either of these two conditions exists, the quantity $A + \theta$ (Eq. 1) is assumed to be of the form $A + F(A) \cdot \theta$ where $F(A) = A/A_k$.

In the original paper by Philip and De Vries, some experimental data from the work of Rollins et al (4) was used as experimental verification of this theory. Additional experimental data accumulated since that time, but previously unpublished, are presented in Figures 1 and 2.

Figure 1 shows the relationship between ratio of the observed vapor transfer to that calculated by the simple diffusion theory as a function of the air-filled voids. The effect of temperature on this ratio is apparent. Simple vapor diffusion predicts an effect of this kind that is further magnified by the theory of Philip and De Vries inasmuch as the ratio of temperature gradient over the system possesses a small negative temperature coefficient.

Figure 2 shows the results of observed moisture transfer compared with the predicted values determined in accordance with the theory of Philip and De Vries. A_k for these calculations has been assumed equal to 0.2. The values on the ordinate for Curve 1 are the ratio of observed transfer to that calculated by the simple theory, while for

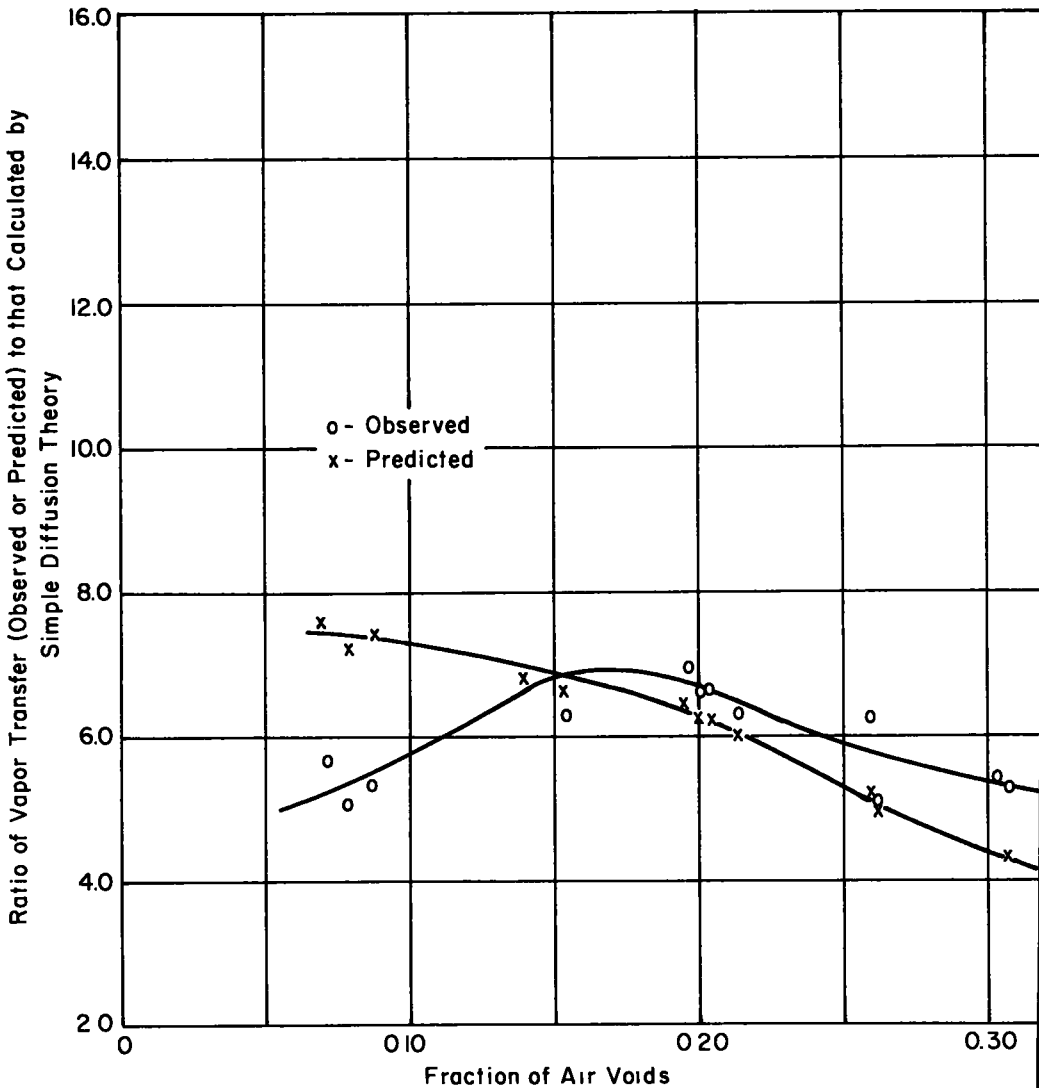


Figure 2. A comparison of observed vapor transfer to that predicted by Philip and De Vries.

Curve 2 the ratio is the quantity of flow predicted by the new theory divided by that predicted by the simple theory. The agreement is noted to be reasonably good to an air filled void fraction of about 0.15. More experimental information will be necessary definitely confirm this theory at low porosities.

The method used to compute the ratios of the temperature gradient across the pore to temperature gradient over the system was based on a method used by De Vries (5) for calculating thermal conductivities in soils.

It is interesting to note that since the symposium in 1958, Woodside and Kuzmak have performed an experimental investigation on the ratio of temperature gradient across the pore to that for the system. For this investigation they constructed an enlarged model of the grain-pore system. A temperature gradient was imposed on the model and temperatures measured at selected points throughout the system when equilibrium had been established. An open packing arrangement of spheres was used in the model and the thermal conductivities of the materials composing the model were se-

ected such that ratios K_s/K_a and K_s/K_w characteristic of the prototype were satisfied in the model. The values K_s , K_a , and K_w are, respectively, the thermal conductivities of the sand, air, and water. Throughout the pore the ratio of the temperature gradient to the over-all gradient varied from 22.4 to 1.9 for the system, solid and air, with an average of 6 over the entire pore. This value was shown to decrease somewhat when a system of air, water, and solid existed. On applying the theoretical method used by Philip and De Vries for determining this ratio to their system, a value of 2.04 was obtained. They conclude that the ratios obtained by Philip and De Vries are too low; however, they postulate a method of vapor transfer similar to those authors.

The maximum net transfer of moisture recorded by Hutcheon (1) is in agreement with others (7, 8, 9) who have noted this condition. It is also noted that the moisture contents at which maximum net moisture movement occurred are near the wilting point. This maximum movement is readily explained. At this moisture content the capillary conductivity is essentially zero. Movement of moisture toward cold side for the systems used must be vapor transfer. Inasmuch as these experiments were performed in a closed system, the observed migration of moisture is net transfer, and at the moisture contents corresponding to maximum flow the transfer is total transfer. The situation changes rapidly when the moisture content increases to the point where the capillary conductivity is significant. Return flow from cold to hot results with a corresponding reduction in net flow. At moisture contents less than that, corresponding to maximum flow, the relative humidity decreases rapidly with a resultant reduction in vapor pressure gradient.

Hutcheon concludes that the major mechanism of moisture movement is by vapor flow, which undoubtedly is true for that system but may not be true for other systems.

The moisture transfer apparatus described by Kuzmak and Sereda (10), in their article "On the Mechanism by Which Water Moves Through a Porous Material Subjected to a Temperature Gradient," appears to be an excellent piece of equipment. Their observation that no flow occurred in the system as long as the gap between the porous plates is saturated is in agreement with Hutchison et al (11) who demonstrated that thermo-osmotic flow in sintered glass discs did not occur. The experiments of Hutchison et al were a repetition of experiments performed by the Russian investigators Derjaguin and Sidorenkov who concluded that thermo-osmotic flow did occur in sintered glass plates. After modifying the apparatus by the Russian worker and thoroughly cleaning sintered plates, Hutchison observed not the slightest movements of water through the disc.

Kuzmak and Sereda also used the salt tracer technique in an effort to prove that no liquid movement occurred in the sand-water system used by them presuming, of course, that if no salt movement occurred then associated liquid flow was also absent. It becomes apparent that the salt tracer technique employed in this experiment is not conclusive in differentiating between liquid and vapor flow in the moisture transfer due to thermal gradient; it is, in reality, vapor transfer in series—parallel with transfer through a discontinuous liquid phase in the form of "islands" as proposed by Philip and De Vries and Woodside and Kuzmak.

A review of experiments on soil moisture movement due to thermal gradients indicates that most of the soils used have been sands, silts, or silty clay with low plasticity characteristics and, hence, the conclusion that no movement in the liquid phase occurs quite correct.

It appears likely that there exist in nature clay-water-gas systems possessing high specific surface and high plasticity characteristics in which movement in the liquid phase, or more specifically stated, the adsorbed phase, would be of considerable importance.

Winterkorn (12) has described such a system as one in which the clay-water system has no appreciable gas phase and the water is present in such proportions that even the molecules most distant from the solid surface are still under a certain relatively small fixation." Hutchison et al (11) have defined the thermodynamic requirement for moisture movement due to thermal gradient for this case. The resulting equation given by these authors is

$$\frac{DP}{DT} = \frac{Q^x}{VT}$$

in which

$\frac{DP}{DT}$ = pressures gradient in the system.

Q^x = heat adsorbed by system at one side and liberated at the other when 1 mole of water is transferred through the membrane.

V = molar volume of water.

T = temperature.

Hutchison states, "For example, if the transfer is affected by the passage through the membrane there may be heat adsorbed Q^x , when the substance dissolves in the membrane at one side and liberation of the same amount of heat when the substance passes out of the membrane at the other side. Since the temperatures are equal, the two entropy terms, $-Q^x/T$ and Q^x/T , exactly cancel and are therefore not usually considered. However, in the case of nonisothermal systems, the two entropy terms do not cancel. The heat effect, Q^x , must be allowed for and is the origin, in a thermodynamic sense, of phenomena such as thermo-osmosis."

Winterkorn (12) has used a similar approach to derive the pressure gradient associated with this type of moisture movement.

Baver and Winterkorn (13) have shown that water adsorbed by different aluminosilicates is a sensitive function of temperature, which implies that the heat of adsorption likewise increases as the temperature decreases. Table 1 taken from the data of Baver and Winterkorn dramatically displays this effect.

TABLE 1
WATER ADSORPTION BY DIFFERENT ALUMINOSILICATES
AS FUNCTION OF TEMPERATURE*

Colloid	Percent H ₂ O Adsorbed at Given Temperature			
	30°	40°	50°	80°
H-Bentonite	32.7	13.0	7.51	2.12
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
Strength of H ₂ SO ₄ -H ₂ O mixture used to maintain constant humidity	10	41.5	52.75	68.75

* Vapor pressures = 30 mm Hg, relative humidity = 94 percent at 30°.

Because the energy of adsorption of coarse textured soils is very low, the effect of a temperature gradient in systems of this kind would not be expected to cause appreciable movement in the adsorbed phase. On the other hand, it appears that the theoretical concept requiring flow of moisture in the adsorbed phase in certain systems as described above is well established and that research efforts could be profitably spent in this area.

REFERENCES

1. Hutcheon, W. L., "Moisture Flow Induced by Thermal Gradients Within Unsaturated Soils." HRB Special Report 40, 113-133 (1958).
2. Philip, J. R., "Physics of Water Movement in Porous Solids." HRB Special Report 40, 147-163 (1958).
3. Philip, J. R., and De Vries, D. A., "Moisture Movement in Porous Materials Under Temperature Gradients." Trans. Amer. Geophys. Union, 38:222-232 (1957).

4. Rollins, R. L., Spangler, M. F., and Kirkham, D., "Movement of Soil Moisture Under a Thermal Gradient." HRB Proc., 33:492-508 (1954).
5. De Vries, D. A., "Het Warmtegeleidingsvermogen van Grond." Med. Landbouwhogeschool, Wageningen, 52:1-73 (1952).
6. Woodside, W. A., and Kuzmak, J. M., "Effect of Temperature Distribution on Moisture Flow in Porous Materials." Trans. Amer. Geophys. Union, 39:676-680 (1958).
7. Smith, W. O., "Thermal Transfer of Moisture in Soils." Trans. Amer. Geophys. Union, 24:511-523 (1943).
8. Jones, H. E., and Kohnke, H., "The Influence of Soil Moisture Tension on Vapor Movement of Soil Water." Soil Sci. Soc. Amer. Proc., 16:245-248 (1952).
9. Gurr, C. G., Marshall, T. J., and Hutton, J. T., "Movement of Water in Soil Due to a Temperature Gradient." Soil Sci., 74:335-356 (1952).
0. Kuzmak, J. M., and Sereda, P. J., "On the Mechanism by Which Water Moves Through a Porous Material Subjected to a Temperature Gradient." HRB Special Report 40, 134-146 (1958).
1. Hutchison, H. P., Nixon, I. S., and Denbigh, K. G., "The Thermo-Osmosis of Liquids Through Porous Materials." Discussion Faraday Society, No. 3:86-93 (1948).
2. Winterkorn, H. F., "Water Movement Through Porous Hydrophilic Systems Under Capillary, Electrical and Thermal Potentials." ASTM Special Publication No. 163:27-35.
3. Baver, L. D., and Winterkorn, H. F., "Sorptions of Liquids by Soil Colloids: II. Surface Behavior in the Hydration of Clays." Soil Sci., 40:403-419 (1935).

Supplementary Statements by Authors of Original SR-40 Papers

Streaming Potential and Moisture Transfer in Soil upon Freezing as a Function of Porosity of Soil

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This article brings up to date the author's work on soil moisture transfer upon freezing and verifies experimentally the existence of various soil moisture transfer mechanism ranges as a function of porosity, as theorized by the author in 1958.

● IN A PAPER presented at the Highway Research Board's International Symposium on Water and Its Conduction in Soils, entitled "Some Concepts Pertaining to the Freezing Soil Systems," the author theorized about various soil moisture transfer mechanisms and their assumed effects on the amounts of soil moisture transferred as a function of porosity of the packing of the soil system. The degree of packing is very important to know, as this gives a clue to what mechanism in the upward soil moisture transfer in the freezing soil system would be most likely to take place; film flow, film-capillary flow, film-vapor flow, or pure vapor diffusion, or a combination of some of the aforementioned flow mechanisms.

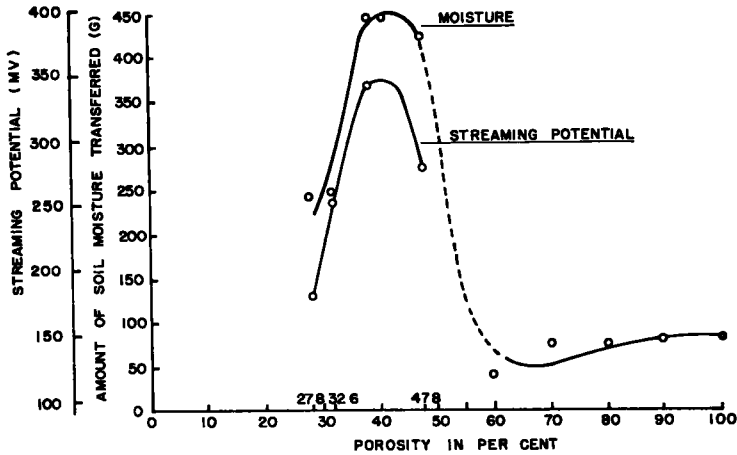
Since 1958 the author has been engaged in experimental studies to establish the porosity ranges of soil packings at which one or another soil moisture transfer mechanism would be most effective. There are, of course, no sharp porosity boundaries at which one kind of flow mechanism would cease and another, different mechanism assume its existence. Rather, there is a more or less pronounced transition from one moisture transfer mechanism to another depending on the porosity of the soil packing. In these transition zones two adjacent effective moisture transfer mechanisms may co-exist.

The instrumentation used in these experiments is described in the author's symposium paper.

The results of such an experimental study are shown in Figure 1. The soil packings were made of Dunellen soil, a silty glacial outwash. The amounts of soil moisture transferred and streaming potential measured in the freezing soil systems are given for the time lapse of 168 hr of freezing at temperatures $T_S = 20$ C at the upper surface of the vertical cylindrical soil system and $T_W = 8$ C at the ground-water table (lower end of the system).

The summary of the test data is also shown in Figure 1. Between porosities of about $n = 27.8$ and about $n = 50$ percent (particles in contact) the effective soil moisture transfer mechanism is by way of film flow; from porosity of about $n = 50$ percent to about $n = 60$ percent there exists simultaneous film and vapor flow (large voids, particles still in contact). From porosity about $n = 60$ percent to about $n = 100$ percent (soil particles not in contact) effective soil moisture transfer mechanism is by way of pure vapor diffusion. Here porosity of $n = 100$ percent means an empty cylinder.

The maximum amount of vapor diffused (at $n = 100$ percent), though, constitutes only about 20 percent of the maximum amount of soil moisture transferred in the effective film phase (at about $n = 40$ percent).



TEST NO		B-6	B-9	B-7	B-5	A-6	A-5	A-3	A-4	A-2
EFFECTIVE MOISTURE TRANSFER MECHANISMS		LOWER POROSITIES THAN N = 27.8 % DIFFICULT TO ATTAIN IN PRACTICE		EFFECTIVE FILM FLOW		FILM AND VAPOR FLOW	PURE VAPOR TRANSFER			
OPTIMUM M C IN %		12.6	15.3	13.8	12.4	-	-	-	-	-
MAXIMUM DRY DENSITY IN LB/FT ³		119.8	119.7	102.1	86.7	63.0	46.5	29.9	13.4	0
VOID RATIO (e)		0.385	0.484	0.636	0.916	1.50	2.33	4.00	9.01	∞
AMOUNT OF MOISTURE TRANSFERRED	ABSOLUTE AMOUNT IN GRAMS	239.0	250.0	445.6	424.0	41.0	77.0	75.0	82.0	83.0
	RELATIVE TO MOISTURE TRANSFERRED AT 100 % POROSITY	2.88	3.01	5.47	5.11	0.49	0.93	0.90	0.99	1.00
STREAMING POTENTIAL IN MV		180	250	340	275					

Figure 1. Moisture transfer and streaming potential in soil upon freezing as a function of porosity.

In conclusion, these experiments in general make clear that:

1. The amount of soil moisture transferred upon freezing as a consequence of an externally applied freezing temperature gradient to the soil system is a function of porosity of the packing of the soil;
2. Depending on the porosity of the packing, moisture may be transferred upward from ground water towards the cold front by way of various moisture transfer mechanisms; and
3. Vapor transfer is a relatively ineffective soil moisture transfer mechanism; that is, soil moisture transfer in the film phase takes place virtually unaccompanied by vapor diffusion.

Water Movement in Porous Solids:

Some Recent Progress

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This report gives some recent contributions to the diffusion analysis of water movement in unsaturated solids, to the thermodynamics of water held in such solids, to moisture movement under temperature gradients, and to the study of the effects of entrapped air*. The latter, rather novel, field of inquiry has theoretical and practical implications of great importance.

● THIS SHORT communication is essentially a footnote to the author's symposium article (1). In accordance with the Chairman's suggestion, certain more recent work with which the author has been associated is reported.

LIQUID FLOW OF WATER IN UNSATURATED POROUS SOLIDS

Early Stages of Absorption and Infiltration

The author's article (1) stated that it is "possible that perceptible deviations from Darcy's law may occur during the very early stages of absorption or infiltration into unsaturated systems." This was expected because the "diffusion analysis" predicts that, very close to the start of these phenomena, the flow rate, and hence the Reynolds number of the system, must be so large that Darcy's law fails. Further, Darcy's law implies a force equilibrium with no resultant to impart momentum to the system, which is initially at rest. These considerations suggested that the diffusion analysis might be open to some question, at least during the early stages of phenomena such as absorption and infiltration.

An analysis based on Newton's second law has been carried out and has resolved these various difficulties. The net result is that the error in the diffusion analysis due to the neglect of inertia effects is entirely negligible, except for a short initial period of less than 10^{-4} sec; the maximum Reynolds number of the motion is shown to be finite and the observed small deviations from the diffusion analysis during the early stages of absorption and infiltration are in the wrong sense to be explained as due to inertia or high Reynolds number. They appear to be due to the effects of entrapped air. This work is fully reported by the author (2).

Viscous Dissipation of Energy During Absorption and Infiltration.

The problem of just when and where energy is dissipated in unsaturated porous solids when they are taking up water does not seem to have been investigated hitherto. An investigation of the viscous dissipation of energy during this process has been carried out, and is an extension of the previous diffusion analysis. One by-product of the study is a novel definition of hydraulic conductivity in which it is related to the point rate of viscous dissipation in the solid. The profiles of energy dissipation reveal a characteristic peak near the "wet front" in terms of energy dissipation. This study is described by the author (3, 4).

* Chairman's note: See statement concerning effect of entrapped air, IRB Special Report 40:335 (1958); also, "Das Verhalten des Bodens gegen Luft," Handbuch der Bodenlehre, Julius Springer Verlag, Berlin, 6:253-342 (1930).

Absolute Thermodynamic Functions in Study of Porous Solids

The potential function commonly used in soil-water studies is equivalent to the specific differential Gibbs function. It has been found (5) that it is more useful in problems in which one wishes to examine changes in the total potential energy of the system to use the absolute form of thermodynamic function. As an example, the differential function does not distinguish between the energy state of water in a saturated porous solid and that of free water at the same level. The absolute function does so.

Mathematics of Concentration-Dependent Diffusion

The mathematics of concentration-dependent diffusion is basic to the diffusion analysis of water movement in unsaturated solids. Hitherto, numerical methods have been necessary to solve these problems, except in certain quite special cases. A general method of solution of problems in concentration-dependent diffusion by analytical means has been developed (6) and promises to make the mathematical problem more tractable. Details of a function entering into this new method are given in a second paper (7).

MOISTURE MOVEMENT UNDER TEMPERATURE GRADIENTS

Although there seems to be general agreement that the theory of moisture movement in porous solids under temperature gradients put forward by Philip and De Vries (8) is broadly correct (9), certain workers appear to have misunderstood some aspects and to have been led into erroneous criticisms (10). De Vries and Philip (1) emphasize the differences between the fine structure of the temperature field and the vapor field and clear up other misconceptions that have arisen.

EFFECTS OF ENTRAPPED AIR IN POROUS SOLIDS

For quite some time now, the presence of entrapped air in naturally saturated porous solids (12) and its effect on hydraulic conductivity of such solids (13) have been clearly recognized. Recognition of the importance of the air-phase in unsaturated solids has been somewhat more tardy.

The possibility that entrapped air would produce nonuniqueness of the moisture potential function in the surface layers of a porous solid was recognized (14) in 1955. This explained the characteristic "dog-leg" transition zone observable in moisture profiles during infiltration (15) and also the observed small deviations from the diffusion analysis (2).

Temperature Dependence of Moisture Potential

Another phenomenon that has long been puzzling is the failure of the temperature dependence of moisture potential to be related in any consistent manner to the temperature dependence of surface tension. A proper understanding of the temperature dependence of moisture potential is necessary before the problem of liquid phase transport under temperature gradients can be studied in a meaningful way.

In the author's symposium paper (1) it was stated that "the explanation seems to be that as temperature 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 experiments and a detailed working-out of the theory confirm the suggestion made in HRB Special Report 40. Peck has been responsible for the experimental program and for going into the details of the theory. He has reported part of the work (16) and has a further paper in preparation.

Effect of External Air Pressure on Moisture Potential

Intimately connected with the temperature effect previously discussed is the effect of changes of the external pressure on the volume of entrapped air, and hence on meniscal configuration and on moisture potential.

Experimental work has confirmed the reality of the effects of external air pressure which the "trapped air" theory demands (16). This effect is also of great practical importance. For example, systematic changes of water table level with atmospheric pressure are to be expected, and have been observed experimentally by Peck (17).

Perhaps of greater importance is the fact that this work indicates that moisture characteristics determined by pressure-plate methods do not necessarily agree with those determined by "suction" methods. There will certainly be important discrepancies at the wet end of the moisture range. It is more difficult to predict the importance of this effect at moisture potentials greater than 1,000 cm.

The significance of this work on trapped air for soil mechanics is that it underlines the importance of treating the soil as a three-phase system—solid, liquid, and gas. Perhaps all have been too prone to work with the two-phase system of just soil particles and water.

REFERENCES

1. Philip, J. R., "Physics of Water Movement in Porous Solids." HRB Special Report 40:147-163 (1958).
2. Philip, J. R., "The Early Stages of Absorption and Infiltration." *Soil Sci.*, 88: 91-97 (1959).
3. Philip, J. R., "Energy Dissipation During Absorption and Infiltration: 1." *Soil Sci.* 89 (1960).
4. Philip, J. R., "Energy Dissipation During Absorption and Infiltration: 2." *Soil Sci.* 89 (1960).
5. Philip, J. R., "Absolute Thermodynamic Functions in Soil-Water Studies." *Soil Sci.* 89 (1960).
6. Philip, J. R., "General Method of Exact Solution of the Concentration-Dependent Diffusion Equation." Submitted for publication, *Austral. Jour. Phys.*
7. Philip, J. R., "The General Function $\text{inverfc } \theta$." Submitted for Publication, *Austral. Jour. Phys.*
8. Philip, J. R., and De Vries, D. A., "Moisture Movement in Porous Materials and Temperature Gradients." *Trans. Amer. Geophys. Union*, 38:222-232 (1957).
9. Gardner, W. R., "Soil Water Relations in Arid and Semi-Arid Conditions." UNESCO Arid Zone Symposium, Madrid (1959).
10. Woodside, W., and Kuzmak, J. M., "Effect of Temperature Distribution on Moisture Flow in Porous Materials." *Trans. Amer. Geophys. Union*, 39:676-680 (1958).
11. De Vries, D. A., and Philip, J. R., "Temperature Distribution and Moisture Transfer in Porous Materials." *J. Geophys. Res.*, 64:386-388 (1959).
12. Smith, R. M., and Browning, D. R., "Persistent Water Unsaturation of Natural Soil in Relation to Various Soil and Plant Factors." *Soil Sci. Soc. Amer. Proc.*, 7:114-119 (1942).
13. Christiansen, J. E., "Effect of Entrapped Air upon the Permeability of Soils." *Soil Sci.* 58:355-365 (1944).
14. Philip, J. R., "The Concept of Diffusion Applied to Soil Water." *Proc. Nat. Ac. Sci. (India)*, 24 A:93-104 (1955).
15. Philip, J. R., "The Theory of Infiltration: 3." *Soil Sci.*, 84:163-178 (1957).
16. Peck, A. J., "The Change of Moisture Tension with Temperature and Air Pressure: Theoretical." *Soil Sci.* (1960).
17. Peck, A. J., "The Water Table as Affected by Atmospheric Pressure." Unpublished manuscript.

Design Correlations for Red and Kenya Red-Brown Soils

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● WITH THE accumulation of further data and especially data in relation to particular roads, it has been necessary to revise the general curves slightly and it has been possible to produce particular curves applicable to specific roads or to lengths of specific roads each of which exists under apparently similar climatic and geological conditions. The new curves so obtained are given in Figures 7 and 8.

In a restricted way they could, perhaps, be described as pedological design curves. The curves for specific roads are, in general, based on points showing remarkably little scatter.

The most clearly defined curves were obtained for the Mau Summit-Kericho road, some 29 mi long, which, for most of its length, climbs up a narrow valley characterized by high rainfall and dark brown surface soils containing appreciable organic matter residues, until it reaches a relatively undulating area of higher rainfall where the Red Tea soils are found. As soon as the tea area is reached the correlation curve changes. Between the two there is a short transition stage in which there is some scatter.

The Thika-Sagana-Nyeri road (some 65 mi) did not lend itself to any simple correlation pattern. This road crosses plains and mountainous country passing through a number of rainfall belts.

The Mau Summit-Eldoret road (64 mi), over very fine light red soils, similar perhaps to Red Coffee soils, calls for an almost constant thickness of pavement 12 in. for Procuro compaction throughout. The rainfall lies wholly within the same belt from one end to the other.

Though reference is made to Red Coffee and Red Tea soils, this does not necessarily mean that the subgrades were invariably constructed in such materials. Where this material was not used—and this seems of importance—they were constructed in material obtained from lower horizons of such profiles. In these relatively young soils, the parent material seems to exercise a control over the road engineering properties of all horizons over that material.

There is the apparent transition between parent material and the subsoil layer which takes the form:

basic tuff————→decomposed tuff containing mainly hydrated halloysite————→dehydrated halloysite where the degree of hydration decreases as the surface layer is approached.

The decomposed tuff appears to contain montmorillonite but there is no known record of the montmorillonite persisting in the soils over that horizon. This presence may well supply an explanation for the worst correlation curves; that is, those calling for high pavement thicknesses, pertaining to decomposed stone, soil adulterated with some decomposed stone, as well as to some black cotton soils. The possibility of allophane being present at some stage or in one of the horizons is not, however, to be ruled out. It has since been ascertained by W. Arthur White, Geologist and Head, Clay Resources and Clay Mineral Technology Section, State Geological Survey Division, Urbana, Ill., that allophane was present in two samples of soil sent him from Kenya.)

A low CBR soil from the Mau Summit-Kericho road was recently investigated to determine, if possible, the reason for its low load carrying capacity. Though the swelling

This paper, printed in HRB Proc., 39:683-694 (1960) represents a logical extension and practical application of the HRB Special Report 40 paper entitled, "Moisture Content and the CBR Method of Design." This is the reason for including these supplementary remarks.

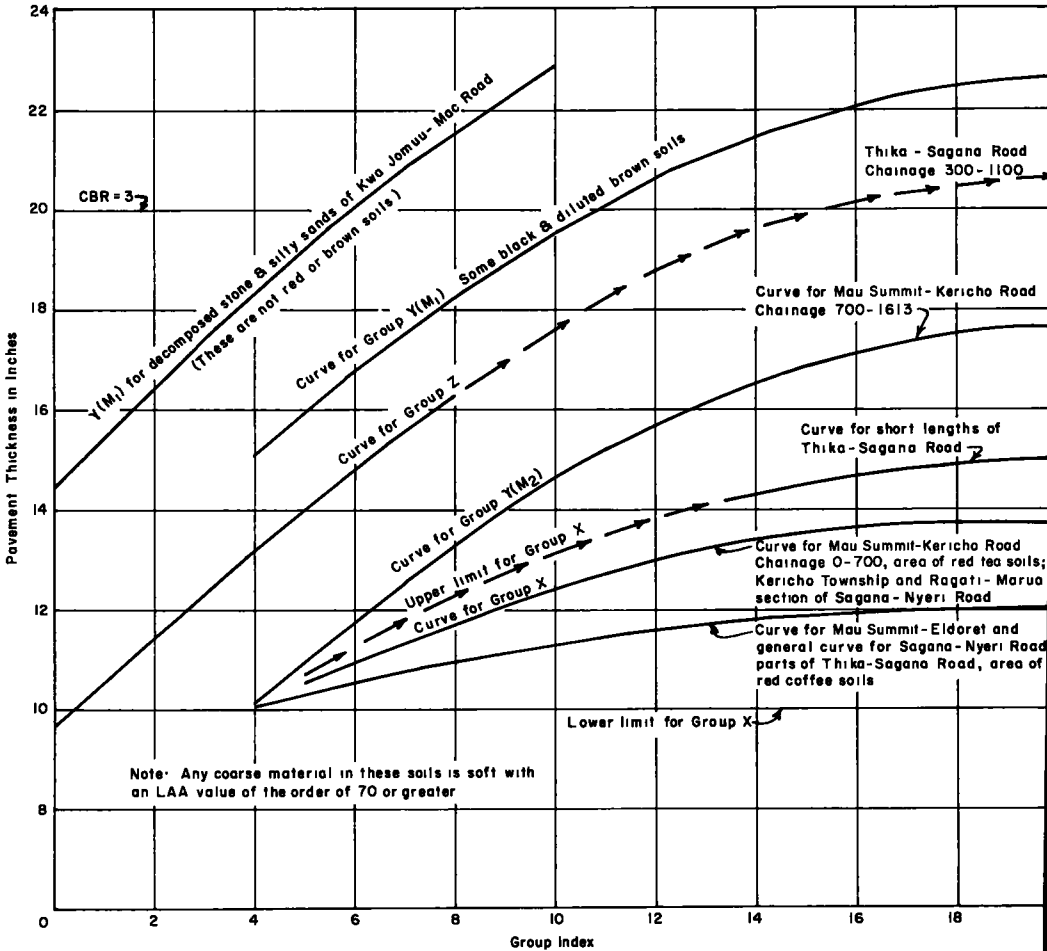


Figure 1. Pavement thicknesses for various subgrade soil groups when compacted to Proctor maximum density (9,000-lb wheel load).

pressure was found to be just under 1 ton per sq ft at Proctor (OMC + MD), the only clay minerals recognized, by X-ray analysis, were metahalloysite and possibly a small amount of hydrated halloysite with feldspar and quartz. (Exposure to the drying action of the sun for a day or two is sufficient to convert thin layers of hydrated halloysite to metahalloysite. Montmorillonite appears to be formed, as an intermediate product, during the more normal weathering of hydrated halloysite to metahalloysite.)

The form of the correlation curves (Figs. 1 and 2) is of interest. A number of curves appear to pass approximately through the common point represented by a constant pavement thickness for a G. I. value of 4 representing a change from a silt-clay material to a granular material under the Don Steele method of classification. For lower G. I. values the pavement thickness required would seem to remain constant, as might be expected. For the other materials, this does not appear to apply in toto and the pavement thickness required continues to decrease as the material becomes more granular. It should be remembered, however, that the so-called granular fraction of the vast majority of Kenya soils consists mainly of soft lateritic material or soft decomposed stone though within the larger particles there may be some small fraction of harder small particles as of iron oxides.

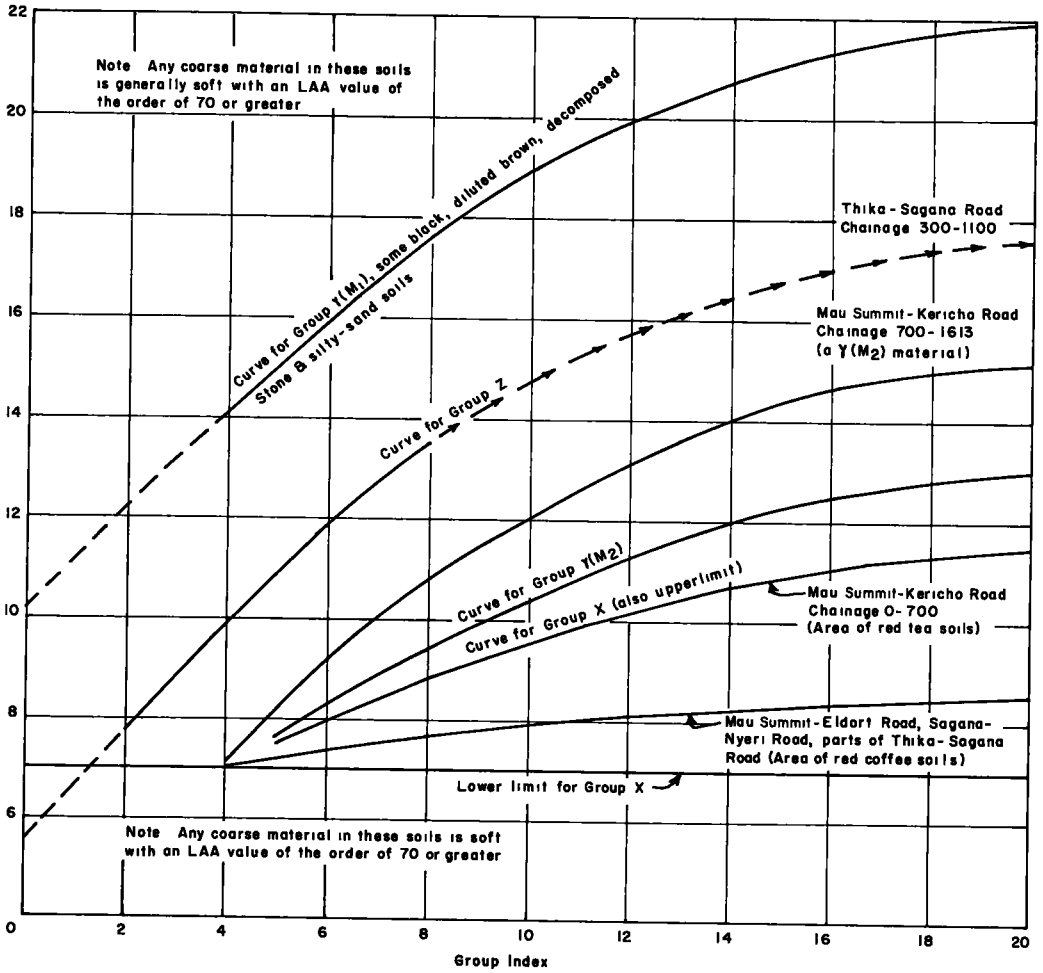


Figure 2. Pavement thicknesses for various subgrade soil groups when compacted to half-modified maximum density (9,000-lb wheel load).

An endeavor was made to group the various materials on the basis of their "clay activity," as determined by $\frac{PI}{100} \times \frac{(-36)}{\text{clay } \%}$, but no recognizable tie-up or semblance of a tie-up was noticeable in respect of pavement thickness.

Water Dislodgment in the Soil

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● THE WATER in the soil, due to the existence of gradients of the principal forces, such as capillary and hydraulic, are in continuous movement, which takes place together with a total or partial dislodgment of the free water present in the soil by the entering water.

The possibility of dislodging the soil solution with the water (or with the solution) is well known in the literature since Schloesing (1). In the course of the last 100 years there have been proposed different variations (2-7). In all these variations the water (or solution, or some other dislodging liquid) fills all the pores of the upper part of the column, and, infiltrating under the hydrostatic pressure, dislodges mechanically the free water present in the soil. Hence, in order to separate the existing water in the soil a high column must be used. In order to reduce the porosity, Kriukov (6) recommends, in addition, to submit previously the soil to a high pressure.

It is evident that in the limit of two solutions a mixture will inevitably be formed due to mutual diffusion. The formation of a mixture will also be favored by the speed of the infiltration and by the structure of the pores.

A disperse system of fine and open pores would be ideal for the complete dislodgment of the free water present in the pores. The failure of many methods proposed formerly for the dislodgment of the soil solution is a consequence of the speed applied.

The dislodgment of the water that is not free (adsorbed) is possible by its substitution with some other miscible liquid, like ethyl alcohol. The dislodgment takes place not by a simple displacement of one liquid by another but by the diffusion of the adsorbed water in the displacing liquid. Liquids which do not mix with water (benzol, etc.) are incapable of dislodging the adsorbed water by the adsorbent and especially by the soil.

Leaving out the dislodgment by infiltration the dislodgment by the capillary movement is considered next. In the course of the capillary saturation the water does not completely fill the pores; therefore, it would be interesting to see to what degree of completeness the dislodgment occurs.

Straprens (8) showed that water in the sand at 3.3 percent moisture begins to move when the limit of capillary elevation is at a distance of 10 cm. This means that the capillary and film water in the sand at that moisture is displaced by the entering water at a distance of 10 cm.

If the sand is well mixed with 2 percent of the solution of a nonadsorbable dye (brophenol green) and a tube is filled and placed for capillary rise, then the entering water dislodges the solution of the dye and pushes it to the extreme point of the upper part. For a tube 10 cm long, the dye accumulates in the upper part at 0 to 2 cm. This experiment shows that the water entering by capillary rise is capable of dislodging the free water that was present there before. To establish the totality of dislodgment a few experiments were made; these are described later.

Some authors (for instance, 9) think that it is difficult to establish the quantity of dislodgeable water. Nevertheless, by starting from some evident assumptions the problem can be solved with sufficient approximation. To begin with, it may be supposed that the undislodgeable is also the adsorbed water and at the same time also that which does not dissolve the indicator whose solution is applied as a dislodging agent (for instance, KCl solution). Then, if the soil contains the dislodgeable water the chloride solution will diminish its concentration, and in the contrary case the KCl concentration will increase. Errors may occur if the undislodgeable but dissolving water for the indicator is contained therein. In this case the real volume of undislodgeable water

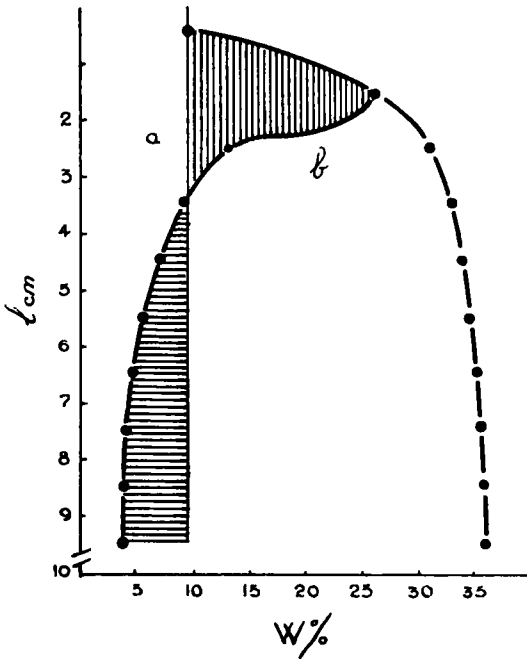


Figure 1. Water dislodgment by the capillary rise of 0.10 N KCl solution in the soil which contained 9.5 percent of water. Ordinate: l —height of the soil column in cm; abscissa: W —water content in percent: a—water content before the capillary rise; a + b)—water content after the capillary rise. Entered water—horizontal lines; dislodged water—vertical lines.

should be somewhat greater than calculated. Such an error would be of insignificant importance here, because in a soil of a 29 percent field capacity there would only remain a small percentage of dislodgeable water, as shown later.

Prairie soil with a field capacity of 29 percent and an exchange capacity of 37 me per g was passed through a sieve of 1mm. Different samples of this soil with a variety of moisture contents as well as different KCl contents were prepared. With these samples plastic tubes of $\phi = 2.5$ and 10 cm long were filled with a homogeneous densification. Soil columns thus obtained were arranged for capillary rise of water or KCl solution. Thus, the soil water was dislodged by 0.10 N KCl and the KCl solution in its turn by the water.

Thereafter the capillary rise samples were taken at each height (every 1 cm of thickness) and the water and KCl contents made it possible to calculate the dislodgment for each height.

First of all, the possibility of obtaining the water (or the solution) without mixing with the solution (or water, respectively) entering by capillary rise was investigated. The following experiment shows that the major part of the water (or solution) that the soil contained was dislodged by the solution (or water) without forming any mixture.

The soil with a 9.5 percent content of water was put to capillary saturation with 0.1 KCl. When the rise reached the surface, the water and KCl content of each cm of column was determined. The results of the calculations of dislodgment for each height are given in Figure 1.

These curves show that layer 0.5 - 1.5 cm contains the water that formerly existed in the soil. The following layers contain a mixture. A simple look at the displacement curve will give an idea about the amount of undislodgeable water, which should correspond or be equivalent to the adsorbed water. As is well known, the quantity of adsorbed water is a function of the concentration of the electrolyte in equilibrium. It may be as-

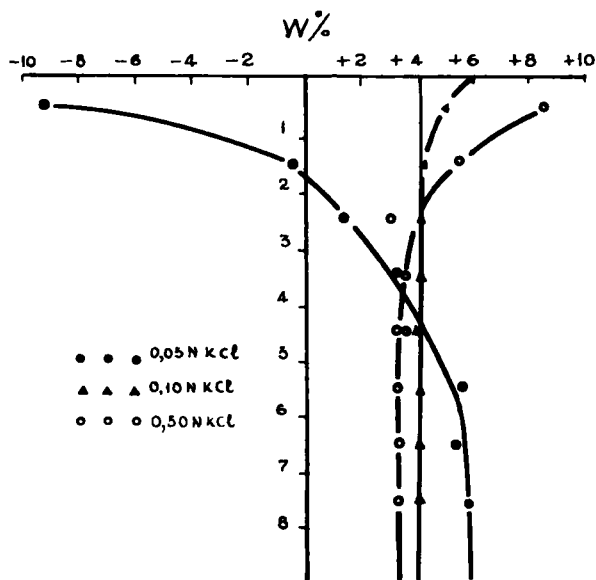


Figure 2. Water dislodgment by the capillary rise of KCl solutions: 0.05 N; 0.10 and 0.50 N in the soil which contained $\frac{1}{4}$ percent of water. Ordinate: l —height of the soil column in cm; abscissa: W —water content (without KCl solutions) after the capillary rise. The negative and positive values give the water quantity with and without which the electrolyte concentration would not change.

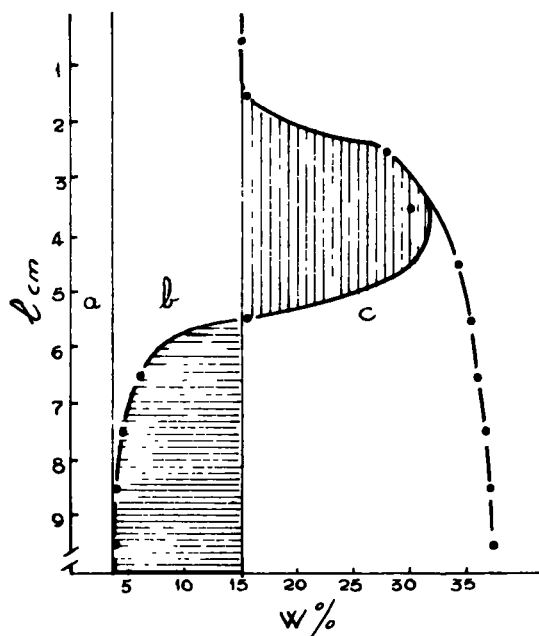


Figure 3. Water dislodgment by the capillary rise of 0.10 N KCl solution in the soil which contained 15 percent of water. Ordinate: l —height of the soil column in cm; abscissa: W —water content in percent: a —adsorbed water content; $(a + b)$ —water content before the capillary rise; $(a + b + c)$ —water content after the capillary rise. Entered water—horizontal lines; dislodged water—vertical lines.

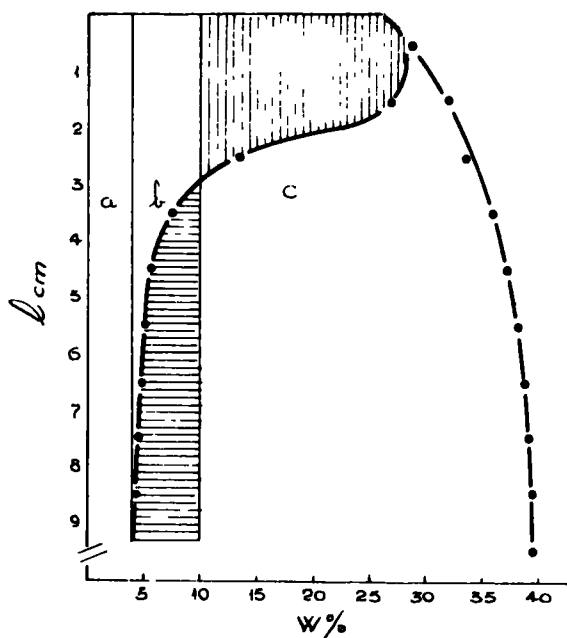


Figure 4. Water dislodgment by the capillary rise of water in the soil which contained 8 percent of water and 6 percent of 0.1 N KCl solution. Ordinate: l —height of the oil column in cm; abscissa: W —water content in percent: a —adsorbed water content; $a + b$ —water content before the capillary rise; $(a + b + c)$ —water content after the capillary rise. Entered water—horizontal lines; dislodged water—vertical lines.

umed that the amount of undislodgable water will also be a function of the concentration of the electrolyte.

Experiments have shown effectively that the amount of undislodgable water is a function of the concentration of the dislodging solution. Thus, when dislodging by the KCl solutions of 0.05 N, 0.10 N, and 0.50 N there were found in this Prairie soil the following quantities of undislodgable water: 5.8, 3.8, and 3.2 percent.

Figure 2 gives the curves of dislodgment of the soil water (4 percent) by the solutions of 0.05 N, 0.10 N, and 0.50 N of KCl. The negative and positive values give the water quantities with and without which the electrolyte concentration would not change. The obtaining of different quantities of the undislodgable water, when applying the solutions of different osmotic pressures, confirms the idea of the existence of the polymolecular layers on the surface of the particles.

Figures 3 and 4 show the results of dislodgement of the water by KCl and, on the other hand, of the KCl solution by the water. By means of capillary rise all the free water in the soil can be dislodged and even a great part of it without forming a mixture.

Finally, Figure 5 shows the dislodgment by capillary rise in sand. According to Radogovski (9), by infiltration 3 to 5 percent remains without being dislodged. By using a column of 9 cm of sand with a 5 percent 0.10 N solution of KCl it was possible to dislodge this almost completely by capillary rise of water.

The method of dislodgment can also be used to calculate the change of free energy (Gibbs energy) in function of water content because the osmotic pressure makes such calculations possible.

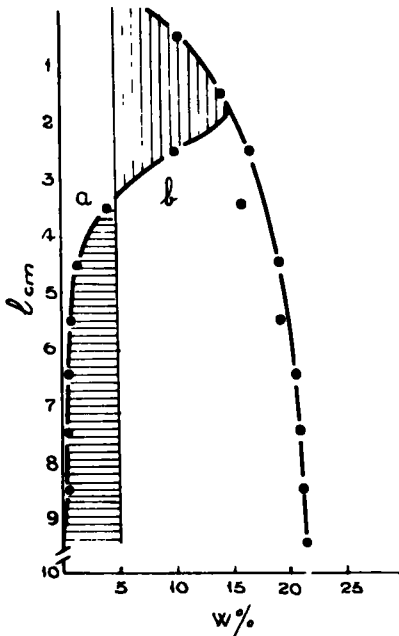


Figure 5. Water dislodgment by the capillary rise of water in the sand, which contained 5 percent of 0.1 N KCl solution. Ordinate: l —height of the soil column in cm; abscissa: W —water content in percent; a —solution content before the capillary rise; $(a + b)$ —solution and water content after the capillary rise. Entered water—horizontal lines; dislodged water—vertical lines.

SUMMARY

1. The capillary movement of water in the soil is accompanied by complete dislodgment of the free water present in the soil.
2. The dislodged water mixes partially with entering water and one part is left without forming any mixture being detained on the wetting front.
3. The amount of undislodgable water is a function of the concentration of the electrolyte in equilibrium.

REFERENCES

1. Schloesing, T., C.R. Acad. Sci., 63:1007 (1866).
2. Ishcherekov, V.I., Zh. op. Agr., 8:147 (1907).
3. Parker, F.W., Soil Sci., 12:209 (1921).
4. Conrad, J.P., et al, Soil Sci., 29:323 (1930).
5. White, L.M., and Rosse, W.H., J. Agr. Res., 59:81 (1939).
6. Kriukov, P.A., "Sovrem. metody isll. f-Khim. sv. pochv." T.4 (1927).
7. Komarova, N.A., Trudy Pochv. Inst., 60:5 (1955).
8. Straprens, V., Migracia kapillarno-sv. vlagi (1954).
9. Budagovski, A.I., Vpityvanie vody v pochvu (1955).

Papers on the Use of Nuclear Magnetic Resonance to Determine State of Water In Soils and Similar Systems

Introduction

HANS F. WINTERKORN

You have seen and heard numerous illustrations of the complex properties of soil-water systems. For the behavior of the water substance in such systems, we must hold the geometric, electric, and magnetic properties of the water molecule responsible that determine the interactions with molecules of its own kind and with ions, atoms, and molecules of different kinds. The latter may themselves be relatively free or fixed in position as in the surfaces of the soil minerals. The pertinent properties of the water molecule and the consequences of these properties with respect to the structure of the liquid water substance are masterfully presented in the paper by Buswell and Rodebush. One of the consequences of the hexagonal layered molecular structure of the water substance vicinal to clay mineral surfaces is the difference in its mechanical resistance properties parallel and normal to these surfaces. Hence, such water may possess a more "liquid" character in one direction and a more "solid" character normal to this direction.

Some may think that to solve our engineering problems we have gone far enough or perhaps too far to be concerned with particles as small as the water molecule. As a matter of fact, nobody knows how far down or how far up one has to go in the size scale to obtain pertinent information. This is well illustrated by the next three presentations. Much can be learned about the water molecule and its interaction with soil minerals from its protons, which are about a thousand times smaller than the water molecule. The method of learning involves radio waves whose wave lengths are more than ten million times the diameter of the water molecule. This refers, of course, to the method of nuclear magnetic resonance. Some time ago I read a very fine paper in the Journal of Geophysical Research entitled, "An Investigation of Shear Strength of the Clay-Water System by Radio-Frequency Spectroscopy," by A. G. Pickett and M. M. Lemcoe of the Southwest Research Institute of Texas. I was so impressed that I asked Mr. Pickett to contribute to the conference.

While in Washington these last few days, I found out that there were two other scientists in attendance who are deeply concerned with the use of nuclear magnetic resonance as a tool to determine the state of restraint of water molecules in clay-water-, portland cement paste-, crystalline hydrates, and similar systems. These gentlemen are Dr. Gaine of the National Bureau of Standards and Dr. Seligman of the Portland Cement Association. They, also, kindly agreed to contribute to the program.

Proton Magnetic Resonance in Clay Minerals

R. L. BLAINE, Inorganic Building Materials Section, National Bureau of Standards

Nuclear magnetic resonance energy absorption line widths within the region of proton resonance were determined for a number of clays and related materials at room temperature. The line widths were calculated from the horizontal distances between the maxima and the minima of the derivative absorption curves obtained with a 1720-gauss proton-magnetic-resonance apparatus. Line widths in order of decreasing proton mobility were found to be approximately 3 gauss for pyrophyllites, 6 gauss for kaolins and halloysites, 9 gauss for a sepiolite, and 11 to 12 gauss for a bayerite and a bauxite. Illites and montmorillonites gave only narrow line widths (0.3 to 0.7 gauss) in the semi dry state, but exhibited some less mobile hydrogen (line width of 2 to 3 gauss) after drying at 200 C. Except for bayerite, bauxite, and sepiolite, the clays did not exhibit the wide lines frequently associated with either hydroxide groups or water of crystallization or as determined for brucite and gibbsite. A sample of montmorillonite frozen with liquid nitrogen and slowly thawed in the apparatus indicated that greatly increased proton mobility began at about -70 C.

● THE ROLE and position of the hydroxide groups and water in clay minerals have been the subject of extensive research for many years. Many techniques have been utilized by research workers in determining the atomic structure of the various types of clays. Grim (1), Marshall (2), Rigby (3), Hendricks (4), and many others have summarized research on the different clay minerals and presented structural arrangements. Hydroxides and water molecules are important groups in most of the proposed structures. However, the nature and position of the hydrogen of the hydroxides or the water in clay minerals are difficult to ascertain and have been the subject of much conjecture.

Nuclear magnetic resonance apparatus, tuned to the proton-resonance frequency (PMR), has been used to study the hydrogen in both organic and inorganic materials. The technique was originally developed, almost simultaneously, by Bloch, Hansen, and Packard (5) and Purcell, Torrey, and Pound (6). Comprehensive reviews of the principles involved have been presented by Andrews (7), Pake (8), Slichter (9), and others.

In the field of silicates, PMR techniques have been used by Kawachi, Murakami, and Herahara (10), French and Warder (11), Watanabe and Sasaki (12), and Blaine (13) in the study of the hydration of portland cement and related compounds. Pickett and Lemcoe (14), have reported on the use of PMR in a study of clay-water systems of rather high water content. Large quantities of free or sorbed water may, however, mask the resonance effect of the protons of the structural water or hydroxide groups which are a part of the crystal structure. It appeared desirable, therefore, to study the application of PMR techniques to semi dry clays and related materials.

APPARATUS

A Schlumberger Model 104 nuclear magnetic resonance analyzer was used for making these tests. This apparatus, which has previously been described by Rubin (15), is of the broad-band type and utilizes a 1720-gauss permanent magnet with a 2-in. gap between the 10-in. diameter pole faces. A sweep coil on the magnet varies the field strength by amounts up to 20 gauss. A crystal-activated radio frequency coil of 7.3

the precession frequency of the hydrogen nuclei in this particular magnetic field) is located between the pole faces of the magnet and contains the test sample in a glass vial of about 1.35-in. outside diameter. As the external field strength is varied from one side to the other of the 1720-gauss field (H_0) corresponding to the resonance frequency of protons, the instrument plots, within certain limitations, the derivative of the energy absorption of the protons in the test sample.

Smooth lines were drawn through the extraneous "noise" of the signals and measurements made of the horizontal distance between the maxima and the minima of the derivative absorption curves. These values, as obtained from the charts, were corrected in accordance with the instrument calibration previously described (13), and are termed the derivative line widths (ΔH). Tests made on a number of polycrystalline, reagent grade chemicals indicated that the ΔH values obtained with this apparatus were consistent with previously published values.

The area under an absorption curve is proportional to the energy absorbed and hence the number of protons in the sample. With the derivative curves the distance of the peaks above and below the base line is related to this area and is used to furnish a rough estimate of the number of protons involved. This value is referred to in this paper as peak signal amplitude or ΔS .

SCOPE

Measurements of nuclear magnetic energy absorption in the region of proton resonance were made on a variety of semi dry and dried clays to investigate the application of PMR to the study of water and hydroxides associated with clay minerals. Measurements were also made of clay constituents such as brucite and gibbsite. Amorphous and ground crystalline silica as well as finely divided alumina, lime, and limestone were tested to assess the effect of sorbed water on these different materials. A limited study was also made of the thawing of water in a frozen sample of semi dry montmorillonite, and a few tests were made of the effect of soil stabilizers such as CaCl_2 and $\text{Al}(\text{OH})_3$ on the water associated with a sample of montmorillonite.

TEST METHODS

Samples of some of the clays were packed into the 1.35-in. o. d. glass vials to a depth of about 2 in., whereas others were pressed into disks slightly smaller in diameter than that of the vials and placed in the vials to a $1\frac{1}{2}$ - to 2-in. depth. Samples were evacuated at room temperature for various periods to remove portions of the water, after which they were dried at 100 C, then at 200 C, and finally at 350 C. After each evacuation or heat treatment the samples were allowed to remain in the stoppered vials for a few hours before weighing and testing in the PMR apparatus. Normally 3 to 5 tests were made of each sample under each condition.

In determining the over-all absorption curve, a 20-gauss field strength was traversed in 4 min, whereas, in determination of the line width of peaks near the resonance frequency field strength, only 1 or 2 gauss were traversed in 4 min. To insure a closely approximate derivative curve, the modulation amplitude employed was less than one-fifth the line width in gauss in all reported values for ΔH . Where double peaks occurred, separate determinations of ΔH were made using the required instrument parameters. The amplification of the signal was adjusted for each test sample to obtain optimum signal-to-noise ratio. Under the most unfavorable conditions reported it is estimated that the signal-to-noise ratio at the peak of the derivative curve for bound water was of the order of 4 to 1, but in most cases it was larger.

Peak signal amplitude values were determined traversing a 10-gauss field in 30 sec. Various signal amplification factors were used but, for comparative purposes the values reported have been corrected to the same arbitrary sensitivity.

The time constant of the apparatus was maintained at $\frac{1}{30}$ of the sweep time or less, necessary requirement for quantitative measurements with the instrument used.

A sample of montmorillonite was frozen in liquid nitrogen in a special glass Dewar flask made to fit in the rf coil between the magnets. The sample was allowed to warm in the Dewar flask while in the apparatus. Alternate determinations were made of the absorption-derivative line-width and the temperature as determined by means of a

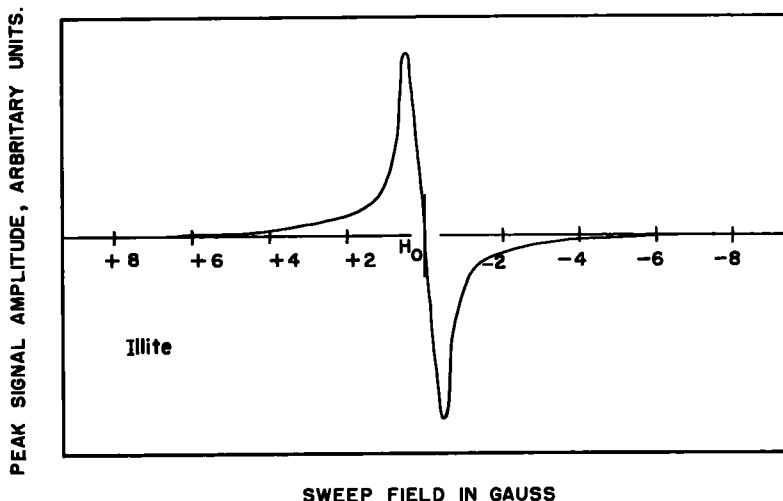


Figure 1. Derivative of absorption curve obtained on illite sample.

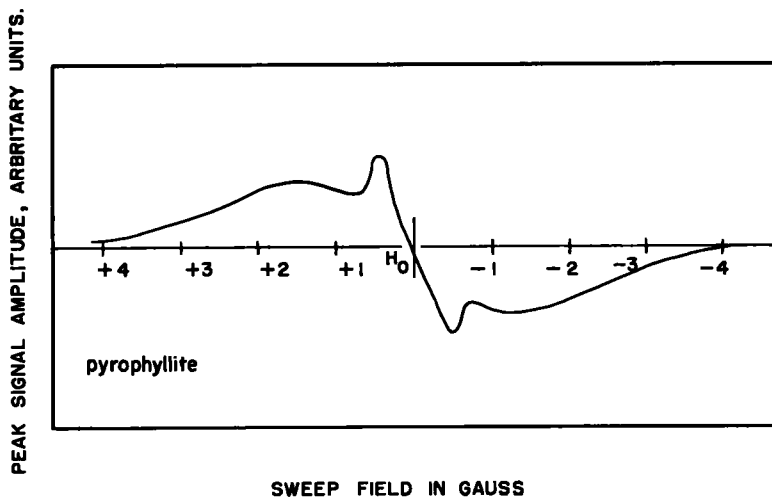


Figure 2. Derivative of absorption curve obtained on pyrophyllite sample.

copper-constantan thermocouple inserted into the sample. Comparative measurements were made with distilled water frozen and cooled to liquid-nitrogen temperature and allowed to warm up in the Dewar in the apparatus.

A sample of montmorillonite was mixed with 20 percent of reagent-grade $\text{Ca}(\text{OH})_2$ and water to a plastic consistency. Another sample of this same clay was mixed with 2.5 percent of CaCl_2 and water. Both samples, as well as one mixed with distilled water, were stored in stoppered vials at 50 C for one week. Measurements were then made of the samples in the PMR apparatus after various periods of drying.

Determinations of the PMR patterns of powdered opal, gibbsite, boehmite, and bayerite were made without addition of water to the samples. The samples of quartz ground to a surface-mean diameter of approximately 2μ , as well as the other powdered materials, were compacted in the test vial containing known quantities of distilled water before the determinations.

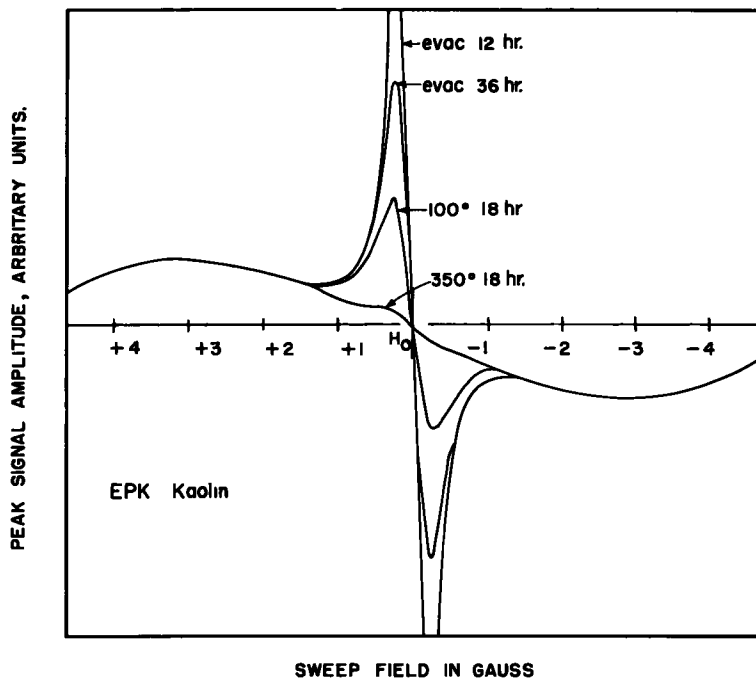


Figure 3. Derivatives of absorption curves of kaolin sample after removal of various amounts of water.

RESULTS OF DETERMINATIONS

Figure 1 shows a smooth tracing of a derivative absorption curve, obtained for a sample of partially dried illite where the field was traversed the nominal ± 10 gauss about the H_0 . Although the instrument parameters used for this test were such that the central portion of the signal was overmodulated (that is, the modulation amplitude was greater than one-fifth of the absorption line width), very little absorption was evident other than the central peaks. The values for the line widths obtained on three samples of illite are given in Table 1.

The patterns obtained with montmorillonites, conditioned in laboratory environment and partially dried, were very similar to those obtained with the illites in that the only apparent absorption occurred very close to the resonance frequency possibly associated with free water. The ΔH values obtained for a number of montmorillonites are also presented in Table 1.

A curve obtained with a pyrophyllite is shown in Figure 2, where two pairs of peaks are apparent. The peaks closest to H_0 , possibly resulted from the presence of adsorbed water, whereas the other peaks are associated with structural hydrogen in the mineral. The line widths obtained with samples of pyrophyllites were approximately 6 gauss, as given in Table 1.

Absorption curves of a kaolin evacuated and dried to remove some of the water are shown in Figure 3. The figure was traced from individual determinations after the various treatments. The sample as well as the instrument parameters were the same for each of the determinations. The broad curve with ΔH of about 6.1 gauss was common to each of the recorded patterns, whereas the height of the central peaks became smaller with evacuation or drying. Values for the line width for a number of kaolins are given in Table 1.

The halloysites gave curves very similar to those obtained with the kaolins, except that the peaks closest to H_0 indicated a slightly narrower line width than those obtained with the illites and montmorillonites.

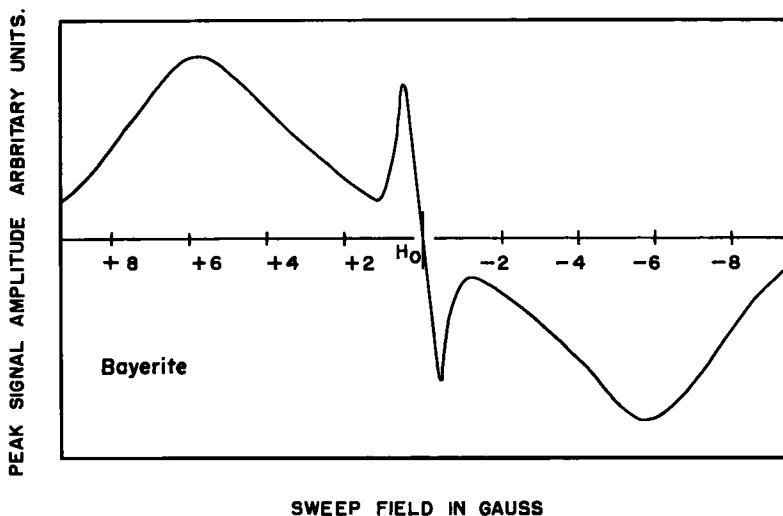


Figure 4. Derivative of absorption curve obtained on bayerite sample.

TABLE 1
ABSORPTION LINE WIDTH (ΔH) OF CLAY SAMPLES TESTED
IN A SEMI DRY CONDITION

Clay Sample	ΔH (gauss)	Clay Sample	ΔH_1 (gauss)	ΔH_2 (gauss)
Illites		Kaolinities		
Oswego	0.29	Putman	6.0	0.18
McAvoy	0.50	Kamec	6.0	0.19
Fresian	0.53	EPK	5.8	0.15
Montmorillonites		Ga 600	5.9	0.20
Hectorite	0.54	Lustra	5.9	0.21
Bentonite #25 Upton	0.48	Dry Branch	5.8	0.14
Bentonite #24 Otay	0.47	(unknown)	6.2	-
Belle Fourche	0.47	Dickite	5.9	-
Belle Fourche	0.38	Georgia	6.0	0.19
Aberdeen, Miss.	0.34	Florida	5.8	0.19
Panther Creek	0.33	Mesa Alta	6.1	0.22
Chambers, Ariz.	0.67	Murfreesboro	6.2	0.16
Nontronite	0.88	Bolivia	7.5	0.10
Wyoming bentonite	0.51	Halloysite dragon	6.1	0.09
Na bentonite	0.49	Halloysite	6.0	0.10
Ca bentonite	0.62	Halloysite hydrated	6.5	-
Pyrophyllite	3.0	Sepiolite	9.1	-
Pyrophyllite 2074	2.8	Bauxite	11.0	-
Pyrophyllite 2089	2.8	Bayerite	11.4	-
Pyrophyllite 2157	2.9			

A single sample of sepiolite tested indicated a line width of 9.1 gauss, whereas bauxite and bayerite (Fig. 4) indicated line widths of about 11 gauss (Table 1).

The line widths obtained on a series of clays from which water was progressively removed, first by evacuation and then by heating at 100, 200, and finally 350 C, are

TABLE 2

ABSORPTION LINE WIDTH (ΔH) OF VARIOUS CLAY SAMPLES DETERMINED AT MOISTURE CONTENT

Clay Type	Determina- tion ¹	Sample									After 350 C Treatment ²
		As Rec'd.	After Evacuation for				After Heating for 18 Hr at				
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C	
Mtman kaolin	Water (%)	2.06	1.76	1.61	1.54	1.50	1.42	1.17	0.63	-	14.8
	ΔH_1 (gauss)	6.00	5.90	6.10	6.00	6.00	6.00	6.10	6.10	6.10	
	ΔH_2 (gauss)	0.18	0.21	0.23	0.27	0.28	0.32	0.34	-	-	
amec kaolin	Water (%)	3.75	3.45	3.25	3.20	3.11	3.02	2.65	1.84	-	14.1
	ΔH_1 (gauss)	6.00	6.00	5.90	5.90	6.00	5.90	6.00	6.00	5.80	
	ΔH_2 (gauss)	0.20	0.20	0.19	0.22	0.22	0.23	0.17	0.11	-	
PK kaolin	Water (%)	2.73	2.27	2.09	2.02	1.87	1.78	1.45	0.66	-	14.4
	ΔH_1 (gauss)	6.00	5.70	5.80	5.80	6.10	5.70	6.00	6.00	6.10	
	ΔH_2 (gauss)	0.15	0.20	0.22	0.25	0.27	0.28	0.28	0.16	-	
a 600 kaolin	Water (%)	0.85	0.66	0.61	0.59	0.56	0.53	0.36	0.18	-	15.3
	ΔH_1 (gauss)	6.00	6.10	6.00	6.00	6.10	6.20	6.10	6.10	6.10	
	ΔH_2 (gauss)	0.20	0.19	0.22	0.26	0.29	0.31	-	-	-	
stra kaolin	Water (%)	0.90	0.70	0.66	0.63	0.60	0.57	0.42	0.25	-	15.3
	ΔH_1 (gauss)	5.90	5.90	6.00	6.00	6.30	6.10	6.00	6.10	6.20	
	ΔH_2 (gauss)	0.20	0.25	0.28	0.26	0.26	0.26	-	-	-	
y Branch kaolin	Water (%)	1.52	1.14	1.01	0.96	0.91	0.85	0.63	0.23	-	15.0
	ΔH_1 (gauss)	5.80	6.20	6.10	6.40	6.00	6.00	5.90	6.10	6.20	
	ΔH_2 (gauss)	0.14	0.21	0.24	0.26	0.29	0.28	0.22	-	-	
agon halloysite	Water (%)	3.36	2.58	2.27	2.12	2.02	1.79	1.25	-	-	14.8
	ΔH_1 (gauss)	6.10	6.20	6.20	6.00	6.10	6.00	6.30	6.00	6.10	
	ΔH_2 (gauss)	0.07	0.09	0.09	0.09	0.10	0.11	0.09	0.06	-	
wego illite	Water (%)	1.16	0.80	0.68	0.63	0.57	0.52	0.18	-	-	4.6
	ΔH_1 (gauss)	-	-	-	-	-	-	-	-	2.60	
	ΔH_2 (gauss)	0.28	0.26	0.14	0.14	0.14	0.11	0.10	0.09	-	
Avoy illite	Water (%)	5.21	3.98	3.42	3.22	3.02	2.78	2.39	0.71	-	4.4
	ΔH_1 (gauss)	-	-	-	-	-	-	1.10	2.40	3.00	
	ΔH_2 (gauss)	0.51	0.61	0.78	0.73	0.77	0.82	0.77	-	-	

¹Water that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at 100, 200, and 350 C, and with percentage based on weight after last drying.
²Based on ignited weight at 900 C.

given in Tables 2, 3, and 4. The moisture content, based on the weight after the 350 C heat treatment, for the respective determinations of line width is also given. In the first column is the percentage moisture (or other material that may be removed) based on the 900 C ignited weight but still present after the 350 C treatment.

The ΔH_1 line width was arbitrarily assigned to the greater of the two values and ΔH_2 values of the peaks closest to the resonance frequency H_0 . As previously indicated for a single sample of kaolin (Fig. 3), the broad lines for the various kaolins and the halloysite did not change appreciably with the removal of water at 350 C or below. The ΔH_2 line width, which is possibly associated with interlayer or adsorbed water, generally increased slightly as water was removed, which is in accordance with published data on other materials (16).

The line widths for two of the three illites and two montmorillonites (Tables 2-4) also increased slightly with decrease in moisture content. These materials exhibited very narrow line widths at the higher moisture contents. However, after drying at 100 and 200 C, a second set of peaks became apparent on samples of the McAvoy and Fithian illites, the two montmorillonites, and the mixtures of illite and montmorillonite of Table 3. The line widths of these peaks increased with decrease in moisture content. For example, the ΔH_1 line width for the McAvoy illite was 1.1 gauss after drying at 100 C, 2.4 gauss after 200 C and 3.0 gauss after the 350 C drying. The signals obtained on these dried samples were, however, very weak. Plotting line widths vs respective moisture contents for an illite (Fig. 5) and a montmorillonite (Fig. 6) indicates rather sharp breaks in both curves. On the basis of the 900 C ignited weight, the illites and montmorillonites have about 4 percent water remaining after the 350 C drying treatment compared to the kaolins and halloysite which had about 15 percent. It was also ap-

TABLE 3
ABSORPTION LINE WIDTH (ΔH) OF MONTMORILLONITE AND ILLITE AND MIXTURES OF THESE
DETERMINED AT MOISTURE CONTENT

Type	Determina- tion ¹	As Rec'd.	Sample									After 350 C Treatment ²
			After Evacuation for						After Heating for 18 Hr at			
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C		
Montmorillonite (Wyoming bentonite)	Water (%)	6.87	6.16	5.35	4.82	4.21	2.98	2.03	0.28	-	4.8	
	ΔH_1 (gauss)	-	-	-	-	-	-	-	3.10	3.60	-	
	ΔH_2 (gauss)	0.51	0.55	0.56	0.51	0.54	0.57	0.49	0.29	-	-	
75 M 25 I	Water (%)	6.23	5.60	5.00	4.56	3.93	2.64	1.81	0.54	-	5.1	
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.70	2.90	-	
	ΔH_2 (gauss)	0.47	0.51	0.57	0.54	0.59	0.59	0.54	-	-	-	
50 M 50 I	Water (%)	5.75	5.05	4.47	4.11	3.65	2.65	2.05	0.79	-	4.8	
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.60	2.90	-	
	ΔH_2 (gauss)	0.43	0.51	0.57	0.58	0.55	0.59	0.58	-	-	-	
25 M 75 I	Water (%)	5.12	4.59	4.05	3.71	3.40	2.76	2.35	0.98	-	4.8	
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.60	2.50	-	
	ΔH_2 (gauss)	0.38	0.42	0.51	0.52	0.54	0.66	0.64	-	-	-	
Illite (Fithian)	Water (%)	4.88	4.26	3.83	3.68	3.50	3.28	2.70	1.43	-	4.7	
	ΔH_1 (gauss)	-	-	-	-	-	-	-	1.00	2.10	2.50	
	ΔH_2 (gauss)	0.42	0.55	0.58	0.58	0.64	0.67	0.72	-	-	-	

¹Water that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at 100, 200, and 350 C, and with percentage based on weight after last drying.

²Based on ignited weight at 900 C.

TABLE 4
ABSORPTION LINE WIDTH (ΔH) OF A MONTMORILLONITE WITH AND WITHOUT CHEMICAL
TREATMENT DETERMINED AT MOISTURE CONTENT

Type	Determina- tion ¹	As Rec'd.	Sample								
			After Evacuation for						After Heating for 18 Hr		
			4 Hr	8 Hr	12 Hr	18 Hr	36 Hr	100 C	200 C	350 C	
Montmorillonite as received	Water (%)	8.06	6.22	4.57	3.61	2.55	1.54	0.71	0.27	-	-
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.80	3.6	-
	ΔH_2 (gauss)	0.44	0.47	0.49	0.43	0.39	0.42	0.31	-	-	-
Montmorillonite ²	Water (%)	8.92	7.37	5.22	3.92	2.54	1.45	0.67	0.31	-	-
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.70	-	-
	ΔH_2 (gauss)	0.46	0.51	0.54	0.47	0.39	0.38	0.37	-	-	-
Mont + Ca(OH) ₂ ³	Water (%)	13.82	8.89	5.85	4.79	4.30	3.59	2.63	0.81	-	-
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.50	2.2	-
	ΔH_2 (gauss)	0.15	0.20	0.32	0.40	0.42	0.46	0.50	-	-	-
Mont + CaCl ₂ ⁴	Water (%)	11.72	10.75	8.90	7.70	6.48	5.44	3.35	0.52	-	-
	ΔH_1 (gauss)	-	-	-	-	-	-	-	2.80	2.9	-
	ΔH_2 (gauss)	0.37	0.38	0.34	0.38	0.41	0.47	0.68	-	-	-

¹Water that is removable by successive evacuation for 36 hr at room temperature, with 18-hr dryings at 100, 200, and 350 C, and with percentage based on weight after last drying.

²Water added stored one week at 50 C.

³20 percent Ca(OH)₂ and water added, stored one week at 50 C.

⁴5 percent CaCl₂ and water added, stored one week at 50 C.

parent from the weak signals of the test patterns that fewer protons were present in the illites and montmorillonites after drying at 200 or 350 C than were present in the kaolins and halloysites.

The relationship of peak signal amplitude to moisture content as determined on typical samples of kaolin, a sample of illite, and a sample of montmorillonite is shown in Figure 7. The moisture content was based on the weight of samples after drying at 350 C. In these tests a 10-gauss sweep field was scanned in 30 sec using an overmodulated signal of 5 gauss. This procedure has been used for determining moisture content of

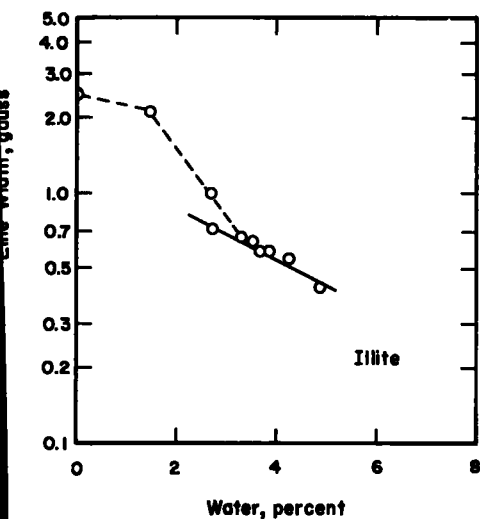


Figure 5. Absorption line width vs moisture content of illite sample.

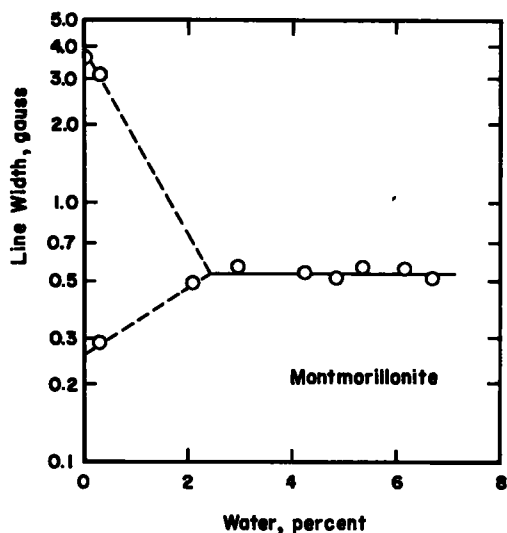


Figure 6. Absorption line width vs moisture content of montmorillonite sample.

various organic materials (15). However, structural hydrogen as well as adsorbed water is included under these conditions. Plotting the signal amplitude vs the moisture content based on the 900 C ignited weight places the kaolins to the right of the illite and montmorillonite but does not remove the curvature of the lines nor bring them together.

TABLE 5

ABSORPTION LINE WIDTH (ΔH) OF MINERALS AND PARTICULATE MATERIALS ASSOCIATED WITH CLAY MINERALS

Material	Water on Dry Basis (%)	ΔH (gauss)
brucite:		
white	-	12.6
blue	-	13.7
gibbsite	-	11.6
boehmite	-	11.0
quartz	30	0.26
opal	10	0.075
silica gel	13	0.036
Al_2O_3	200	0.019
hydrated lime:		
nonplastic	50	0.038
plastic	50	0.030
t., calcium carbonate	32	0.025
ground Limestone:		
E	15	0.038
E	15	0.10

When samples of montmorillonite were mixed with $Ca(OH)_2$ or $CaCl_2$ and allowed to react at 50 C for a week, the ΔH values were not greatly different from those obtained with this clay as received or with water added before the determination and then dried. In every instance, a line width at 2 to 3 gauss became apparent after the 200 C drying treatment. It was noted that the clay treated with the $Ca(OH)_2$ was fairly hard or set after the 50 C curing period, whereas the $CaCl_2$ -treated clay and that with water added were still plastic.

The curves obtained with brucite crystals that had been pulverized are shown in Figure 8. The line widths of both the blue and the white crystalline material were approximately 12 gauss. The curve obtained on gibbsite is also shown in this figure.

The ΔH values obtained with gibbsite, boehmite, opal, silica gel, ground quartz, hydrated lime, precipitated calcium carbonate, pulverized limestone, and a finely divided Al_2O_3 are given in Table 5. The line widths of the materials containing sorbed water were sensitive to the amount of water present. With silica gel, for example, the values for line width increased markedly with lower moisture content, as shown in Figure 9.

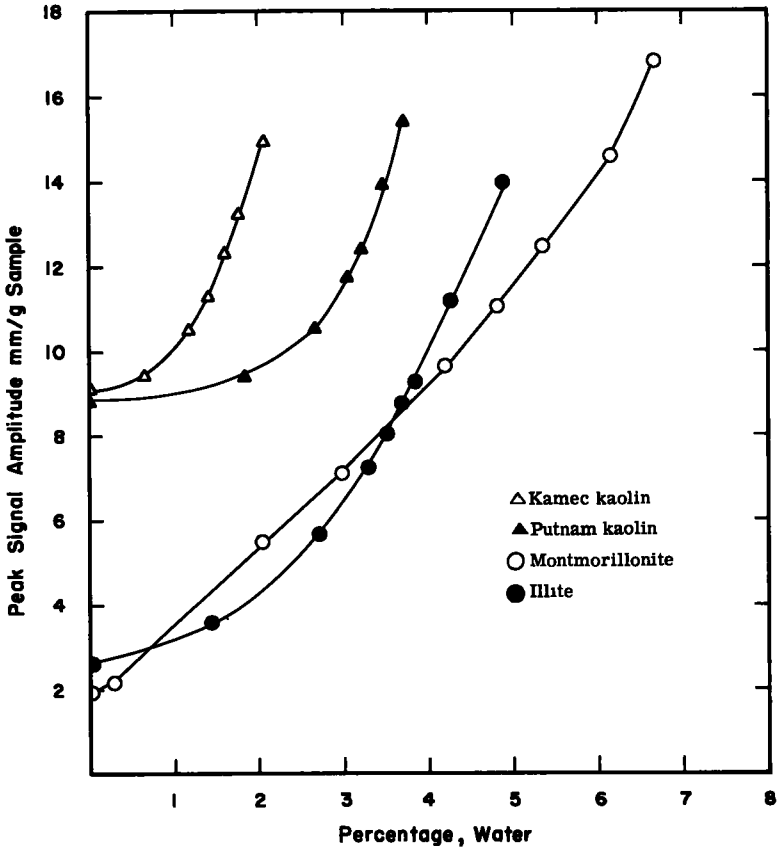


Figure 7. Peak signal amplitude vs moisture content of samples.

PEAK SIGNAL AMPLITUDE, ARBITRARY UNITS.

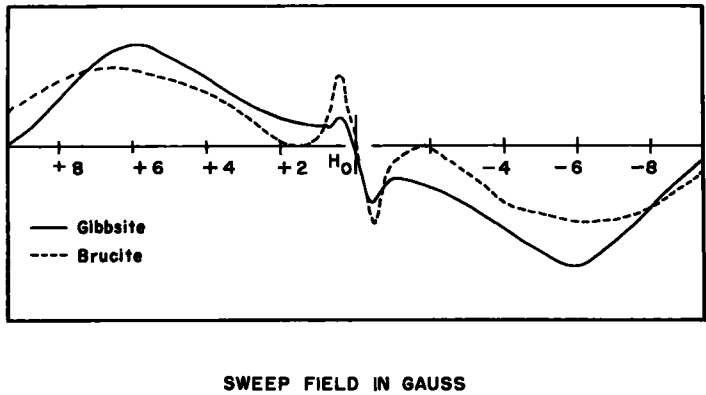


Figure 8. Derivatives of absorption curves for samples of brucite and gibbsite.

A graph showing the line widths obtained on a sample of montmorillonite frozen with liquid nitrogen and allowed to warm up in the apparatus is shown in Figure 10. In this figure is shown also the peak signal amplitude as calculated from the recorder chart values and instrument parameters. It may be noted that a break was obtained in each of these curves at about -70°C , but that the change in line width with temperature was fairly gradual. Smooth curves were obtained in each determination with no evidence of any secondary peak as would be obtained with free water. Presented also in this graph are tests obtained with ice frozen in liquid nitrogen and permitted to thaw under similar conditions. A sharp break in the curve is apparent in the -10°C region. The temperature of both the ice and the montmorillonite were measured near the center of the sample, and the material near the edges may have been considerably warmer and contributed to the apparent line width. It may be noted, however, that the ΔH value for montmorillonite at liquid nitrogen temperature was less than half that of ice.

DISCUSSION

Many of the structures proposed for clay minerals include, in addition to interlayer water, brucite and gibbsite layers and hydroxide groups as well as water of crystallization. The line widths of both brucite and gibbsite were found to be about 11 to 12 gauss.

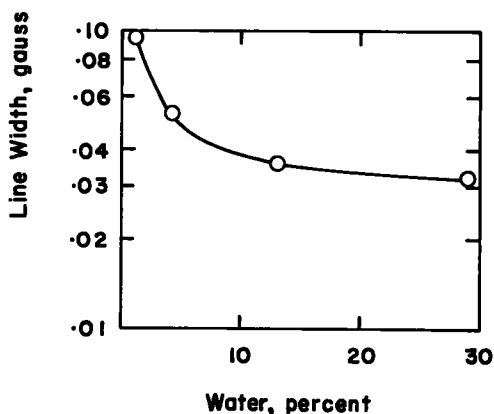


Figure 9. Relationship between derivative line width and moisture content of silica gel sample.

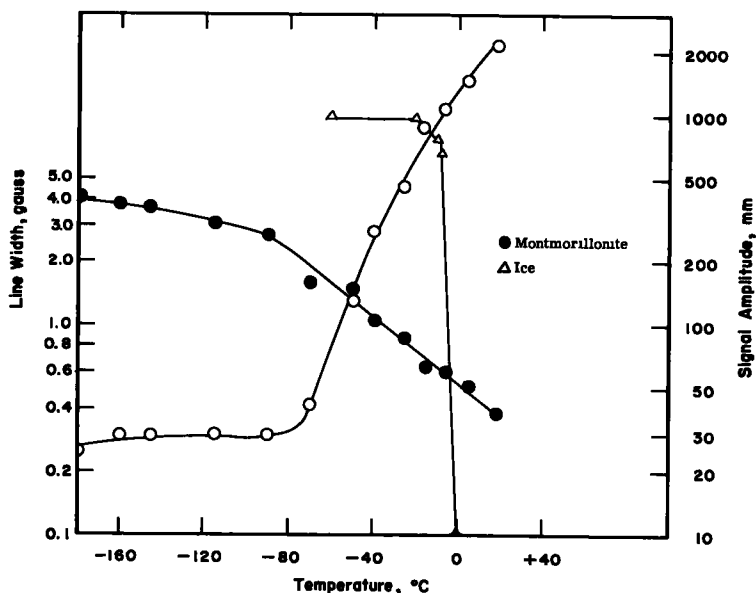


Figure 10. Relationship between derivative line widths and temperature and relationship between signal amplitude on montmorillonite sample and temperature.

Tests made with this apparatus on a large number of reagent grade inorganic polycrystalline hydroxides and compounds with water of crystallization indicated line widths for a great majority of the compounds in the 10- to 16-gauss range when tested at room temperature. The ΔH values for bayerite and bauxite were within this range. However, measurements on illites, montmorillonites, pyrophyllites, kaolins, and halloysites did not exhibit any peaks in the curves with line widths in the 10- to 16-gauss range. It is recognized that in interpretation of PMR data, many unknown factors are involved. It appears, however, that for these clays, the apparatus used was not sensitive enough to determine the presence of any structural hydrogen held either as hydroxides or as water of crystallization in the quantities present.

Nakamoto, Margoshes, and Rundle (17), in a paper on stretching frequencies as a function of distance in hydrogen bonds, reported the bond distance of a number of compounds. A few of these compounds (reagent grade) were tested in some preliminary work with this apparatus and ΔH line widths of 2 to 10 gauss were obtained—the smallest values for ΔH being obtained for those compounds reported as having low values for the O-H-O distance.

The ΔH values for pyrophyllites, kaolins, halloysites, and sepiolite fall within this 2- to 10-gauss range as do the ΔH values for the montmorillonites and illites after drying at 200 C. However, the signals for the montmorillonites and illites were very weak in this region compared to those of the other clays.

The explanation of the role of sorbed water or interlayer water associated with clay minerals also presents some interesting problems. Water adsorbed on amorphous silica such as gel or opal exhibited a relatively small ΔH value, whereas powdered crystalline quartz with a water content of 30 percent indicated a larger line-width value. The fact that rather narrow line widths were obtained with the very fine materials such as silica gel, fine Al_2O_3 powder, lime, and precipitated calcium carbonate would seem to indicate that a large surface area as such is not a major factor in contributing to the ΔH value. Crystalline silica appears to immobilize the water to a greater extent than amorphous silica and may be responsible for the strong adsorption of water leading to ΔH values in the range of 0.3 to 0.7 gauss as found for the illites and montmorillonite and the ΔH values of 0.1 to 0.2 gauss for the kaolins. The ΔH values obtained for the interlayer adsorbed water on halloysite were appreciably lower than those obtained for the previously mentioned clays. These lower values may indicate a different type of surface adsorbing the water or a surface with a different energy.

Although samples of montmorillonite tested at room temperature had only small ΔH values which suggested highly mobile protons, the sample tested at liquid nitrogen temperature exhibited a ΔH value less than half that determined for ice similarly tested. Tests of frozen samples of other clays may furnish further information of the nature of the water in these materials. The results obtained with the broad-band proton-magnetic resonance apparatus are relatively insensitive with polycrystalline materials and give the effect of the different types of bonding of the hydrogen nuclei. For example, Pake (8) has reported that $CaSO_4 \cdot 2H_2O$, which has two types of water molecules, exhibits double derivative peaks with a single crystal but only one set of peaks in the powder form. It cannot, therefore, be definitely stated that the ΔH values of 2 to 10 gauss obtained with these clays are caused by hydrogen bonding. Further tests with highly oriented silicate minerals appear necessary to the study of water and hydroxides in clay.

It may be noted that the line widths obtained on the clay minerals appear to fall into a pattern of multiples of 3 gauss; namely, approximately 0, 3, 6, 9, and 12 for illite, pyrophyllites, kaolins, sepiolite, and bayerite, respectively. Minor constituents, impurities, instrumental variations, and inaccuracy of measurements may have accounted for the different ΔH values that occurred within each group, but the differences between the groups appear real.

SUMMARY

Determinations were made at room temperature of the proton magnetic resonance absorption derivative line widths of a variety of clays and related minerals.

The line widths of illites and montmorillonites were in the 0.3- to 0.7-gauss range when tested in a semi dry condition. These values correspond to line widths associated with

strongly adsorbed water. When these materials were dried at 200 C or higher, line widths of about 3 gauss became apparent, but no absorptions corresponding to those normally obtained with hydroxides or with water of crystallization were obtained with this apparatus. The line widths of samples of pyrophyllite were also about 3 gauss, whereas ΔH values of about 6 gauss were obtained with kaolins and halloysites. Smaller ΔH values normally associated with adsorbed or interlayer water were also obtained with these clays. Line widths in the 2- to 8-gauss range are similar to those obtained on reagent chemicals having various O-H-O distances and are considerably lower than those obtained with brucite or gibbsite or with most other hydroxides or salts with water of crystallization. A sample of sepiolite gave a line width of 9.1 gauss, and samples of bayerite and a bauxite gave line widths of 11.4 and 11.0 gauss, respectively, which fall within the range normally associated with hydroxides or water of crystallization.

Removal of water by evacuation or by heating up to 350 C did not affect the line width attributed to structural water in kaolins but tended to increase the line width associated with the adsorbed water. The interlayer water or that adsorbed on different clays exhibited different degrees of line broadening and also greater line widths than were obtained with other finely divided minerals such as silica gel, ground quartz, or precipitated calcium carbonate. Adsorbed water on crystalline silica exhibited a greater absorption line width than that sorbed on either amorphous opal or silica gel.

A sample of montmorillonite frozen with liquid nitrogen and allowed to thaw in the apparatus indicated a decrease in line width (that is, an increase in proton mobility) at about -70 C. Samples of a montmorillonite clay mixed with calcium hydroxide or with calcium chloride and stored at 50 C for one week did not exhibit line widths greatly different from clay samples without the chemical treatment.

Although the results reported in this study may not be considered quantitative with respect to either structure or possible hydrogen bonding of the clay minerals, the use of proton magnetic resonance techniques appears to offer possibilities for a better understanding of these materials.

REFERENCES

1. Grim, R. E., "Clay Mineralogy." McGraw-Hill (1953).
2. Marshall, C. E., "The Colloidal Chemistry of the Silicate Minerals." Academic Press (1949).
3. Rigby, G. R., Trans. British Ceramic Soc., 48:1 (1949).
4. Hendricks, S. B., and Jefferson, M. E., Amer. Mineral, 23:863 (1938).
5. Bloch, F., Hensen, W. W., and Packard, M. F., Phys. Rev., 70:474 (1946).
6. Purcell, E. M., Torrey, H. C., and Pound, R. V., Phys. Rev., 69:37 (1946).
7. Andrews, E. R., "Nuclear Magnetic Resonance." Cambridge University Press (1956).
8. Pake, G. E., Amer. Jour. Physics, 18: 438-452, 473-486 (1950).
9. Slichter, C. P., Annals N. Y. Acad. Sci., 70:769 (1958).
10. Kawachi, K., Murakami, M., and Herahara, E., Bul. Fac. Engr. Hiroshima Univ., 4:95 (1955).
11. French, G. M., and Warder, J. F., Jour. Appl. Chem., 9:561 (Nov. 1959).
12. Watanabe, K., and Sasaki, T., 4th Internat. Symposium on the Chemistry of Cement.
13. Blaine, R. L., 4th Internat. Symposium on the Chemistry of Cement.
14. Pickett, A. G., and Lemcoe, M. M., Jour. Geophys. Res., 64:1579 (1959).
15. Rubin, H., Jour. ISA (Jan. 1958).
16. Shaw, T. M., and Elsken, R. H., Jour. Chem. Phys. 21:565 (1953).
17. Nakamoto, K., Margoshes, M., and Rundle, R. E., Jour. Amer. Chem. Soc., 77:6480 (1955).

A Study of Absorbed Water on Clay by Steady State Nuclear Magnetic Resonance

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● THE CONCEPT of water film strength, reported by Terzaghi (1) in his earliest works on soil mechanics and developed into a more elaborate theory by such investigators as Winterkorn (2, 3), Forslind (4, 5), and Grim (6, 7) may be summarized as follows:

1. An adsorbed film of strongly oriented water molecules is firmly bound to the clay surface.
2. The water molecule orientation extends for some distance into interparticle water.
3. The oriented water molecules resist deorientation and this resistance to deorientation is a significant part of the shear strength of a wet clay soil.

The source of this bonding and orienting force is the polar nature of the water molecule itself and a similar property of the clay crystal surface. Although an atom is electrically neutral, the formation of an ionic valence bond in which electrons are "borrowed" from one atom to help fill the outer electron shell of another causes a dislocation of electric charge, the donor atom becoming positively charged and the borrower negatively charged. The asymmetric water molecule behaves, therefore, as a body with oppositely charged ends, one of which is attracted and the other repelled by the clay crystal surface which is charged by a similar mechanism. The enormous surface area of clays, estimated by Hendricks, Nelson, and Alexander (8) as being in the neighborhood of 8×10^6 sq cm per g for a montmorillonite, offers this force the opportunity of being a very important parameter of shear strength. Opposing the development of orientation, however, is the Brownian movement, which is also of consequence at this phenomenological level and the estimates of the resultant thickness of strongly oriented layers and their resistance to a shearing stress—based on theoretical analyses by various investigators—vary widely. It has been conclusively demonstrated, however, that the polar bonding forces are of real significance in the resistance of materials to shearing stresses and that they can be measured by appropriate techniques. In particular, Debye delineated their role as "dashpot" elements in viscoelastic materials and demonstrated that a measurement of their relaxation times by any means also described the functions in determining the mechanical properties of a material.

The unique feature of the electrostatic linkage is the immobilization of the hydrogen atom. This immobilization can be measured in terms of resistance to shearing stress (viscosity or shear strength) by steady state nuclear magnetic resonance.

Steady state nuclear magnetic resonance (NMR)(9) measures two relaxation times. T_1 , called the thermal relaxation time, is the time required for the energy absorbed by a nucleus whose equilibrium has been disturbed to be dissipated to the lattice. T_2 , called the spin-spin relaxation time, is a time constant associated with the influence of the magnetic field of one nucleus on another nucleus, which is a measure of the proximity of nuclei. Bloembergen, Purcell, and Pound (10) and Grant (11) showed that T_2 is also a measure of the potential resistance of an assemblage of water molecules to shearing stress.

The great advantage of this technique is that it is nondestructive and measures water film strength directly. The viscosity of intralayer water of montmorillonite is measured as easily as that of the interlayer water, for example.

In order to limit the variables, clays of well-known properties were prepared and tested. These clays were (a) Georgia kaolin, (b) homionic Wyoming bentonites, and

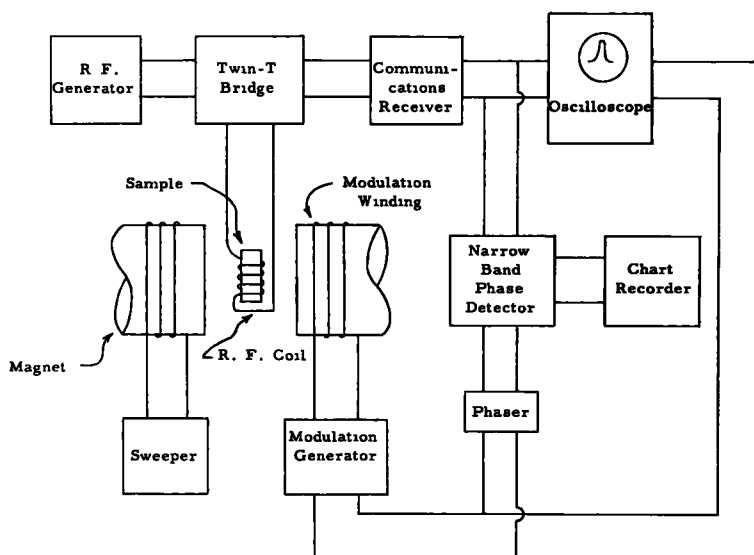


Figure 1. Block diagram of NMR equipment used.

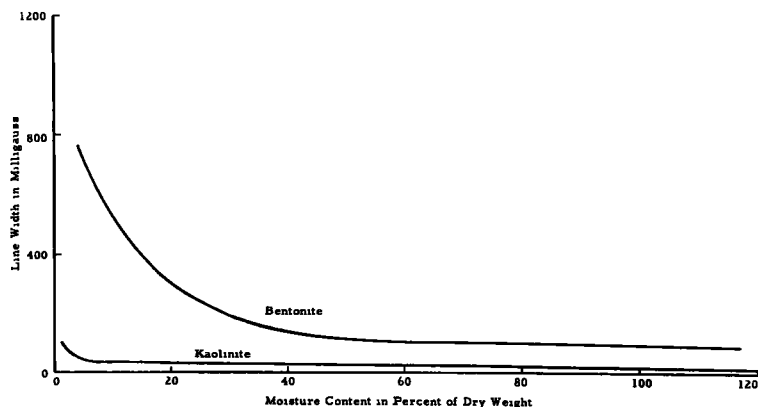


Figure 2. Moisture content, natural bentonite and natural kaolinite.

treated homionic montmorillonites. These clays were prepared at various moisture contents, and the line width of the recorder derivative signal (equal to $1/\sqrt{3}\pi T_2$) was measured and plotted as a function of moisture content. Stored at constant moisture content (in sealed bottles), the samples exhibited no change in line width despite noticeable changes in strength properties (caused by thixotropic behavior and remodeling) that resulted from aging and agitation. The only measurements made by NMR were of line width. The moisture content was measured by standard oven-drying technique. Figures 1 through 5 show the equipment used, typical NMR signals, and the final results. The magnitude of this bonding force, compared with Ice 1, is low—indicating that the contribution to shear strength is relatively small. For example, ice at -2°C (Bloemrogen, Purcell, and Pound (10)) has a line width of 4,000 milligauss and sodium montmorillonite has line widths of 1,600 milligauss at 0.48 percent moisture content by dry weight and 950 milligauss at 3.46 percent. It is interesting to note that comparable line widths were measured in dry, aged portland cement concrete, and that some organic thixotropic gels exhibited no increase in line width on setting up. From experiments on

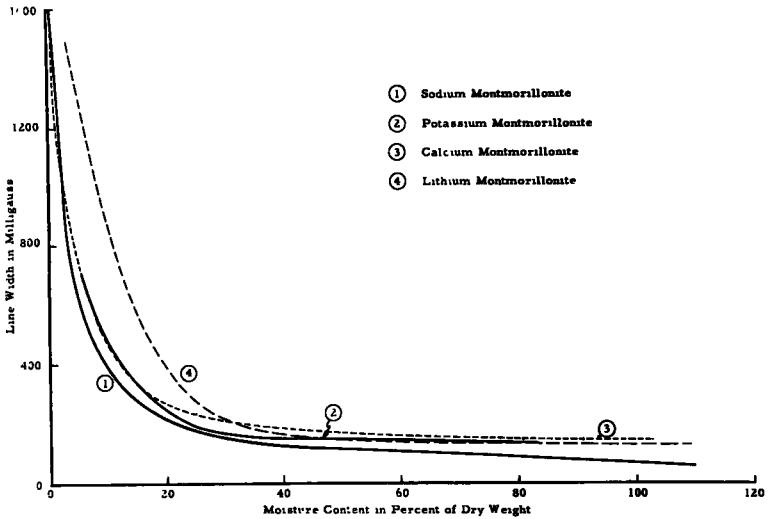


Figure 3. Moisture content, homoionic clays.

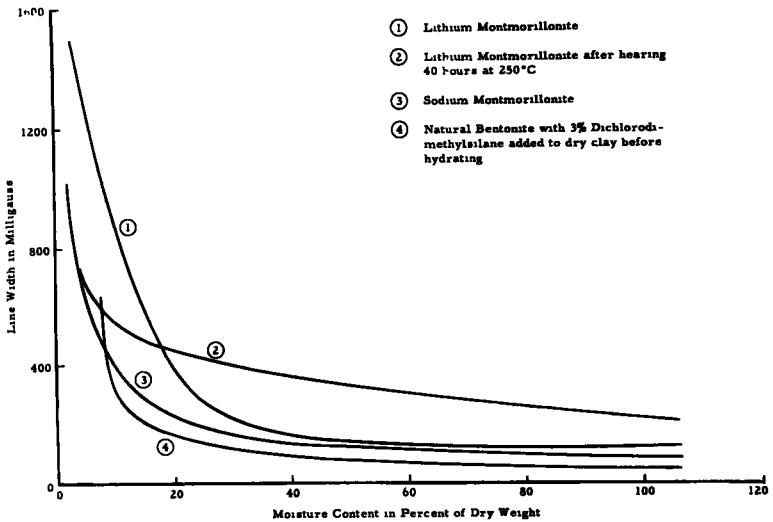


Figure 4. Moisture content, modified clays.

clays, it was concluded that the major bonding forces in clays were other than water film strength.

The modified clays were prepared to investigate the difference in the condition of water on the different surfaces of montmorillonite crystal stacks. The lithium montmorillonite, after heating, has no intralayer water. The silaned clay has intralayer water, but has no exterior water film. However, no difference was observed in modulus or energy of bonding between the two systems.

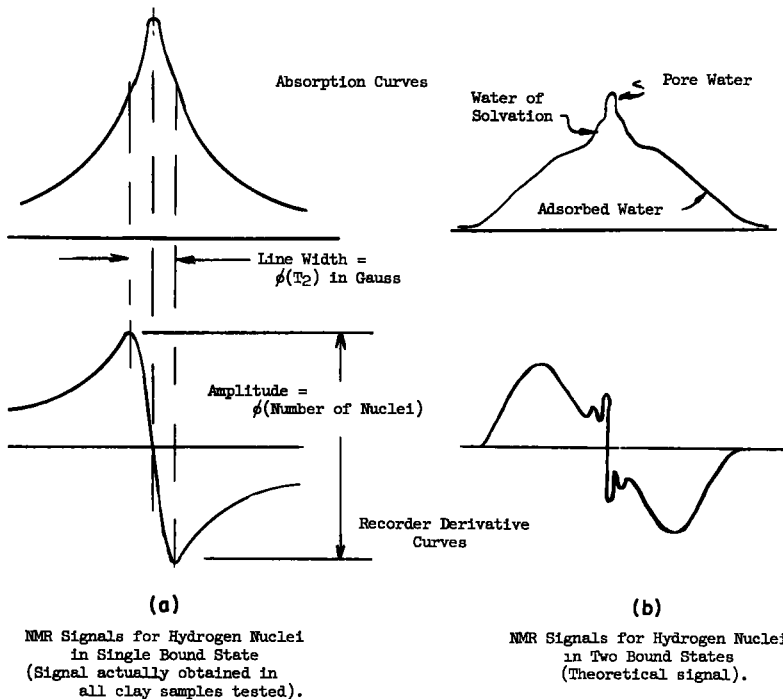


Figure 5. Measured and theoretical NMR signals, with frequency constant and field strength varied.

REFERENCES

- 1. Terzaghi, C., "The Static Rigidity of Plastic Clays." *Jour. of Rheology*, 2 (1931).
- 2. Winterkorn, H. F., "A Fundamental Approach to the Stabilization of Cohesive Soils." *HRB Proc.*, 28:415-422 (1948).
- 3. Winterkorn, H. F., "The Conditions of Water in Porous Systems." *Soil Sci.*, 55: 109-115 (1952).
- 4. Forslind, E., "A Theory of Water, The Clay-Water System: II." *ACTA Polytechnica*, Vol. 115 (1952).
- 5. Forslind, E., "Water Association and Hydrogels." *Proc.*, 2nd Internat. Congress on Rheology.
- 6. Grim, R. E., and Cuthbert, "The Bonding Action of Clays." *Univ. of Ill., Eng. Exp. Sta., Bull.* 357.
- 7. Grim, R. E., "Clay Mineralogy." McGraw-Hill (1953).
- 8. Hendricks, S. B., Nelson, R. A., and Alexander, L. T., "Hydration Mechanisms of the Clay Mineral Montmorillonite Saturated with Various Cations." *Jour. Amer. Chem. Soc.*, 62:1457 (June 1940).
- 9. Andrews, E. R., "Nuclear Magnetic Resonance." Cambridge Univ. Press.
- 10. Bloembergen, N., Purcell, E. M., and Pound, R. V., "Relaxation Effects in Nuclear Magnetic Resonance Absorption." *Phys. Rev.*, 73:679 (1948).
- 11. Grant, E. H., "Relationship Between Relaxation Time and Viscosity for Water." *Jour. Chem. Physics*, 26:No. 6 (June 1957).
- 12. Zimmerman, Holmes and Lasater, "A Study of Adsorbed Water on Silica Gel by Nuclear Resonance Techniques." *Jour. Phys. Chem.*, 60:No. 9 (Sept. 1956).
- 13. Hauser, E. A., "Colloid Chemistry of Clays." *Chem. Rev.* (October 1945).
- 14. Pickett, A. G., and Lemcoe, M. M., "An Investigation of Shear Strength of the Clay-Water System by Radio-Frequency Spectroscopy." *Jour. of Geophys. Res.*, 64:1579-1586 (Oct. 1959).

SELECTED BIBLIOGRAPHY ON NUCLEAR MAGNETIC RESONANCE

Prepared by the Physics Department, Southwest Research Institute, San Antonio, Texas.—The following bibliography was assembled in late 1954 to provide an introduction to the literature on nuclear magnetic resonance for technical persons contemplating the use of NMR techniques for measuring moisture in hygroscopic solids. Inasmuch as over 400 articles on NMR had been published by January 1954 alone, no attempt has been made to cover the field completely. A sufficient number of references has been included to provide a general background, and those interested in pursuing the subject further are referred to the extensive bibliographies contained in the review articles listed in Part II.

The majority of NMR papers published in the United States are found in Physical Review and Journal of Chemical Physics. More recently, papers on applications of NMR to chemical problems have begun to appear in the chemical journals. The major source of republication information on new advances in the field are the several meetings of the American Physical Society, held at major cities during the year. Advance announcements and abstracts of the papers to be presented are contained in the Bulletin of the American Physical Society. For more detailed information on equipment and experimental techniques than is usually presented in the published papers, one can take advantage of the many doctoral theses on NMR usually obtainable on microfilm at small cost from the university concerned.

Part I: General Theory and Experimental Methods

1. Bloch, F., "Nuclear Induction." *Phys. Rev.*, 70:460 (1946).
2. Bloch, F., Hansen, W.W., and Packard, M., "The Nuclear Induction Experiment." *Phys. Rev.*, 70:474 (1946).
3. Bloembergen, N., Purcell, E.M., and Pound, R.V., "Relaxation Effects in Nuclear Magnetic Resonance Absorption." *Phys. Rev.*, 73:679 (1948).
4. Pake, G.E., "Fundamentals of Nuclear Magnetic Resonance Absorption: I & II." *Amer. Jour. Phys.*, 18:438-452, 473-486 (1950).
5. Hahn, E.L., "Spin Echoes." *Phys. Rev.*, 80:580 (1950).

Part II: Review Articles and Books

1. Soutif, M., "Nuclear Paramagnetism." *Rev. Sci.*, 89:203-42 (1951). In French.
2. Gorter, C.J., "Radiofrequency Spectroscopy." *Experientia*, 9:161-175 (1953).
3. Rollin, B.V., "Nuclear Paramagnetism." *Rep. Phys. Soc. Prog. Phys.*, 12:223 (1948-49).
4. Smith, J.A.S., "Nuclear Magnetic Resonance Absorption." *Quart. Rev. (London)*, 7:279-306 (1953).
5. Pound, R.V., "Nuclear Paramagnetic Resonance." *Prog. Nuclear Phys.*, 2:21 (1952).
6. Gutowsky, H.S., "Nuclear Magnetic Resonance." *Annual Rev. Phys. Chem.*, 4:333-356 (1954).
7. Ramsey, N.F., "Nuclear Moments." John Wiley (1953).
8. Andrews, E.R., "Nuclear Magnetic Resonance." Cambridge Univ. Press (in press).
9. Darrow, K.K., "Nuclear Magnetic Resonance." *Bell Systems Tech. Jour.*, 32:99 (1953). Especially recommended for the layman.
10. Black, F., "The Principle of Nuclear Induction." *Science*, 118:425-30 (1953).
11. Purcell, E.M., "Research in Nuclear Magnetism." *Science*, 118:431-36 (1953).

Part III: Equipment

A. R-F Bridge Systems

1. Bloembergen, N., Purcell, E.M., and Pound, R.V., (see Ref. I-3).
2. Anderson, H.L., "Precise Measurement of the Gyromagnetic Ratio of He³." *Phys. Rev.*, 76:1460 (1949).

3. Smaller, B., "Precise Determination of the Magnetic Moment of the Deuteron." *Phys. Rev.*, 83:812 (1951).
4. Thomas, H.A., Driscoll, R.L., and Hipple, J.A., "Measurement of the Proton Moment in Absolute Units." *Jour. Res. N.B.S.*, 44:569 (1950).
5. Grivet, P., Soutif, M., and Gabillard, R., "The Double T Bridge in Nuclear Magnetic Resonance." *Physics*, 17:420 (1951). In French.

B. Induction Systems

1. Bloch, F., Hansen, W.W., and Packard, M., (see Ref. I-2).
2. Proctor, W.G., "On the Magnetic Moment of T^{203} ," *Phys. Rev.*, 79:35 (1950).

. Regenerative and Superregenerative Spectrometers

1. Roberts, A., "Two New Methods for Detecting Nuclear Radio-Frequency Resonance Absorption." *Rev. Sci. Instr.*, 18:845 (1947).
2. Sheriff, R.E., and Williams, D., "Nuclear Gyromagnetic Ratios." *Phys. Rev.*, 82:651 (1951).
3. Pound, R.V., and Knight, W.D., "A Radiofrequency Spectrograph and Simple Magnetic-Field Meter." *Rev. Sci. Instr.* 21:219 (1950).
4. Ginsberg, J., and Beers, Y., "Circuit for a Radio-Frequency Spectrometer." *Rev. Sci. Instr.*, 24:632 (1953).
5. Knoebel, H.W., and Hahn, E.L., "A Transitron Nuclear Magnetic Resonance Detector." *Rev. Sci. Instr.*, 22:904 (1951).
6. Gutowsky, H.S., Meyer, L.H., and McClure, R.E., "Apparatus for Nuclear Magnetic Resonance." *Rev. Sci. Instr.*, 24:644 (1953).

Spin Echo Equipment

1. Hahn, E.L., (see Ref. I-5).

Part IV: Moisture Measurement by NMR

- Shaw, T.M., and Elsken, R.H., "Nuclear Magnetic Resonance Absorption in Hygroscopic Materials." *Jour. Chem. Phys.*, 18:1113 (1950).
- Shaw, T.M., and Elsken, R.H., "Investigation of Proton Magnetic Resonance Line Widths of Sorbed Water." *Jour. Chem. Phys.*, 21:565 (1953).
- Shaw, T.M., and Elsken, R.H., "Determination of Water Content of Solids by Nuclear Magnetic Resonance." Abstracts of papers, 123rd Meeting of American Chemical Society, Los Angeles, Calif., p. 1A (March 15-19, 1953).
- Shaw, T.M., Elsken, R.H., and Kunsman, C.H., "Moisture Determination of Foods by Hydrogen Nuclei Magnetic Resonance." *Jour. Assoc. Official Agric. Chemists*, 36:1070 (1953).
- Rollwitz, W.L., and O'Meara, J.P., "Determination of Moisture by Nuclear Magnetic Resonance: I. Theory and Design Considerations for a Practical Instrument." Abstracts of papers, 124th Meeting of American Chemical Society, Chicago, Ill., p. 13D (Sept. 6-11, 1953).
- O'Meara, J.P., and Rollwitz, W.L., "Determination of Moisture by Nuclear Magnetic Resonance: II. Experimental Results on Products of the Corn Wet-Milling Industry." Abstracts of papers, 124th Meeting of American Chemical Society, Chicago, Ill., p. 13D (Sept. 6-11, 1953).
- Shaw, T.M., and Elsken, R.H., "Techniques for Nuclear Magnetic Resonance Measurements on Granular Hygroscopic Materials." *Jour. App. Physics* (in press).
- Shaw, T.M., and Elsken, R.H., "Determination of Hydrogen in Liquids and Suspensions by Nuclear Magnetic Absorption." *Jour. Chem. Physics* (in press).
- O'Meara, J.P., and Rollwitz, W.L., "Determination of Moisture by Nuclear Magnetic Resonance." Abstracts of papers, 1st International Instrument Congress, Philadelphia, Pa., September 13-23, 1954, *I.S.A. Jour.*, p. 75 (Sept. 1954). *I.S.A. Proc.* (in press).

Part V: Commercial Manufacturers of NMR Equipment

Varian Associates, 611 Hansen Way, Palo Alto, Calif. Useful technical data and various bulletins can be obtained from Emery H. Rogers, Special Products Sales Manager.

Laboratory for Electronics, 75 Pitts St., Boston 14, Mass. Technical data may be obtained from A. Carl Westbom.

DISCUSSION

Question: With respect to the differences in line width at 100 percent moisture in the case of the homoionic clays, do these widths signify that you have differences in the orientation of the water molecules at moisture contents of 100 percent?

Pickett: The observed differences were so small that I do not know whether to attribute them to experimental error, the inhomogeneity of the magnetic field, or the rather large samples used. The samples were 1.5 in. in diameter and the inhomogeneity in the sample, the way it was placed, was of the order of about 50 milligauss. The differences at 100 percent moisture were in the order of about 30 to 40 milligauss. Therefore, I really cannot give a definite answer on this point.

Question: When you compared the viscosity of the absorbed water to the viscosity in ice or free water, is not what you measured an average viscosity of the entire water in this clay piece?

Pickett: Yes, that is right. These graphs give the average viscosity of all of the water. It would take a bit of mathematics to go from layer to layer as you build up layer after layer to reduce the data down to the viscosity of specific layers.

Question: Could this not be done by using different degrees of saturation of the mineral?

Pickett: Well, you see we ran these samples from about 0.5 percent moisture to something over 100 percent in rather small increments.

Question: But your data could be evaluated.

Pickett: They could be, but we have never done it.

Winterkorn: In such an evaluation, it should be kept in mind that the viscosity of a particular water layer depends not only on its distance from the mineral surface but also on the distance to an existing air-water interface.

Question: Has anybody attempted to start with a fairly well-characterized clay hydrate and first analyzed it by X-ray diffraction; then after determining that he was dealing with, perhaps, a monolayer hydrate, run it in a nuclear magnetic resonance (NMR) machine to see what he got in the way of water configuration? He could have gone back and prepared a two-layer hydrate and tested this in the NMR machine, and forth. I should think that if he started out with fairly well-purified clay mineral and hydrates which he had characterized by some standard means, such as X-ray diffraction, this would greatly simplify the interpretation of the results from the NMR machine.

Pickett: I do not know of any study on clays that has been that complete. Our laboratory has done some work that has been that complete on silica gels, but not on clays. Does anyone here know of anybody who has had that much money?

Answer: I do not know of anyone, but the fact that you went through water contents with mono- and dual-layers usually form and got no discontinuities in your curves suggests that the continuous change in the NMR line width represents the viscosity.

Pickett: Thank you. I felt that way, but I cannot prove it.

Winterkorn: I feel that the fog is lifting and that we are getting right at the crux of the problem. Certainly, the NMR method will have an important role to play in its ultimate solution. Mr. Pickett mentioned the money angle involved in this kind of

Money is indeed a very important factor. Several years ago, I applied to the National Science Foundation and to other agencies for funds to do this kind of work in the manner suggested. I did not get it and the same thing probably happened to others that were on the same scent. This is why I was so happy when I read Mr. Pickett's work on this subject and why I asked him to speak to us today. Universities are no longer rich enough to provide funds for this kind of work and it seems that we have to hope that the large government and industry laboratories will do it and produce data which we can use.

Dr. Blaine and Mr. Pickett have introduced us to the NMR method and have shown us why and how it can be used for our purpose. Now Dr. Seligmann of the Portland Cement Association Research Laboratories will tell us more about the "why" and also about the advantages and limitations of this method.

Interpretations and Limitations of Nuclear Magnetic Resonance

PAUL SELIGMANN, Portland Cement Association

● **ALTHOUGH** the interest of the Applied Research Section of the Portland Cement Association has centered primarily on the possible use of nuclear magnetic resonance for determining the states of binding of the water in hydrated cement paste, the conclusions drawn as a result of study and the few experiments that have been conducted for the Section are of interest. This belief is based on the fact that most of the hydration products of portland cement are, like the clay fraction of soils, of a colloidal nature (1). In fact, the system concerned is at least as complex as the soil-water system. In addition to the phenomena associated with changes in adsorbed water content, there are the chemical reactions of continued hydration of the cement and the reactions of the hydration products with atmospheric carbon dioxide. No technique has yet been developed for determining the precise states of physical and chemical binding of the water in hydrated cement paste.

The Section's interest in nuclear magnetic resonance was first aroused by the appearance of a paper (2) in 1955 dealing with the different proton resonance patterns that appear at various degrees of hydration of cement-water pastes. It appeared from this work that physically adsorbed and chemically combined water could be distinguished, at least semiquantitatively. A careful study of the potentialities of this method was therefore initiated; this study was completed at about the same time that an earlier speaker, Raymond Blaine, obtained his equipment. The conclusions from this study pertinent to the Section were (a) if the instrument could distinguish no more types of water than were indicated in the 1955 paper, the technique would not be useful either routine work or as a research tool, and (b) in view of this apparent limitation, there would be little or no justification to make the considerable effort required to develop techniques for use of the equipment or to develop detailed theoretical interpretations of the patterns obtained.

The first conclusion is based on a variety of results obtained from shrinkage data and X-ray diffraction patterns showing that the portion of the paste water that is evapable at 105 C cannot be a homogeneous adsorbed phase, and further that the precision of proton resonance measurements was not sufficient for this technique to be used as replacement for the time-consuming, routine adsorption methods now in use. The second conclusion was based in part on the scope of the work of the Section and in part on the extreme difficulty of precise interpretation of nuclear magnetic resonance patterns.

The proton resonance frequency depends on the difference in energy between two proton states representing two possible orientations with respect to the magnetic field. This energy difference, in turn, depends on the field strength as is shown by the following formula:

$$\gamma = \frac{\Delta E}{h} = \frac{\mu H}{h} (\cos \theta_1 - \cos \theta_2)$$

in which

- γ = the resonance frequency
- ΔE = the energy difference between the two proton orientations
- H = the magnetic field strength
- μ = the magnetic moment of the proton
- θ_1, θ_2 = the angles between the magnetic field and the magnetic moment of the proton in the two orientations
- h = Planck's constant

If the magnetic field were completely homogeneous, the resonance pattern would consist of only one infinitesimally thin line at the resonance frequency given by the formula. The pattern would therefore be the same for all materials containing hydrogen and would be useful at best only for the quantitative determination of hydrogen content. The real utility of the instrument is based on the fact that the local magnetic field strength at the positions of individual protons is a resultant of the external magnetic field and the magnetic fields produced by neighboring electrons, nuclei, and other atoms and molecules. The actual pattern obtained, therefore, results from the particular environments in which the protons find themselves, and consequently the patterns themselves when properly interpreted indicate the states of binding of the protons in the material under study. Although qualitative conclusions can be readily drawn, as has been shown in the two preceding discussions, a more detailed interpretation is exceedingly difficult.

The effect of binding can be illustrated by a description of the difference in patterns between a liquid and a solid. In a solid, the atoms are rather tightly bound; they are not free to move and as a result the local field may vary considerably from point to point within a lattice. As a result, there is a large range of resonance frequencies because there is a wide variety of local magnetic field strengths. In a liquid, on the other hand, much greater freedom of motion is possible; the application of the external field causes the nuclei and atoms to align themselves in such a way as to cause the local field to be much more nearly like the external field. The line width is, therefore, considerably narrower and all portions of the pattern are very close to the frequency that could be calculated from the external field strength by Eq. 1.

Really precise interpretations of proton magnetic resonance patterns have been made only for single crystals of known structure where all the components of the local magnetic field could be precisely determined. The cement-water system, like the soil-water system, is far from meeting the prerequisites for such detailed analysis.

It must be recognized, however, that the phenomenon of nuclear magnetic resonance can be used in a variety of techniques. The discussions of Blaine and of Pickett were based on the so-called "wide line" technique, which is very adaptable to the study of solid material. There is another technique known as the "spin-echo" technique that is less well known but has been successfully used in determining the states of binding of adsorbed water in various colloidal systems without a precise knowledge of the local magnetic field strengths.

Of great interest in this connection is a paper on the state of water adsorbed on silica (3). At low moisture contents, three distinct classes of water were found in place of the single, previously assumed class. Of equal significance is recent work (4) on the state of binding of adsorbed water on cellulose. In this system, two distinct types of adsorbed water could be distinguished and the frequency of transition between the two could be determined.

Because of the great promise of this new technique, samples of a particular hydrated cement paste with different evaporable water contents were submitted to the manufacturer of a spin-echo proton magnetic resonance apparatus that has recently become commercially available. Unfortunately, it was found that the local magnetic fields produced by the small quantity of ferric oxide in the cement distorted the patterns sufficiently to destroy their value. It is believed, however, that the method still holds great promise for the study of colloids containing no iron. Unfortunately, the iron usually present in cement minerals would cause this technique to be of little value in work with the systems of interest to this audience.

Although the conclusions reached herein appear very discouraging, one further technique is being investigated; namely, the study of dielectric constant and dielectric loss measurements as a function of frequency. In both of the applications of spin-echo technique cited, the results confirmed preliminary indications obtained by studies of the dielectric constant of the same materials. Inasmuch as local magnetic fields are not expected to interfere with the ability of a polarized water molecule or hydroxyl group to resonate with an external electromagnetic field, this technique appears to hold promise. Anticipated difficulty is that the results obtained depend not only on protons but rather on all polar or polarizable constituents of the material under study. A recent paper (5)

on measurements of halloysite and kaolinite shows the difficulties in interpretation that may be encountered. It is encouraging, however, that studies on the materials of interest to this audience are being undertaken.

REFERENCES

1. Powers, T.C., and Brownyard, T.L., "Studies of the Physical Properties of Hardened Portland Cement Paste." *Jour. Amer. Concrete Inst.* (Oct. 1946-April 1947); *Proc.*, 43:101-132, 249-336, 469-504, 549-602, 669-712, 845-889, 933-992 (1947), *PCA Res. Bull.* 22.
2. Kawachi, K., Murakami, M., and Hirahara, E., "Studies on the Hydration and Hardening of Cement (Experimental Studies on Nuclear Magnetic Resonance of Water Molecules in Cement)." *Bull. Faculty Engineering, Hiroshima Univ.*, 4:95-101 (1955).
3. Zimmerman, J.R., Holmes, B.G., and Lasater, J.A., "A Study of Adsorbed Water on Silica Gel by Nuclear Resonance Techniques." *Jour. Phys. Chem.* 60:1157-1161 (1956).
4. Sasaki, M., Kawaii, T., Hirai, A., Hashi, T., and Odajima, A., "A Study of Sorbed Water on Cellulose by Pulsed NMR Technique." *Jour. Phys. Soc. Ja* 15:1652-1657 (1960).
5. Goldsmith, B.J., and Muir, J., "Surface Ion Effects in the Dielectric Properties of Adsorbed Water Films." *Trans. Faraday Soc.*, 56:1656-1661 (1960).

General Discussion

L. F. Winterkorn, Chairman:

We have gone a long way trying to find solutions for our macroscopic soil-water problems by passing to systems of ever smaller dimensions and ending up with the proton spin. Now, we have to ask: What good is all this for working engineers? Or rather, which available concepts and facts are directly useful to us and what is the best way of using them?

First of all, the laws of material behavior on a certain level of structure in order to be useful must be derived or at least expressed on the level of application. To gain a better understanding of such laws and obtain a mastery of their use, it is often necessary and always desirable to underpin them with knowledge derived from the study of a lower level of structure. Thus, we underpin the laws for the macroscopic level by those obtained at the microscopic, and so on, until we arrive at the nuclear or even intranuclear level. In this procedure, two important points must be realized:

1. Even if we understood perfectly the properties and behavior of the components of a system, the behavior of the system is not a simple summarization but contains an organizational or structural factor that may not be obvious a priori. Even in the relatively simple case of gases, one may have to use Maxwell-Boltzmann statistics under one set of conditions, Bose-Einstein statistics under another, and Dirac statistics under still another set.
2. There exists no a priori reason why the laws derived and valid on a particular dimensional level should be of a greater intrinsic certainty than those derived on a level of larger dimensions. As a matter of fact, the most exact physical laws were derived from the behavior of heavenly bodies whereas, on the other end of the size scale, one of the most important findings of modern science is the uncertainty principle of Heisenberg.

The lesson to be drawn from this situation is apparent. With all the justified eagerness to learn from the knowledge of material behavior on the levels of smaller dimensions, with all the acknowledged need for such knowledge to serve as underpinning for a better understanding and optimum use of soil on the dimensional level on which we work, it must be kept in mind that all this knowledge is ancillary to the job of coordinating this knowledge into practical phenomenological laws that are valid for engineering purposes. Engineers, especially the workers in the purer sciences, cannot be expected to do this for themselves. Much of the details furnished by them will, of course, have to fall by the wayside. To do this job, there is need for your cooperation if only in the form of questions, but any other form will also be appreciated.

I was somewhat taken aback when I heard the review of my paper entitled "Mass Transport Phenomena in Moist Porous Systems as Viewed from the Thermodynamics of Reversible Processes." This title may have been somewhat presumptuous and not entirely fitting, but it was intended to be provocative. Here is a good and promising method but some people have blown it up too big and promised too much without laying down the strict conditions necessary if the promises are to be realized. I tried to show the use of this methodology in the larger field of thermodynamics and to indicate the type of experimental data that has to be accumulated before this methodology can be honestly and sensibly applied for our purpose. I am happy to be able to state that Dr. Taylor of the Agricultural Experiment Station of Utah is already busy along these lines and that the proceedings of the Seventh International Soil Science Congress will contain a paper by him on this subject. Probably, additional papers by him and his co-workers will be published in the Proceedings of the Soil Science Society of America.

L. H. Fink, Philadelphia Electric Co.:

Our company has been very much concerned with the movement of moisture in soil under the influence of thermal gradients because of the influence of such movement on the thermal resistivity of soils and consequently on the heating of our underground cable systems.

I would like to ask for at least a qualitative statement of opinion on a question on the lack of agreement concerning the relative importance of movement in the liquid and vapor phases. Reading the papers in this symposium and related papers in the literature, I have gotten the impression that the evidence, at least that presented by the proponents of movement in the vapor phase, tends to indicate that it is impossible for there to be much movement in the liquid phase in open systems—at least for there to be enough to cause any appreciable results. On the other hand, the evidence presented to show that movement in the liquid phase is possible, could perhaps be interpreted as also supporting the Smith-Philip-De Vries hypothesis that movement is stepwise in vapor and liquid, alternately. At the same time, this hypothesis could also be consistent for instance, with the results obtained by Mr. Flood, referred to by Prof. Low.

The question is, is it correct that the Philip hypothesis presents a consistent explanation for the otherwise apparently conflicting data cited by the proponents of the vapor and liquid movement hypotheses, respectively?

P. F. Low, Department of Agronomy, Purdue University:

My own profession is largely the physical chemistry of soils more than the transfer of water by mass flow; therefore, I do not regard myself as an expert in this area. It is a possibility in Mr. Flood's work, of course, that part of the movement was in the vapor phase. The question arises whether in the voids of his carbon rod he had a vapor transfer between necks joining the carbon particles or between water necks at the point of contact between the carbon particles. I can only answer honestly that I do not know. Dr. Rollins has reviewed some of this work.

I would like to make one general comment in this regard: The path by which water moves through a porous system, whether it be in the films along the particle surface or in the vapor phase in the voids, will depend on the energy necessary for that movement. It can be visualized that a moving molecule has to surmount a potential energy barrier in going from one equilibrium position along the path of movement to the next. If movement along the liquid surface requires movement over a smaller potential energy barrier than movement in the gas phase, then movement will occur in the liquid phase. The path that is taken will largely depend on the energy required for movement to occur. As the liquid films get thicker, the outermost layer of the water molecule should move with less and less resistance because the forces of adsorption would decrease. It is conceivable that both mechanisms might occur simultaneously.

One other factor, and Prof. Flood made this point, when there is an adsorption potential so that the potential energy of the water is less next to the clay surface or the carbon surface than out in the middle of the pore, if there is a vapor pressure gradient in the center of the pores, this gradient may be a million times less than that along the surface, because the pressure build-up toward the surface might be a thousand times and when there is one vapor pressure, for example, at the inlet face and another at the outlet face and a given vapor pressure gradient in the voids, the fact that the vapor is adsorbed on the surface and its pressure can build up on the surface by reason of the attractive forces can lead to a gradient along the surface that might be a million times the gradient in the vapor. Even though the viscosity of the water on the surface is maybe a hundred times higher than that of normal water, according to Prof. Flood there is so much larger gradient present that water can still flow in the films.

The problem may be looked at in terms of Darcy's Law for unsaturated systems. In the films there is a conductivity, a transmission constant, that in the saturated state is called the permeability or conductivity. That constant may decrease a great deal as the surface of the clay particles is approached. Thinking of Darcy's Law, the flow would be expected to go down. But as the surface is approached, the pressure gradient could go up far more than the transmission constant could go down, or might go up

more than the transmission constant would go down, with the net effect that the transfer along the surface might be a lot higher than would be normally anticipated. I hope that Prof. Rollins will care to comment because he has worked in this area.

R. L. Rollins, Brigham Young University:

In addition to what Prof. Low has said, I would like to make a couple of comments. The type of system must be considered when we examine any research that has been performed in this particular field. After reviewing the research of the workers who have been proponents of the vapor transport theory, it seems that they have been dealing with soils that are primarily nonplastic or of very low plasticity. Under these conditions it would be expected that vapor transport would be the predominant mechanism of flow. On the other hand, the work of Dr. Winterkorn, and perhaps of one or two other individuals, was performed on systems that were highly plastic or bordering on the montmorillonite-type clays. Under these conditions, it would seem that the predominant mechanism would be flow in the liquid phase.

A few years ago, I performed some research on the movement of soil moisture due to a thermal gradient which attempted to measure quantitatively in an open system the amount of vapor flowing. The soils used were of low plasticity. Comparing the observed flow rates with the theory advanced by Philip and De Vries, there appears to be a fairly good correlation between theory and experiment, except below air-filled voids of 5 percent. For systems below this percentage, the correlation was not good. Above this figure, there is a fairly good correlation. The type of system dealt with in attempting to make any general conclusion as to the type of flow mechanism must be considered. I agree with Prof. Low that it is possible to have systems where both of these mechanisms would occur to some degree simultaneously, with liquid flow in highly plastic systems and vapor flow predominating in the less plastic systems.

Sereda, Division of Building Research, National Research Council of Canada:

We must realize that Prof. Flood's work, discussed by Prof. Low, and thermomigration of moisture in soils, discussed by Mr. Penner, are two different cases. Dr. Flood worked under isothermal conditions. He established a high vapor pressure at one end of a carbon rod and a low vapor pressure at the other. By condensation, a thicker film was formed on the internal carbon surface at the high pressure end than at the low pressure end. This resulted in a suction potential under which the condensed water tended to redistribute itself. This procedure is analogous to putting together at the same temperature two samples of a material, one of which has a higher moisture content than the other.

The situation about which Mr. Penner was speaking is quite different. In systems where the large, thermally activated flows have been observed, it is a matter of dealing with near-saturated conditions in which the relative humidities approach 100 percent. In the experiment, a homogeneous sample of clay or sand at a given, uniformly distributed moisture content, which usually corresponds to the high pressure end of the isotherm, is taken and then different temperatures are applied to the ends of the sample. Under these conditions, the high spreading suction obtained under isothermal conditions for different moisture contents of the samples cannot be expected, as in Dr. Flood's experiments.

But this does not mean I am arguing that there is no liquid flow involved when a thermal gradient is applied to a moist soil sample. Prof. Winterkorn has already pointed out that this isotherm changes at different temperatures, as in fact it moves up with a decrease in temperature. He has published his experiments and his reasons for thinking that there should be some liquid flow.¹ His pertinent statement in HRB Special Report 40 says that the water "shifts" in the sample because of the change of isotherms from one temperature to the other.

¹ Soil Science, 38:No. 4 (1934); 40:No. 5 (1935); 41:No. 1 (1936). HRB Proc., 27:443-445 (1947).

H. F. Winterkorn:

I would still like to have some more discussion about the problem brought up by Mr Fink, for what may appear to be fine points of theory are actually decisive factors with respect to proper design of soil structures for various purposes. Mr. Fink's problem and that of the electric power industry is how to prevent the drying out of soil around buried power cable conduits. Such drying lowers the thermal conductivity of the soil, which in turn leads to overheating and eventual burning out of the power cables with great direct and often greater indirect economic loss.

C. M. Johnston, Bureau of Public Roads, U.S. Department of Commerce:

There seems to be an argument between one group and another as to whether thermally activated water movement went through the vapor or liquid phase. Possibly, both groups are right. Now, one speaker said that the adsorbed water was held so tightly that water movement had to take place in the vapor phase. In such tightly held films, would it be possible for a molecule at one end, possessing a large amount of free energy, to bump all the way through so that this molecule would take the place of its next neighbor and this, that of its neighbor, and so on until finally on the other end there is a free molecule?

H. F. Winterkorn:

The possibility of such a mechanism has been discussed in the literature as far back as the times of Grotthus, but there are some serious objections if the hydrogen linkage of the water molecules is taken into account. There are, however, a large number of possible and actually occurring types of flow in these systems. As a reference, the extremes of "plug" flow as in certain electro-osmotic systems and of molecular diffusion in zeolites have been studied by M. H. Hey in England and results published during the early thirties in the Mineralogical Magazine. Hey's work and conclusions might be pertinent with respect to moisture movement in hardened cement pastes.

E. Penner, Division of Building Research, National Research Council of Canada:

To add one further note on the confusion between liquid and vapor phase, it seems that at the time when Gurr, Marshall, and Hutton² published their work, they showed fairly definitely that if salt is added to a moist soil and then a temperature gradient applied to this soil, all the salt accumulates at the hot end. What this means is that the salt cannot be any continuous liquid flowing from the hot end to the cold end. It must all have gone through a vapor phase. Now there is certainly "back-wicking," which is flow from the cold side to the hot side. In the case of Gurr, Marshall, and Hutton, this was done with closed systems. It is true that we did not use material—in our open system—which would be akin to the clays referred to, but rather to silts and sands. What Gurr, Marshall and Hutton used was a loam.

H. F. Winterkorn:

A loam and washed fine sand.

E. Penner:

There was no evidence at all that the complete movement is in the vapor phase from the hot to the cold end under temperature gradients. This means that there can be segments of liquid but they are always separated by a vapor phase. These gaps are in fact barriers to salt movement from the hot side to the cold side.

H. F. Winterkorn:³

The results of the experiments by the Australian workers are not as clear cut as they appear to be and lend themselves to interpretations that are at variance with those that have been offered. Also, as has been stated, they were performed on loams and sands.

² Soil Science, 74:No. 5, pp. 335-345 (1952).

³ The following comments are an expanded version of the oral discussion in order to avoid low specific reference to the actual experimental data of Gurr, Marshall and Hutton.

not on clay soils. The physical characteristics of the materials used by the Australian workers were as presented in Table 1.

Enclosed cylindrical soil samples 10 cm long and 14 cm in diameter were submitted to temperature gradients of about 1.6 C per cm. One set of tests with the loam soil involved 10 different moisture contents ranging from 1.7 to 24.4 percent subjected to the temperature gradient for 5 days. Maximum differences in water content at the end of the tests were observed in the samples of the original uniform moisture contents of 5.3 and 7.9 percent, respectively. This, according to the authors, placed the maximum

TABLE 1

Properties	Loam Soil	Washed Fine Soil
Particle size distribution (percent):		
2-0.2 mm	1.9	20
0.2-0.02 mm	50.2	80
0.02-0.002 mm	31.3	0.0
<0.002 mm	16.6	0.0
Total soluble salts (percent)	0.077	—
Chloride content/100 g of soil in me	0.14	—
Moisture equivalent (percent)	20.0	2.5
Permanent wilting (percent)	6.3	—
Plastic limit	15.8	—

or water transmission at about one-third of the moisture equivalent or about 6.7 percent of water. The permanent wilting point is at 6.3 percent.

The experiments made at 5.3 percent moisture content showed a maximum in chloride content about 3 cm from the cold end, those made at 7.9 percent moisture showed chloride peak at the same distance and a maximum value at the hot end. At higher moisture contents, the chloride contents form a plateau lying between 3 and 7 cm from the cold side, the height of the plateau corresponding to from about 7 to 10 percent of the original uniform chloride content. The highest absolute values for chloride concentration at the hot end occurred in the samples with original uniform moisture contents of 14.3 and 16 percent, respectively. Significantly, practically no water shifting took place at these moisture contents.

An experiment in which this loam soil was submitted at a water content of 11.3 percent to the temperature gradient for 18 days resulted in a reduction of the chloride content to about 15 percent of its original content in the colder half of the specimen, to about 40 percent at 7 cm distance from the cold side, and increased it 7 times the original concentration at 1 cm from the warm side. The accompanying water shift was only one-half that obtained in the 5-day experiment at the optimum water content for water shifting.

Ten-day experiments with the washed sand to which NaCl was originally added at the cold end made at 5.8 and 7.9 percent of water, respectively, gave an irregular pattern of water shifting with differences between cold and warm side of 1 and 0.5 percent, respectively, and a chloride concentration peak at a distance of about 5 cm from the cold side and a maximum concentration at the warm side for an initial water content of 8 percent. For the sample with 7.8 percent water, there was an absolute chloride concentration maximum at about 3 cm from the cold side, and the absolute minimum concentration fell within the first 2 cm from the warm side.

It should be quite obvious that these experimental data have as yet not been completely evaluated; also, that the addition of NaCl has complicated rather than simplified the interpretation of the experiments.⁴ To the speaker, the most significant fact brought

The system may be further complicated by "Soret" effects and by related phenomena that are treated in "The Structure of Electrolyte Solutions," Walter J. Hamer, Ed., John Wiley (1959).

out in the Australian experiments is that maximum moisture transfer occurred at water contents at about the permanent wilting percentage. Up to this percentage, the water is in such a state of organization or restraint that it cannot be utilized by plants. Lowering the temperature will bring more water into this restraint and increasing the temperature will bring less. Organization of molecules into a restrained structure, which is akin to crystallization, results in decrease or loss of its solvent properties, a phenomenon utilized in purification of chemicals by zone-melting.

Taking a soil sample of uniform moisture content at about the wilting or similarly significant point (indicating that most of the water molecules are in a restrained condition at the particular temperature), make one end of the sample warmer and the other colder. Because the restraining power of the mineral surface increases in depth with decreasing temperature and vice versa, the water will shift from the warmer side having less restraining power, to the colder side. If more water is available than necessary to satisfy the mineral surfaces, then this will be distributed in uniform thickness above the restrained layer. If this free water is of a sufficiently large amount, its presence may hide the fact that larger amounts of the total water are under restraint on the cold than on the warm side and the distribution of the water substance will remain uniform. On the other hand, because the strongly restrained water may not serve as solvent, only the free water can contain the electrolyte and, as in the Australian experiments, a great shift in electrolyte content may occur without apparent shift in total water content. There will be, of course, special effects at the ends of the samples due to the abrupt change in condition and to "thermal shock" at the beginning of the experiment. This also is exemplified by the Australian experiments as well as by those made by Trejo for his 1946 master's thesis in the speaker's laboratory at Princeton.

I would like to state categorically that those of us who believe in the indicated water shift toward the cold end in the liquid phase do not deny contributions by vapor transport and other means. Rather, because evaporation and condensation phenomena are so apparent and are ever-present in our daily life, their very obviousness seemed to make it unnecessary to talk much about them, especially because they are well covered in the classical soil science literature. There is sufficient experimental evidence to permit the statement that every transport mechanism imaginable in accordance with established physical laws will actually participate in the total phenomenon to an extent that is controlled by its activation energy. It is the degree of participation that is still to be established for different materials and conditions. Of considerable pertinence in connection with the effect of thermal gradients on moist soils is the symposium paper by Kolyaso and Gupalov. With respect to thermal conductivity of moist soils, the speaker expects to show in a forthcoming paper⁵ the necessity of having several transportation mechanisms acting at the same time in order to account for the actual magnitude of the total effect.

⁵ "The Behavior of Moist Soils in a Thermal Energy Field." 9th Annual Clay Symposium, National Research Council (1961).

Supplementary Note on Work of Caron and Szuk

Before this bulletin went to press, communications were received from Claude Caron, Chief of the Research Laboratory of Solétanche, Paris, and Geza Szuk of the Hungarian Scientific Institute for Structural Engineering, Budapest. These communications resulted from a Seminar by Correspondence organized by Professor L'Hermite on behalf of RILEM on moisture-measurement in materials and structures. They are of considerable importance with respect to the condition of moisture in sands and soils and to electric and thermal resistivity of soil-water systems.

Caron investigated the possibility of using the thermal probe (1) as a nondestructive method of moisture determination. He employed a thermal probe of 2 mm outside diameter and 120 mm length containing an electric heating wire and a thermocouple. Heating was done by a 6-volt battery regulated with a rheostat so that the heating current remained constant at 300 or at 600 milliamp. The increase in temperature of the needle as a function of time was measured with an electronic voltmeter (Philips GM 6010).

The water content of a soil specimen is related to its thermal resistivity; the resistivity is represented by the slope of the line obtained if the thermocouple voltage is plotted as the ordinate and the log of time as the abscissa. One selects the straight part of the curve between 1 and 10 min.

Figure 4 (reproduced herein as Fig. 1) of Caron's paper (2) gives the water content of a sand as a function of the tangent of the slope of the experimental temperature-log time curve. The relationship is very good for low moisture contents. The method may also be applied to determine the porosity of saturated sands.

The paper by Caron elicited the following discussion, written by Geza Szuk:

"Caron discusses in his paper results obtained with the method of moisture determination based on thermal conductivity. When evaluating the diagrams, it is striking that the tangent (tg 0.46) of the sample with a water content of 4.77 percent does not seem to fit into the other results of the test series.

"In the first section of straight lines determining the tangents, scatter is noteworthy where the measured points are not in accordance with the straight lines. Caron is of the opinion that this scatter is due to the heating of the probe and can be neglected.

"In Figure 1, the relation between tg α and the percentage of moisture can be seen, plotted as a continuous curve.

"If the diagram in Figure 1 is plotted on the basis of the actual experimental data, a marked inflection is observed at 5.3 percent of water (Fig. 2, Curve 1). This phenomenon can also be observed in Figure 1 of Caron's paper.

"The diverging values, measured in the first period of the straight lines determining the tangents, are doubtless a consequence of the heating period. But if the character of this scatter is better investigated, it is found that stopping times for the scatter first increase with increase of moisture percentage and later, after a maximum between 5 and 6 percent, begin to decrease (Table 1).

"Plotting these times against the percentage of humidity (Curve 2) a very interesting U-shaped curve is obtained. This curve has no peak, because there is no data between 4.77 and 6.55 percent. Comparing Curves 1 and 2, it is found that the inflection point of the tg curve (Curve 1) appears at the same place where the peak of Curve 2 is thought to be (5.3 percent).

"If the scatter is due solely to heating, it would have another character. It seems probable that this phenomenon is connected with other properties of the sand becoming wet.

"With our conductimetric measurements, it was found that by increasing the moisture content, the electrical resistance curve of the sand shows an inflection at a certain moisture percentage (3).

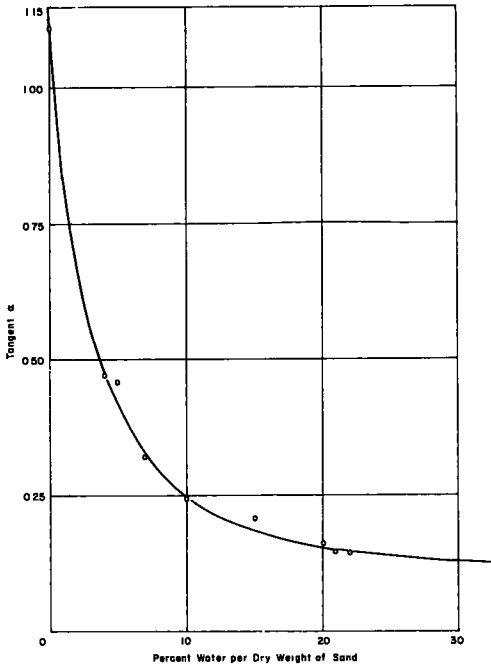


Figure 1. Water content of sand as function of tangent α .

TABLE 1

H ₂ O (%)	tg α	End of Scatter (min)	(sec)
0	1.11	0	40
3.85	0.47	-	-
4.77	0.46	2	00
6.55	0.32	2	00
9.1	0.245	1	00
13.0	0.205	0	40
16.65	0.160	-	-
18.00	1.145	-	-

"This point was called wetting point and it has been proved that this point determines the water requirement of the aggregate.

"The resistance curve of 0- to 0.5-mm sand is shown in the diagram as Curve 3. With this size, the inflection is found to be at 5 percent. Plotting the curve of denser decrease relative to the dry sand material of similar size above the curve against moisture content (Curve 4), a very valuable

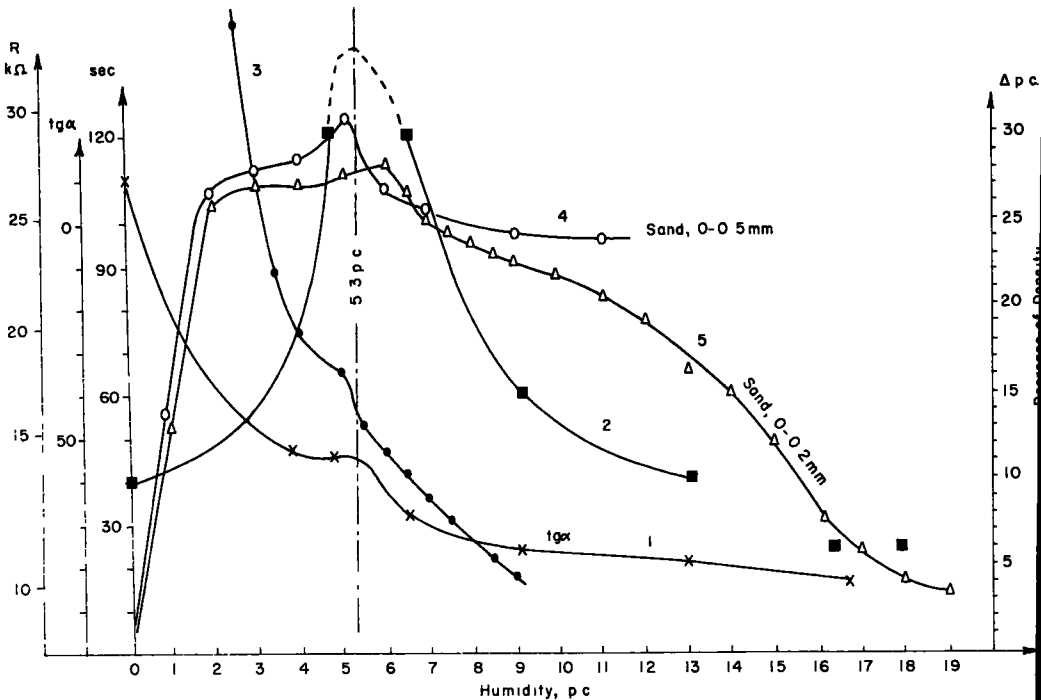


Figure 2. Resistance, tg α , and other properties of sand as function of water content.

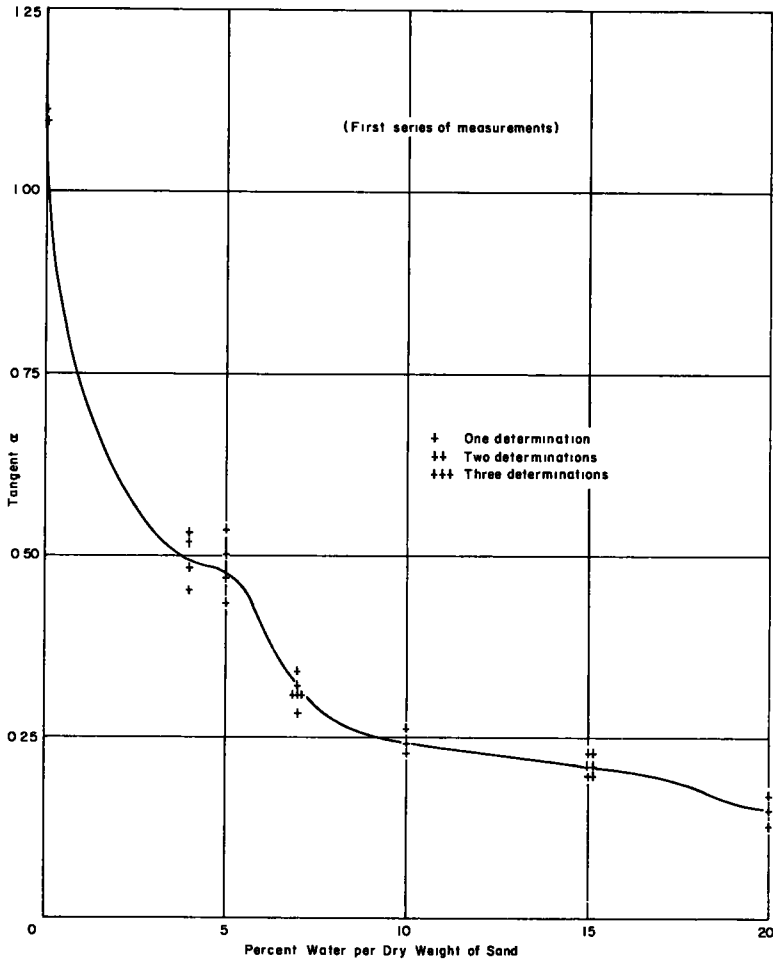


Figure 3. Variation of probe heating as function of moisture content of sand, first series of measurements.

lation is obtained; that is, decrease of the density shows a maximum value at the inflection point of the conductimetric curve.

"These measurements were taken with 0- to 0.5-mm Danube sand. Considering the above statements, a relation between these phenomena is very probable. In the diagram, the curve of change in density of 0- to 0.2-mm Danube sand is also plotted. As can be seen, the peak of the diagram is shifted in direction of the higher percentage moisture. This phenomenon was observed also when the wetting point of the sand is determined conductimetrically.

"Caron used 0- to 0.4-mm sand for his experiments. With this grading, the wetting point and the minimum of density has to be in a somewhat higher moisture zone than is found in our experiments with material of 0.5-mm size.

"Caron's curves show indeed irregularities at 5.3 percent. It would be interesting to repeat the test with 0- to 0.4-mm sand of 5.3 percent moisture content, as it could verify our suppositions."

Caron's response to the observations by Szuk was as follows:

"Your contribution to the conference on the measurement of water content by electric resistivity and your comments on our own report have been of greatest interest to us.

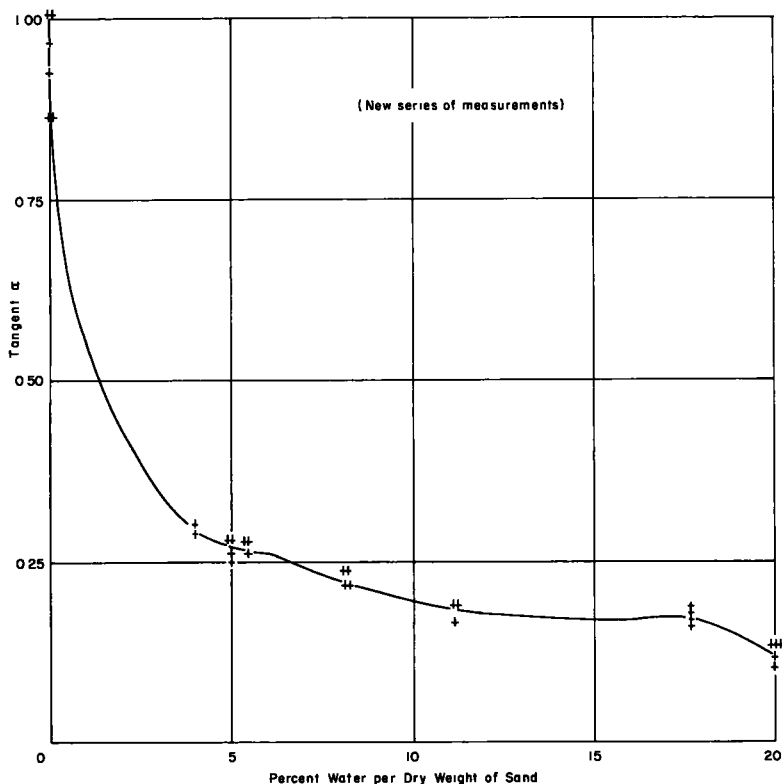


Figure 4. Variation of probe heating as a function of moisture content of sand, new series of measurements.

"The discontinuity that you have observed on the curve representing the electric conductivity as a function of the moisture content and that you have interpreted as representative of the water required for wetting of the material (sand or silt) is indeed very interesting.

"Interpreting several water content curves by variation of the thermal capacity which we had given in our report, you have found a double discontinuity:

1. The curve that represents the rate of heating as a function of the water content would flatten out in the vicinity of the content required for wetting in analogy with the respective observation in the case of electric resistivity.

2. The curve that represents the time passed before the heating curve becomes linear as a function of the water content exhibits a maximum just at the water content required for wetting. To give you more information on these two phenomena, we are sending you our complete series of measurements. On the four curves that will be discussed subsequently, we have reported the water content as a percentage of the dry weight of the material which in all cases is a sand that passes the 0.4-mm sieve.

Curve of the Slope of the Temperature-Log Time Relationship as a Function of the Moisture Content

"Figure 3 gives all the data obtained in the original investigation, of which only a portion was reported in our previous communication. Figure 4 gives a new series of data obtained with another thermal probe. One can notice a slight tendency of inflection at a water content of about 5 percent, but we do not dare to be as categorical about it as in your measurements on electric resistivity, since we recognize the lower sensitivity of our thermal method.

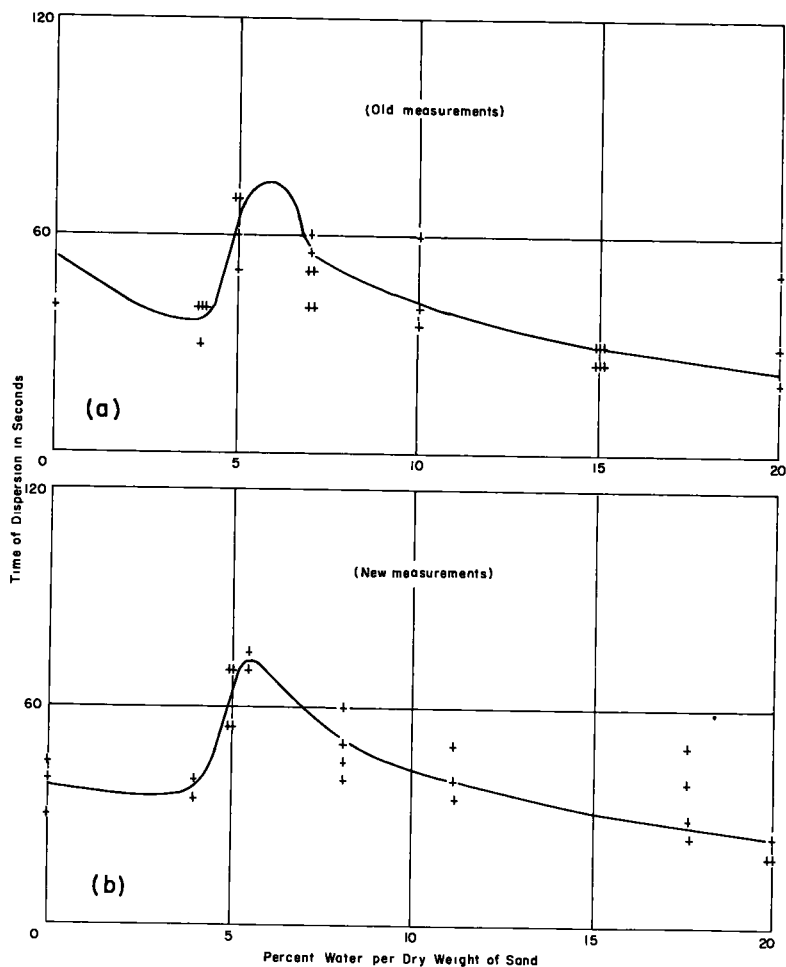


Figure 5. Variation of time of dispersion as function of water content of sand, (a) old measurements, and (b) new measurements.

Curve of the Time of Dispersion as a Function of the Water Content

"As in your communication, we designate as time of dispersion the time passed before the plots of the temperature versus log time become linear; that is, before they begin to obey the theoretical law. We have found that the first points do not align themselves with the data taken after 1 min. It is possible to draw a straight line through these first points. This line has a different slope than the theoretical straight line obtained between 1 and 10 min. The time of dispersion has been defined by us as the time at which these two lines cross. Precise determination of the dispersion time is obviously not possible, since the first straight line is quite ill-defined. Consequently, the intercept is also ill-defined and so is the curve resulting from plotting the dispersion times versus the moisture content.

"Nevertheless, despite this fact which is true not only for our first determinations (Fig. 5a) but also for our second series (Fig. 5b), one can obtain a type of bell-shaped curve whose maximum is in the vicinity of the water percentage required for the wetting of the sand. Therefore, a discontinuity appears to exist at the moment at which the sand-water-air system passes from what is essentially a two-phase sand-air system (in which the water has not yet wetted the sand grains completely and formed a continuous water phase) to a three-phase sand-air-water system. This discontinuity will be more important, the finer the particle size of the material."

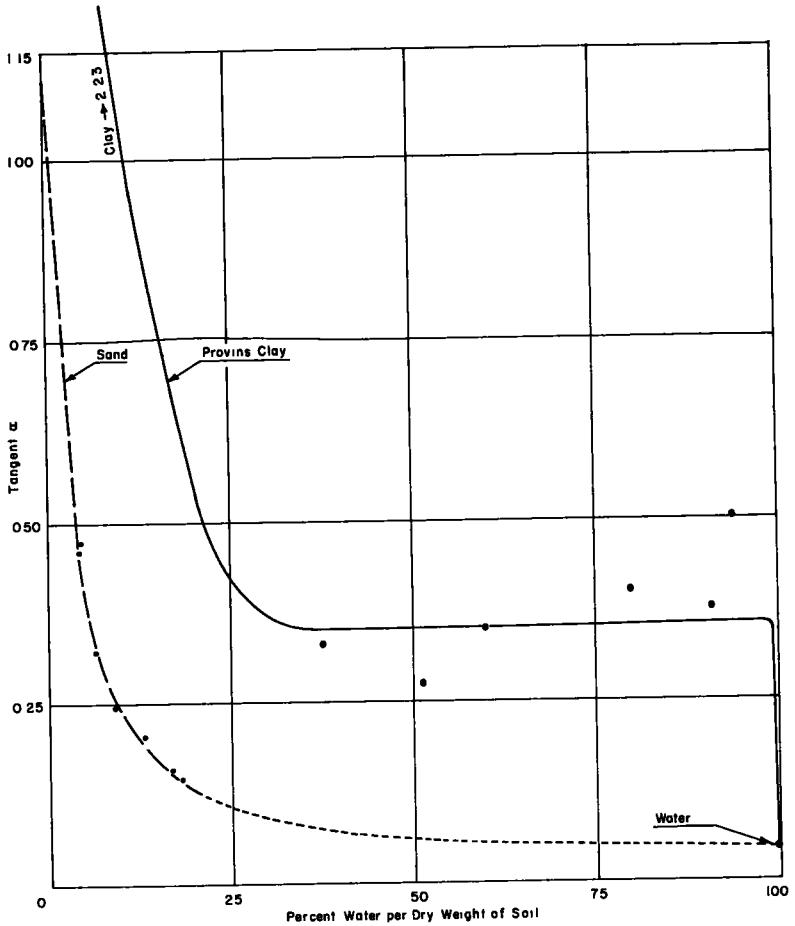


Figure 6. Tangent α as function of water content of sand and clay.

It should be very enlightening with respect to the controversy on the thermal moisture movement in sands to reanalyze available data by taking the findings of Caron and Szuk into account and also to run new experiments with sands having moisture contents that straddle those at which the observed discontinuity occurs.

Caron also attempted to apply the method of moisture determination by means of thermal resistivity tests in the case of clay soils. He made numerous determinations of the same precision as those on sand. However, on plotting the tangents of the \ln -log time curve versus the moisture contents, two anomalies were observed:

"Instead of the points defining a continuous curve as in the case of sands, there are points that deviate considerably. The tangent values, which are proportional to the thermal resistivities, are very high even for very low clay contents (with 75 g of clay or 10 g of bentonite per liter of water, one obtains tangent values that are ten times larger than those for pure water).

"At first we thought that small air bubbles entrained in the clay suspension came in contact with the hot thermal probe and formed some insulating patches. However, carefully de-aired suspensions gave the same high values. We thought to have found an explanation in the high viscosity of the clay suspensions which are pseudo-liquid in which convection phenomena may occur. As a matter of fact, if one applies the same method to glycerine, one finds a tangent value that is fifteen times larger than that for water although the specific heat of glycerine is about 40 percent less. On the other

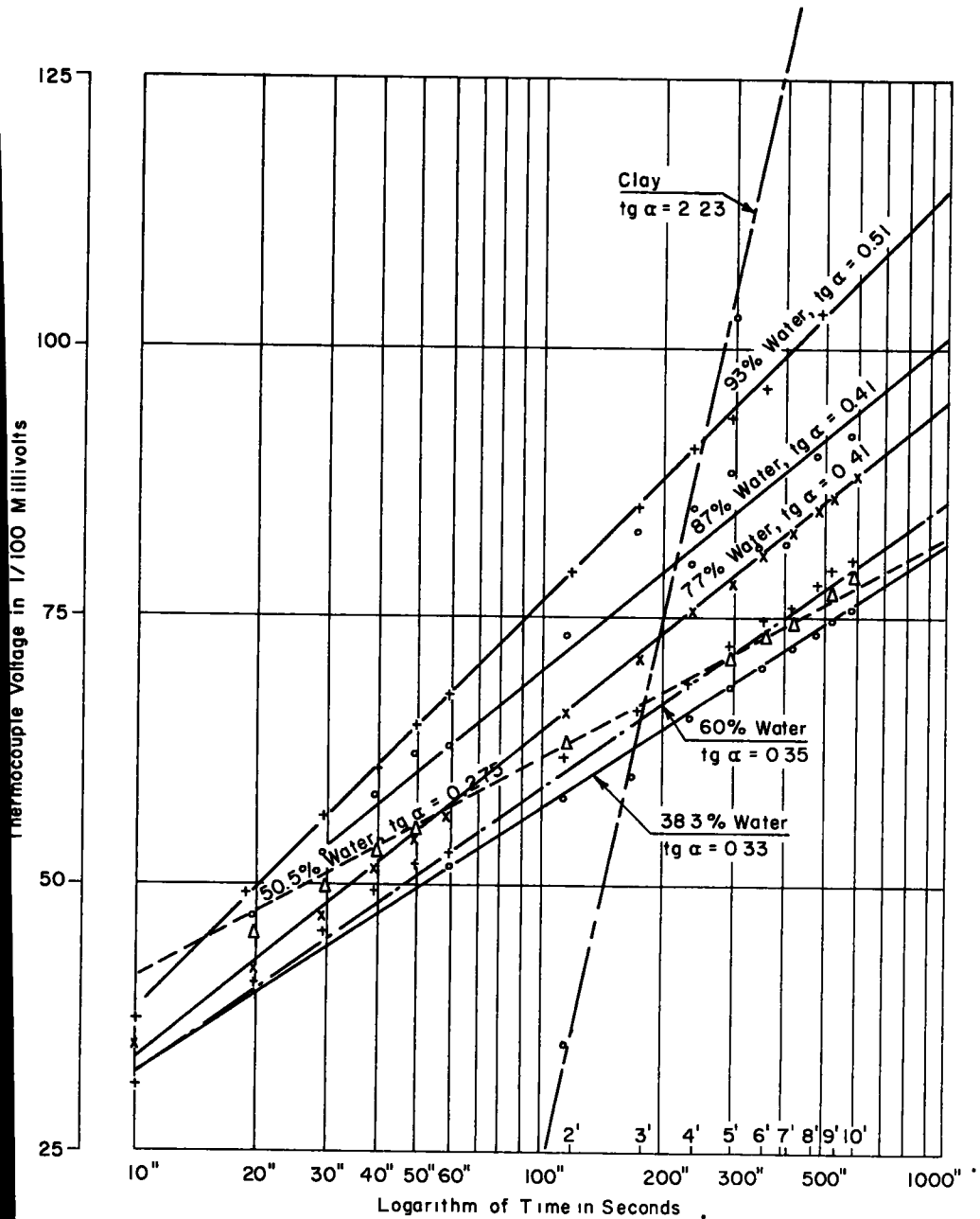


Figure 7. Thermocouple readings in Provins clay at various water contents.

d, the tangent value found with a viscous sodium silicate solution was ten times
her than that for water.

"Measurement of moisture content by thermal diffusion seems to be feasible only if
particles are not affected by convection currents of the medium. Such a conclusion
only be tentative. More extensive studies must be undertaken to clear up this anom-
ous behavior of clays.

"But if the viscosity of the medium causes this anomaly, why do the data for pure
er fall so well in the extrapolated curve for sands (see Fig. 6)? If it is the inter-

stitial water that must be able to move freely and not be bound to the particles, why does the glycerine, which is so much more viscous than water, show anomalous behavior? The problem remains in its fullness and much research is necessary to resolve it."

The findings of Caron with respect to the doubling of the thermal resistivity of water by the addition of 1 g of bentonite per liter and the increase to ten times the water value by dispersion of 75 g of Provins clay in a liter of water are of greatest interest with respect to the problem of thermal and moisture conduction in clay-water systems (Fig. 7). Giving due consideration to the large body of thermal resistivity data on clay soils collected by Sinclair, Buller, and Benham (4) and analyzed by Winterkorn (5) and keeping in mind that the average thermal resistivity of clay minerals at random orientation should be quite close to and possibly less than that of water, the tremendous increase in the thermal resistivity of water by the presence of dispersed clay, as observed by the thermal probe test, must be due to either or both, the disturbance of the water structure by the presence of the clay particles and a special geometric arrangement of the clay particles in the vicinity of the thermal probe. In view of the magnitude of the change in thermal resistivity, it is felt that its most probable cause is a circular arrangement of the clay platelets at a small distance from the probe surface in the shape of a cylinder that is concentric with the thermal probe. Such a structure could function as a thin wall and impede the loss of heat from the water phase between it and the surface of the probe, in a manner similar to that described and analyzed already by Fourier (6). However, as Caron states, this problem deserves further thorough experimental investigation and theoretical evaluation.

REFERENCES

1. Van Rooyen, M., and Winterkorn, H. F., "Structural and Textural Influences on Thermal Conductivity of Soils." HRB Proc., 38:576-621 (1959).
2. Caron, C., "Determination of Moisture Content in Soils." No. 237.722, RILEM, Paris (March 28, 1961).
3. Szuk, G., "Conductimetric Moisture Determination of Building Materials." Paper presented at RILEM Conference.
4. Sinclair, Buller, and Benham, "Soil Thermal Resistivity— Typical Field Values and Calculating Formulas." Soil Thermal Characteristics in Relation to Underground Power Cables. Report of the AIEE Insulated Conductors Committee, Amer. Inst. of Elec. Engineers, pp. 31-42 (1960).
5. Winterkorn, H. F., "The Behavior of Moist Soils in a Thermal Energy Field." 9th Annual Clay Symposium, National Research Council, pp. 85-103 (1961).
6. Fourier, J., "The Analytical Theory of Heat." Section 6, On the Heating of Closed Spaces, Cambridge Univ. Press (1878).

Closing Remarks by Chairman

With all due respect for our modern, highly refined, physical methodologies, especially those involving electromagnetic and corpuscular radiation, we must keep in mind that the picture obtained by their use is often in a similar relationship to the object of our interest as is an X-ray picture to the real thing. As a matter of fact, better pictures or models of the "reality" obtained within the range of dimensions in which the engineer is interested are often derived with some of the more old-fashioned tools of physical and colloid chemistry. This seems to be true especially for the case of the strained or bound water that has lost its solvent properties. There exists a large literature on this subject dispersed in various scientific fields. An excellent critical view, covering significant Western work on this subject and supplementing it with the more recent Japanese research results, was published in 1955 by Ken'iti Higasi (1). Also, this subject is well covered by M. W. Tschapek (2) in his most recent book, the entire contents of which are very pertinent for the present conference.

I should also mention in this connection the recent, small, but pregnant book entitled "Relations Between Water and Soil" by T. J. Marshall (3) of Australia written from an agricultural point of view and the proceedings of a conference on "Water in Porous Media" (4) held in 1959 in Paris under the chairmanship of Robert L'Hermite, Director of the Institute of Building Research and Public Works of France. The papers contained in these proceedings breathe the spirit of modern engineering material science.

To return to some specific aspects of the soil-water problem and crawl around the atoms and molecules in order to observe them more closely. One may start out with a single crystal flake of montmorillonite in as dry a condition as possible without affecting its behavior toward water. In this condition, it will still have some strongly adsorbed water molecules on the surface and also, if the material is surrounded by air, some adsorbed oxygen molecules probably arranged so as to continue, as well as possible, the pattern of the adsorbed water molecules, inasmuch as hydrophilic materials are generally oxophilic. In this state, the exchangeable cations will be located within the void surface of the mineral. If water is added in small increments, possibly by adsorption from atmospheres of increasing water vapor pressure, this water will tend to reduce the pattern of the first adsorbed layer with disturbances of the organization becoming greater as the thickness of the water film increases. The degree of restraint exerted by the molecules in the various layers manifests itself in a lower specific and latent heat as compared with that of normal water, the difference being given off as heat of wetting.

As the water film reaches a certain thickness, the more energetic of the exchange ions are induced to leave their places within the solid mineral surface and venture into the water. These are followed by others, with increasing water film thickness, in a manner that the actual concentration of the exchange ions in the water remains constant over a considerable range. This has been known for a long time from pH measurements made at different water contents. Depending on their size and charge, the cations bind or restrain vicinal water molecules which again will manifest itself in heat of hydration that will add to the total amount of the heat of wetting of the soil. The displaced cations now give rise to osmotic swelling if in contact with free water. The impermeable wall normally required for osmotic swelling is simulated by the electric field that issues from the surface of the mineral and holds the cations within its sphere of influence (5, 6). The different "types" of water that may exist in an aqueous dispersion of clay minerals have been enumerated in my symposium paper.

As the water content of a clay water system is decreased from a condition where there is plenty of room for the hydrated exchange ions to swim freely in the water phase to the initial condition of dryness, then various hysteresis phenomena will be encountered because the hydrated cations will require time to shed their hydration hull and

return to their proper places within the mineral surface. Hence, depending on the rate of wetting and drying, respectively, mineral-water systems may at the same water content exhibit markedly different properties if this content is reached by wetting in one case and by drying in the other.

There is another interesting point that deserves mentioning. The bond energy per mole of water is 3600 calories. The average heat of wetting per gram of water, as determined on clays dried over powdered phosphor pentoxide is 50 to 90 calories, or about 900 to 1600 calories per mole. While this is less than one-half of the bond energy of liquid water, it is of the same order of magnitude as the heat released in the freezing of water under normal conditions. Hence, hydration of soil particles under release of the indicated heat of wetting may be expected to have a similar effect on the consistency of the water involved as has the freezing of normal water. Now, Pickett referred to an apparent paradox that relatively large effects of water bonding on the consistency of clay-water systems are associated with relatively small effects of such bonding with respect to the viscosity of the restrained water itself.

Of course, very thin water films between mineral particles may act as strong cementations, but appreciable effects on consistency properties of soils are observed even with a water content that falls within the range where osmotic swelling predominates. Here, the tendency of the exchange ions to get as far away as possible from the charged surfaces may induce the soil minerals to form cell-like structures (like houses made of playing cards or honeycombs) that are stabilized by the mutual repellency of the exchange ions deriving from the mineral surfaces. Analogies to this picture are the turgidity of healthy plants, as compared with the lower mechanical resistance properties of wilted plants and the stiffness of a well-filled air mattress.

In line with these comments, there exists a good body of evidence that the differences in consistency properties of monoionic variations of the same clay mineral at the same moisture content is due more to differences in state of dispersion and structure of the clay minerals, affected by the ions in interplay with the water present, than to the direct effect of the ions on the viscosity of the water involved.

There is so much more that we should discuss this afternoon, but our time has already run out. It may be pertinent to mention here that while still under the fresh impression of the symposium as given in January 1958, I had an opportunity to formulate a synoptic picture of the subject matter on occasion of a Water Supply Conference at Princeton University. This was printed in Bulletin 12, Water Supply, the Princeton University Conference 1958, which is available on request. The paper was deemed of sufficient importance to have been translated into German and has already been reprinted in Germany and Austria in three different publications.

REFERENCES

1. Higosi, K., "Studies on Bound Water." *Borderland Problems between Physical Chemistry and Physiology*, Res. Inst. of Applied Electricity, Hokkaido Univ., pp. 9-35 (1955).
2. Tschapek, M. W., "El Agua en el Suelo." *Coleccion Cientifica del Inst. Nac. de Tecnologia Agropecnaria*, Buenos Aires (1959).
3. Marshall, T. J., "Relations Between Water and Soil." *Commonwealth Bureau Soils*, Harpenden, England, Tech. Commun. 50 (1959).
4. "Reunion d'Information sur l'Eau dans les Corps Poreux." 2 parties, Assoc. Francaise de Recherches et d'Essais sur les Materiaux et les Constructeurs, Paris (1960).
5. Winterkorn, H. F., "Studies on the Surface Behavior of Bentonites and Clays." *Soil Science*, 41:No. 1 (1936).
6. Ruiz, C. L., "Osmotic Interpretation of the Swelling of Expansive Soils." *HRI Bull.* 313, (in press).

ERRATA

SPECIAL REPORT 40

Page 5, line 7: "nessitatem" should read "necessitatem."

Page 61, line 25: "-50 C" should read "-5 C."

Page 123, line 42: the column numbers "17 and 30" should read "17 and 31."

Page 123, line 48: "column No. 32" should read "column No. 13."

Page 160: reference 23 should read "Simultaneous Transfer of Heat and Moisture in Porous Media." Trans. Amer. Geophys. Union, 39:909-916 (1958).

Page 162: reference 64 should read "Unpublished manuscript."

Page 166 Eq. 10b should read:

$$\frac{x^2}{d^2 \text{Cosh}^2 \Psi} + \frac{y^2}{d^2 \text{Sinh}^2 \Psi} = 1 \quad (10b)$$

Page 170, line 7: "(u, V) plane" should read "(u, v) plane."

Page 176: Eq. 21 should read:

$$K = \frac{R_0}{4T} \ln \frac{ht_1}{ht_2} \quad (21)$$

Page 278, line 16: "hydration" should read "hydratation."

Page 278: "T₁" and "T₂" in drawing should read "r₁" and "r₂."

Page 283, line 8: "permanent design" should read "pavement design."

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