



# University of Arizona

COLLEGE OF AGRICULTURE  
AGRICULTURAL EXPERIMENT STATION

## STUDIES IN SOIL STRUCTURE VI. WATER BOUND BY INDIVIDUAL SOIL CONSTITUENTS AS INFLUENCED BY PUDDLING

By

T. F. BUEHRER AND D. G. ALDRICH, JR.

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# WATER BOUND BY INDIVIDUAL SOIL CON- STITUENTS AS INFLUENCED BY PUDDLING

BY T. F. BUEHRER AND D. G. ALDRICH, JR.

## INTRODUCTION

In a previous bulletin by Buehrer and Rose (4) it was shown that when a soil is puddled within a narrow range of moisture content in the vicinity of the moisture equivalent, a portion of the water becomes "bound," in the sense that it fails to freeze as determined by the dilatometer. The amount of water thus bound by a puddled soil is considerably greater than that held under similar conditions by the normal, unpuddled soil. The extent of binding of water is much greater in soils of low organic matter content. It was found that such binding attains a maximum when the soil is puddled with an amount of moisture corresponding to its moisture equivalent. The binding of water by soils is influenced to a marked degree by the cation with which the soil happens to be saturated. Soils from different geographical regions were found to bind water to an extent that suggested a specific influence of the clay mineral present in dominant amount in the colloid fraction.

In view of these observations it seemed of interest to carry the bound water investigations further to determine the part played by the various soil constituents when puddled under similar conditions. The following classes of constituents were accordingly studied: the simple soluble salts, nonelectrolytes, colloidal sols and gels, the organic matter fraction, and the various types of clay minerals.

## REVIEW OF THE LITERATURE

Although published work concerning bound water in biological systems is fairly extensive, there is relatively little information available concerning the binding of water by the soil, and particularly the part played by the individual soil constituents. Gortner (12) found that lyophilic sols and gels contain both free and bound water. He concluded that part of the bound water is held by adsorption on the surface of the colloidal particles, and part by orientation around the ions that are held as exchangeable bases by the colloid or are present as ions in the intracellular solution. Working with inorganic gels of iron and aluminum hydroxides, Shuruguina (35) found that when such gels are heated or allowed to "age" at ordinary temperatures, the amount of water bound by them decreases, thus confirming the findings of Buehrer and Rose (4) on puddled soils. Similar effects were observed by Chrysler (6) with the organic colloids in kelp, and by Fells and Firth (10) with bound water in silicic acid gel.

A number of investigations in the field of plant physiology have yielded results that have a bearing on the behavior of the dissolved salts in soils on the binding of moisture. Maximov (23) and Rosa (32) have shown that in plant tissues and sap, where salts and sugars are present in true solution, water is bound against freezing chiefly through the hydration of ions and molecules. Gortner (12) considered the water of imbibition of plants as water that is bound, in the sense that it does not, or cannot, dissolve sugars or salts. The amount of water bound by sugars seems to be fairly definite. Philip (30) found that 5 molecules of water are associated with each molecule of sucrose, while Scatchard (34), from vapor pressure measurements, found it to be 6 molecules of water per mol of sucrose. Newton (25) showed that the hardness of winter wheat could be attributed to the amount of "unfree" water in plant tissue. Levitt and Scarth (19) also worked on the frost-hardening process and correlated frost resistance with changes of free to bound water in the tissues.

Newton and Gortner (26) used the freezing point method to distinguish between free and bound water in plant saps. And Newton and Martin (27) studying the drought resistance of a number of cereal grasses and other plants concluded that the imbibition pressure of the hydrophilic colloids in plant tissue is the most significant factor in retaining moisture, and that drought-resistant varieties can be distinguished from the nonresistant by determining their bound water content. In a similar manner the colloidal matter of the soil, both organic and inorganic, may be expected to influence the extent to which water is bound.

The binding of water by granular materials has also received attention at the hands of investigators. Parker (29), using the freezing point method, and Foote and Saxton (11), the dilatometer method, showed that binding of water occurs in systems of finely divided materials such as lampblack, silica, and aluminum and ferric oxides, and hence must be related to the amount and nature of the surfaces exposed by the particles. Parker showed further that there is a depression in the freezing point of a liquid when it is caused to exist in a film around solid particles, and that the freezing point depression of the solid material of the soil, however heterogeneous, is additive. From a practical standpoint his results pointed to the principle that the true concentration of the soil solution cannot be measured by the freezing point method except at high moisture contents where the amount of unfree water is relatively small. At lower moisture contents the extent of binding is higher, and therefore the concentration of the true soil solution as determined by the freezing point procedure will always appear to be higher than it really is. These studies on effect of particle size emphasize the fact that one may expect a greater degree of water binding in the finer textured soils.

The experiments of Woodruff (37) have shown that water is held by attractive forces of different magnitude by the different

kinds of particles of which the soil is composed. For example, in sands and silts, the water appears to be held primarily by forces of capillarity. As the particle size decreases there is a transition from water held by capillarity to water held much more rigidly by the forces of sorption on the surfaces of colloid particles. This phenomenon was also indicated by the experiments of Buehrer and Rose (4) who found that the amount of water bound by a normal soil is a function of time of contact and does not immediately attain a maximum value. Therefore they suggested that there must be several slower processes taking place, chief among which are the hydration of soil minerals and the formation of hydrophilic gels through which the water moves, though slowly, by diffusion. The same type of transformation of water undoubtedly occurs when a puddled soil is allowed to age, in which there is a slow change from bound to free water.

The findings of Buehrer and Rose (4) showed further that in field soils having a relatively low organic matter content, there is no correlation between the percentage of organic matter and the amount of water bound. The extent to which the clay fraction controls the binding of water points to the importance of the minerals of which the clay fraction is composed. The well-known phenomenon of swelling of montmorillonite, which in some cases has been observed to be as high as twenty times its original volume, as well as the expanding character of the montmorillonite lattice, suggests that water binding in this case might be due to the orientation of water molecules between the layer packages, which in the limit brings about an increase of about 12 Å. in the c-dimension of the lattice. It is, therefore, of great interest to determine the part played by the dominant minerals of the soil that make up the fine colloid fraction.

#### EXPERIMENTAL RESULTS

This investigation is based upon the determination of bound water on individual classes of soil constituents by the dilatometer technique developed by Buehrer and Rose (4, 5). Certain changes or improvements in the technique were made to permit greater ease of handling the sample material.

#### WATER BINDING IN SIMPLE SALT SOLUTIONS

In saline soils the soluble salts consisting chiefly of chlorides and sulfates of sodium, calcium, and magnesium, may be present in amounts varying from 0.1 to 10 per cent. At low moisture contents, in the neighborhood of the moisture equivalent, the salt concentration is far too high for adequate crop growth, from the standpoint of specific toxic effects on the plant, and particularly the osmotic relationships which are such that the plant has difficulty in absorbing moisture from such solutions. This latter effect has been conclusively demonstrated in a recent paper by Wadleigh (37). For example, a soil containing 5 per cent of soluble salts (considered as NaCl) in a moist soil at its moisture

TABLE 1.—WATER BOUND BY SOLUTIONS OF SIMPLE SALTS

Salt	Nor- mality	Wt. sample	Wt. water	Water frozen	Water bound exptl.	Water bound calc.*
				per cent	per cent	per cent
KCl	0.25	6.0759	5.990	79.76	20.74	20.94
	0.10	5.9783	5.946	88.48	11.52	7.88
	0.05	5.9836	5.919	98.98	1.02	3.87
	0.025	5.9781	5.970	99.66	0.34	2.01
	0.01	6.1667	6.161	99.87	0.13	1.40
NaCl	0.25	5.0069	4.920	75.00	25.00	36.38
	0.10	6.1585	6.122	88.23	11.77	10.49
	0.05	6.1585	6.122	94.85	5.15	5.85
	0.025	6.0908	6.082	96.86	3.14	2.98
	0.01	4.6640	4.660	112.70	-----	1.80
LiCl	0.25	6.1020	6.102	71.09	28.91	34.19
	0.10	5.9988	5.972	84.97	15.03	14.09
	0.05	6.0644	6.044	97.71	2.29	7.44
	0.025	6.0873	6.079	99.02	0.98	4.29
	0.01	6.1754	6.171	100.29	-----	2.24
BaCl <sub>2</sub>	0.25	6.2723	6.041	71.00	29.00	30.87
	0.10	6.4257	6.323	84.18	15.92	13.02
	0.05	6.1533	6.105	93.34	6.66	6.32
	0.025	6.0411	6.016	96.96	3.04	3.36
	0.01	6.1470	6.137	102.8	-----	1.37
CaCl <sub>2</sub>	0.25	6.0231	5.570	92.83	7.17	-----
	0.10	5.9596	5.757	95.17	4.83	-----
	0.05	6.0901	5.987	100.06	-----	-----
	0.025	6.0181	5.966	102.6	-----	-----
	0.01	5.9897	5.963	104.98	-----	-----
MgCl <sub>2</sub>	0.25	6.1304	6.052	92.63	7.37	-----
	0.10	6.1459	6.123	98.59	1.41	-----
	0.05	6.1850	6.173	100.8	-----	-----
	0.025	6.1965	6.188	103.6	-----	-----
	0.01	6.1467	6.144	101.3	-----	-----
MgSO <sub>4</sub>	0.25	5.9616	5.755	94.96	5.05	-----
	0.10	6.0799	5.972	100.7	-----	-----
	0.05	5.9978	5.921	107.5	-----	-----
	0.025	6.0663	6.041	106.2	-----	-----
	0.01	5.9257	5.915	101.7	-----	-----
Na <sub>2</sub> SO <sub>4</sub>	0.25	-----	-----	-----	-----	-----
	0.10	7.0884	6.989	94.51	5.49	-----
	0.05	5.9836	5.942	91.70	8.30	-----
	0.025	5.9054	5.880	105.3	-----	-----
	0.01	5.9788	5.970	102.3	-----	-----

\*Calculated from freezing point lowering as illustrated on pp. 68-9.

equivalent (30 per cent), would have a salt concentration in its soil solution of about 3-normal. If the soil were puddled, so that 95 per cent of its water were bound, the concentration would be considerably above that of a saturated solution and some of the salt would actually crystallize out. Even if the original salt concentration in the dry soil were only 0.1 per cent, the soil with a moisture equivalent of 30 per cent would, when puddled, have a soil solution with a concentration of about 1.2-normal. It is therefore obvious that puddling, by reducing the amount of free water, can bring about unusually high salt concentrations in the soil solution which will be detrimental to the growth of plants.

Such salts have in themselves the power of binding a certain amount of water. This fact is demonstrated by the lowering of vapor pressure. In a thermodynamic sense the lowering of vapor pressure and of freezing point by dissolved salts is due to a lowering of the activity of the water in such solutions. Evidence for this effect was found by Buehrer and Rose (4) in their freezing point studies on puddled and unpuddled Pima clay, of which the salt content was known. It seemed of great interest, however, to investigate this point further by the dilatometric procedure, by using simple salts with cations and anions of different valences, and making the determinations over a range of concentrations. For this purpose the following salts were employed: LiCl, NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, BaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>. The salts were recrystallized, and solutions made up ranging between 0.01-normal and 0.25-normal. The upper limit represents the highest concentrations capable of being frozen at -3 degrees C., the temperature at which all of the dilatometer determinations were made. In the case of NaCl, for example, this range of concentrations would lie between about 600 p.p.m. at the lower limit and about 15,000 p.p.m. at the upper limit. The results of this study are assembled in Table 1.

The data in Table 1 show that the greatest degree of water binding occurs in solutions of the uni-univalent salts and in barium chloride representing the bi-univalent salts. Magnesium and sodium sulfates showed very little tendency to bind water as measured by the dilatometer. Confining our attention to the four salts given at the top of the table, KCl, NaCl, LiCl, and BaCl<sub>2</sub>, in which the most pronounced binding was observed, we have plotted per cent water bound against normality of solution, as shown in Figure 1.

It will be noted that a series of sigmoidal curves is obtained, each exhibiting a sharp increase in binding with concentration of the solution. Binding of water in such salt solutions is generally looked upon as due primarily to ionic hydration, hence we should find the curves arranged in a sequence according to the hydration of their cations, which is not the case. The hydration values for these cations have been determined cryoscopically by Bourion, cited by DuRietz (8, p. 77), in solutions of their chlorides at 0.5-

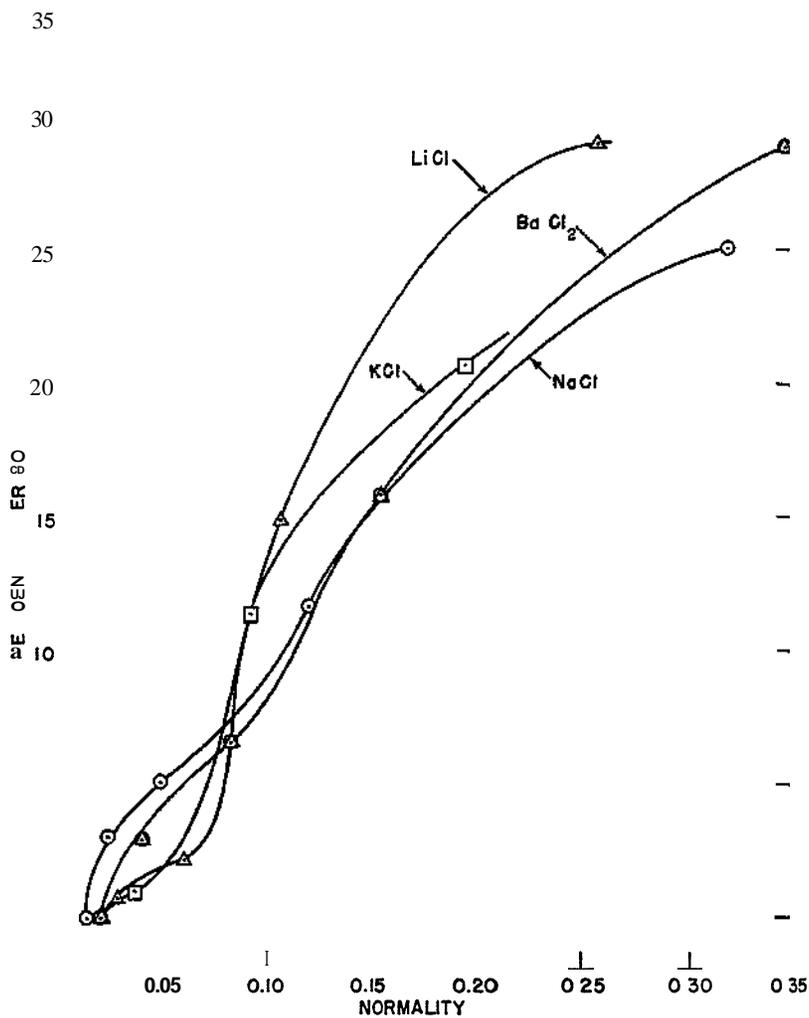


Figure 1.—Water binding in aqueous salt solutions as a function of concentration.

TABLE 2.—HYDRATION OF CATIONS IN AQUEOUS SOLUTION

Cation	Hydration		Ionic radius A.
	0.5-N	1-N	
	<i>mols H<sub>2</sub>O per gram-ion</i>		
K+	4.7	5.7	1.33
Na+	9.3	11.1	0.98
Li+	11.1	13.3	0.78
Ba <sup>++</sup>	18.3	20.1	1.43
Ca <sup>++</sup>	19.2	21.6	1.06
Mg <sup>++</sup>	20.3	22.6	0.78

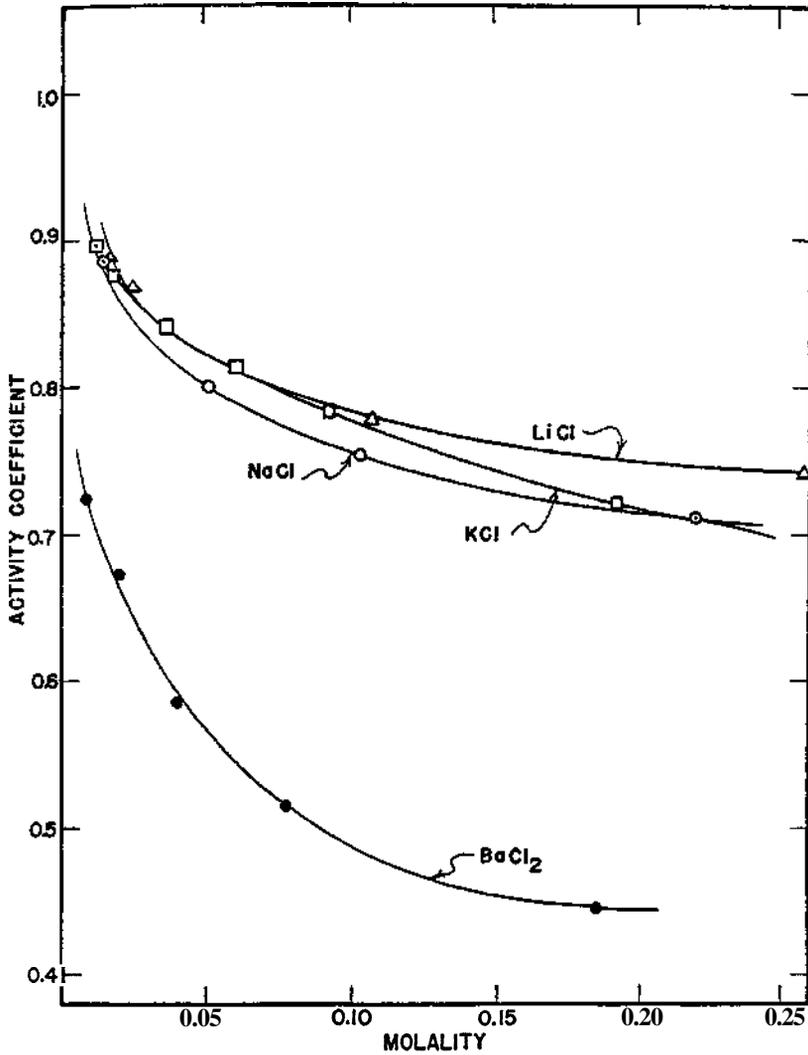


Figure 2.—Activity coefficients of several salts as a function of concentration.

normal and 1-normal concentration, and are reproduced in Table 2.

These hydration data show that binding of water may be due to an orientation by electrostatic attraction of water molecules around a cation, and therefore the dilatometric values should fall in the order of the ionic hydrations. In order to clarify this problem we must consider that these salts have different activity coefficients, and the factor that governs such hydrations is the *activity* rather than the gross concentration. Plotting the activity

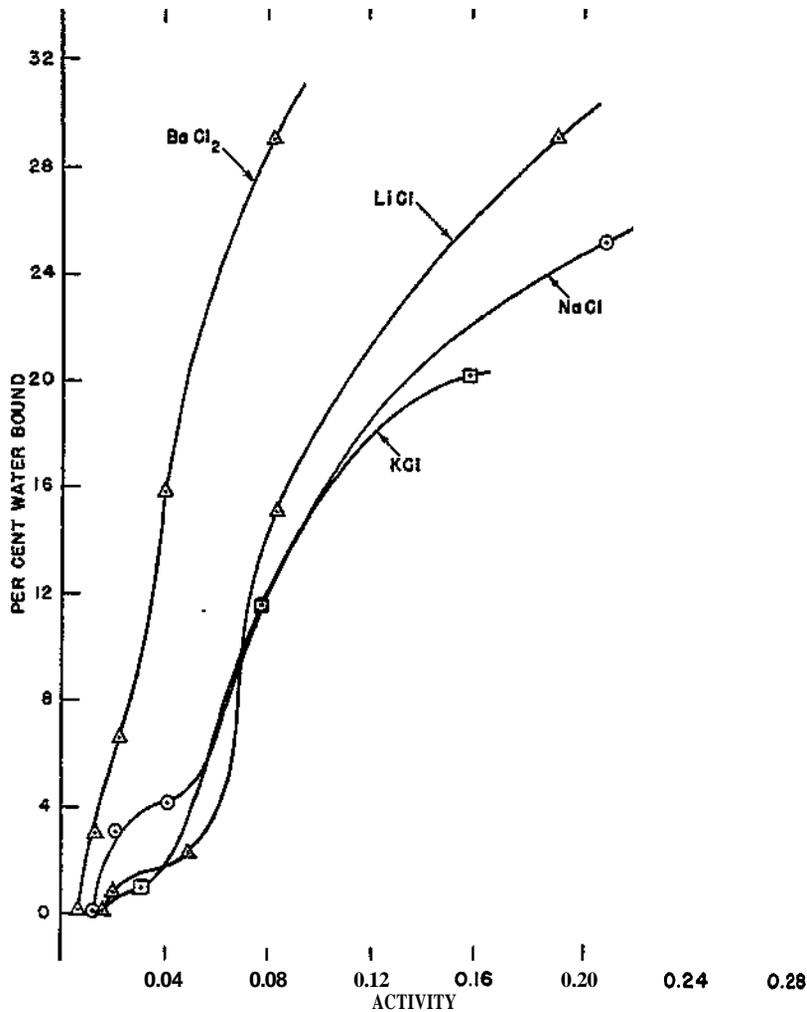


Figure 3.—Water binding in aqueous salt solutions as a function of activity.

coefficients according to Randall (31) against molality, we obtain the curves for these salts in Figure 2. If the activity coefficients of the salts obtained from these curves are multiplied by the respective molalities, we obtain the activity values for each salt. Plotting the percentage of bound water against these activity values, we obtain the curves in Figure 3. It will be seen that the curves now arrange themselves strictly in the order of the cationic hydration of each salt and afford evidence that water binding as determined by the dilatometer is essentially a process of hydration which increases with increasing concentration.

In this connection, Gurney (14) considering the nature of the

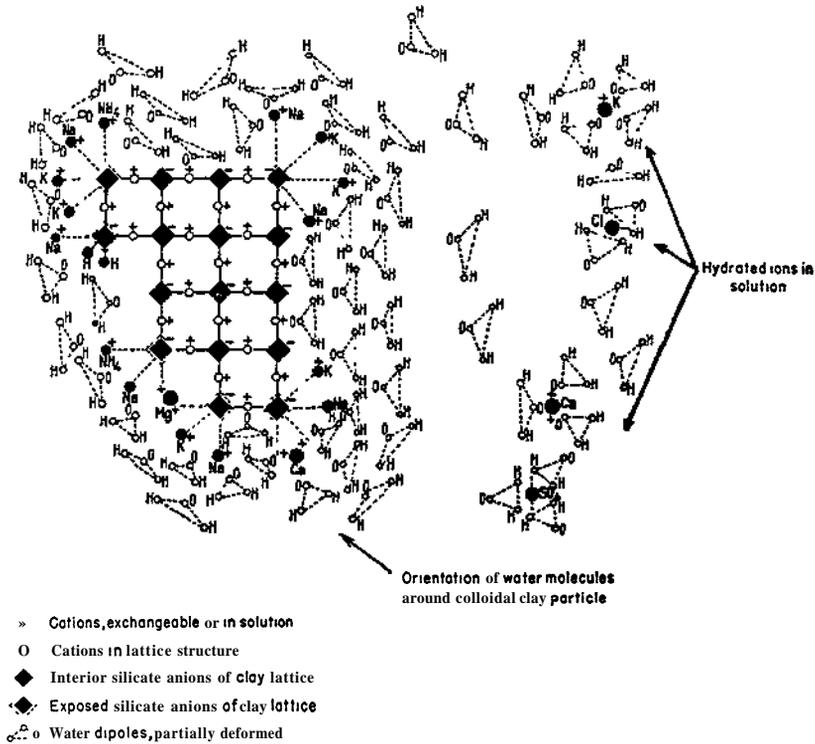


Figure 4.—Orientation of water molecules around clay particles and ions in solution (after Vageler).

water dipole provides a lucid picture of this phenomenon. He holds that both cations and anions are hydrated in solution, but that cationic hydration always exceeds that of the anions. Vageler (36) uses the established concept of the water molecule as being triangular in shape, the angle between the lines connecting the hydrogen atoms to the oxygen being on the average 105 degrees but capable of varying between 102 and 109 degrees. This makes it possible for water molecules to undergo a small degree of distortion in orienting themselves around charged ions. A pictorial representation of such orientation of water molecules around ions is presented by Vageler (36), and is reproduced in Figure 4. It is evident that in the hydration of cations, the water dipoles must be so oriented that the oxygen atom is attracted by, and hence closest to, the positive ion. The maximum number so oriented will depend upon the size of the ion (ionic diameter) and upon the available space (concentration), hence will vary from cation to cation. In the case of anions, the more positive end of the water dipole will be attracted toward the ion, and since this involves the two hydrogen atoms of water, the number will be definitely limited. From geometrical space considerations, anionic

hydration must in general be less than cationic hydration. Thus the bound water curves for the four salts are consistent with the hydrations and ionic dimensions of the cations in question. In reference to these salts we might with equal justification have called the degree of water binding the degree of hydration.

It is possible to calculate the amount of water that fails to freeze from the simple conditions of the freezing process, since during freezing only water is extracted from the solution and separates out as ice. The remaining water is of course present in the unfrozen solution. In the dilatometric determination we freeze the solution at -3 degrees C., therefore if we know the concentration of the solution remaining after freezing at -3 degrees C. has ceased, we should be able to calculate the percentage of the water present which fails to freeze by the simple equation:

$$\text{Per cent water bound} = \frac{\text{Mass water unfrozen}}{\text{Mass original water}}$$

A sample calculation will illustrate this point. Consider the 0.25-normal solution of potassium chloride (Table 1).

Mass of solution used	6.0759 gm.
Mass of salt present	0.0859 gm.
Mass of water present	5.990 gm.
Mols of KCl present	0.001149

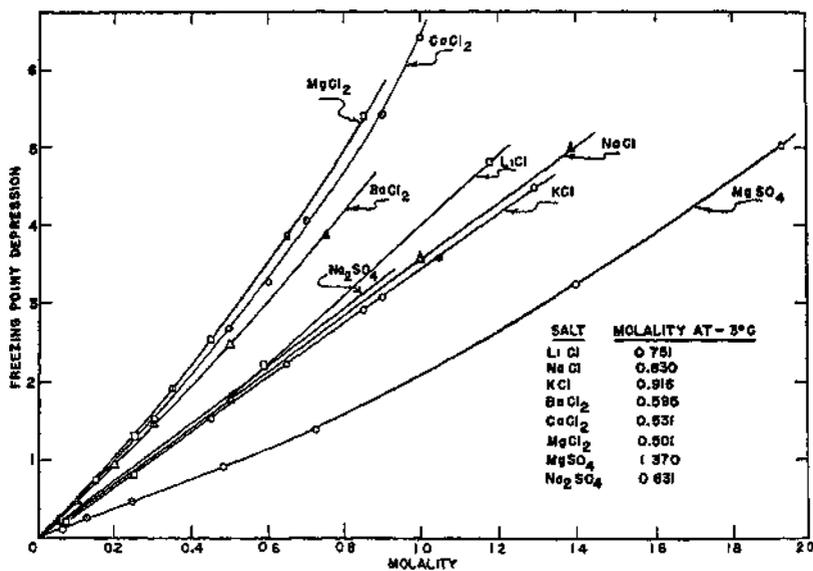


Figure 5.—Freezing point depression curves for various salt solutions.

To calculate the mass of water in the solution remaining after freezing at -3 degrees C., we must obtain the concentration from freezing point data, by plotting freezing point depression against

molality. This has been done in Figure 5 using the data of Stein quoted by Jones *et al.* (18). Interpolating on these curves to obtain the molality at -3 degrees C., we find the value for KCl to be 0.916 mol per 1,000 gm. of water. The mass of water associated with 0.001149 mol KCl in the final solution is obtained by the simple proportion:

$$\frac{0.001149 \times 1000}{0.916} = 1.254 \text{ grams H}_2\text{O}$$

Whence:  $\text{Water bound} = \frac{1.254}{5.990} = 20.94 \text{ per cent}$

which agrees favorably with the value 20.74 per cent obtained by the dilatometer. Other calculated values are tabulated for KCl, NaCl, LiCl, and BaCl<sub>2</sub> in the last column of Table 1. They indicate how closely this principle reproduces the measured values. Good agreement is obtained in more than 50 per cent of the cases, which is probably as good as the experimental method will allow.

From a practical standpoint the hydration of salts in the soil to bind water manifests itself as an indirect effect upon the plant in retarding or inhibiting the process of water absorption. There is evidence, however, to indicate that ionic hydration influences the tendency of clays to disperse and to become puddled, but this effect is offset to some extent by the magnitude of the cationic charge. For example, calcium ion has twice the hydration of sodium ion, yet it is a much more powerful flocculating agent toward soil colloids and is particularly effective in the formation of stable aggregates.

#### WATER BINDING IN SOLUTIONS OF NONELECTROLYTES

Organic matter applied to the soil either as manure or a green cover crop usually carries a certain amount of the soluble sugars and other organic nonelectrolytes. It was considered of interest to determine the extent of water binding in such solutions. For this study solutions of glycerine and sucrose were chosen, ranging in concentration between 0.25- and 1.5-molal. Solutions at concentrations above 1.5-molal will not freeze at a temperature of -3 degrees C., the temperature at which the dilatometer determinations were carried out.

It was found that such solutions show freezing characteristics markedly different from those of electrolytes. Crystallization on freezing takes place at an unusually slow rate and the ice crystals form in parallel planes until the mass has entirely solidified. The results are shown in Figure 6, in which the points for both of these solutes fall on the same straight line, within limits of error of the measurement. There is a marked tendency to bind water and the fact that the graph is a straight line suggests that there may be a definite molal ratio of water bound to amount of solute present. To test this conclusion a calculation was made in the case of glycerine, as shown in Table 3.

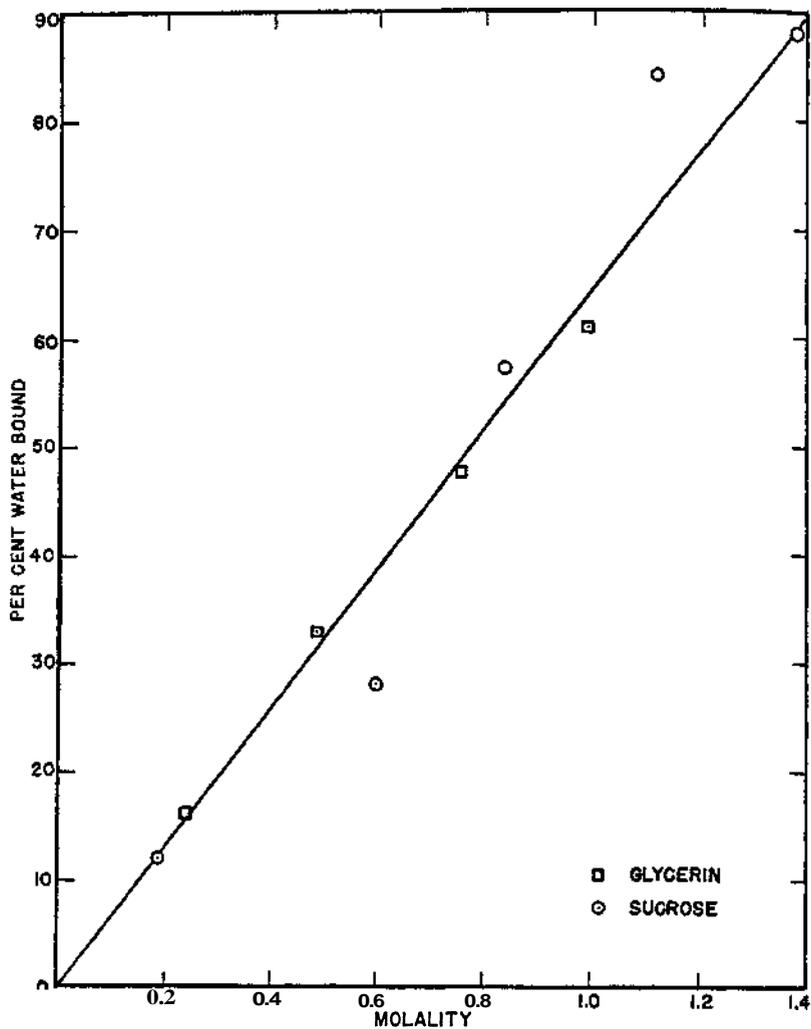


Figure 6.—Water binding in solutions of nonelectrolytes.

TABLE 3.—MOLAL RATIO OF BOUND WATER TO GLYCERINE IN AQUEOUS SOLUTIONS

Molality	Wt. water <i>gm.</i>	Water bound <i>per cent</i>	Wt. glycerine <i>gm.</i>	Wt. water bound <i>gm.</i>	Mols water bound	Mols glycerine	Molal ratio
0.993	5.678	66.1	2.26	3.76	0.208	0.024	8.4
0.758	5.506	47.7	1.72	2.63	0.146	0.018	8.1
0.493	5.523	32.9	1.13	1.82	0.101	0.012	8.2
0.242	5.480	16.3	0.55	0.89	<b>0.049</b>	0.006	8.2

The data of Table 3 show that 8 mols of water are associated with 1 mol of glycerine, which amount is independent of concentration. The points for the sugar solutions fall fairly well on the same line in Figure 6, hence the hydration of sucrose by the dilatometric procedure is 8 mols of water per mol of sucrose, as compared with the values of Philip (30) and Scatchard (34) previously cited. These findings are also consistent with those of Newton (25) and other investigators on the binding of water by plants in sap and tissue. While there may be likelihood of water binding by the fresh active organic matter in soils, the effect is doubtless temporary in view of the rate at which the soluble organic compounds are decomposed or metabolized by soil microorganisms.

#### WATER BINDING IN COLLOIDAL SOLS AND GELS

Numerous investigations have been made on the binding of water by colloidal systems, particularly that of gelatin and silicic acid gels, by Gortner (12) and others, most of which have been concerned with the biological functions and behavior of such systems. It has been shown by Martin (20) that organic gels are formed in the soil but they are only temporary in duration and never exist at any high degree of concentration at any one time. Nevertheless it seemed of interest to get an idea of the magnitude of their effect in binding soil moisture.

This study was made with agar and gelatin, in concentrations ranging from 0.1 per cent to 2 per cent. The samples were prepared by weighing out predetermined amounts of the colloid into the freezing tube and adding to each 5 cc. of distilled water. The tubes were then placed on a water bath and left until the colloid was brought uniformly into solution. They were then frozen and the dilatometer expansion measured. The results for the agar system are given in Table 4.

TABLE 4.—WATER BINDING IN THE AGAR-WATER SYSTEM

Concentration of agar	Wt. water present	Dilatometer reading, initial	Dilatometer reading, final	Water frozen
<i>per cent</i>	<i>gm.</i>			<i>per cent</i>
2.0	4.398	6.15	32.95	101.1
1.5	4.144	5.75	31.95	101.8
1.0	4.178	8.25	34.90	102.8
0.5	4.054	6.40	32.25	105.9
0.1	3.941	9.55	36.55	110.3

The data in Table 4 show that within limits of error the entire amount of water initially taken was frozen. This would mean that there was no binding of water in an agar gel. Most other investigators, notably Gortner (12), Newton and co-workers, and others, have reported extensive binding both in agar and gelatin gels. The apparent variance of these results lies in the fact that relatively dilute gels were here used, that is, gels at concentrations

which would permit freezing at -3 degrees C. It is evident that with stiffer gels much lower temperatures would be necessary to induce the formation of ice crystals. The fact that the expansions observed yielded results for the percentage of water frozen in excess of 100 per cent might be due in part to the colloid itself undergoing a slight expansion in passing from the gel to the solid state. Since all of the water freezes, it must be concluded that the structure of the gel and the forces maintaining that structure must be rather weak and unable to withstand the forces which tend to make the water molecules disengage themselves from the gel and orient themselves in the ice lattice.

It was observed, incidentally, that, unlike the samples of bentonite or Pima clay, a protuberance of ice was forced out at the top of the agar or gelatin gel sample on freezing, suggesting that a stretching of the gel fibrils had occurred, or possibly an actual rupture of the fibrils. At any rate, there seemed to be no resistance to the formation of the ice crystals, and the water behaved, to all intents and purposes, as free water. It is not justifiable, however, to conclude from these limited experiments that one would observe no binding in more rigid structures such as cellulose or lignin, or even in more concentrated gels than those involved in these experiments. Vapor pressure data certainly show that binding occurs in such systems. It is probable that the technique used is not adapted to the study of such elastic systems.

#### EFFECT OF ORGANIC MATTER ON THE BINDING OF WATER IN PUDDLED SOILS

The effect of organic matter in improving soil structure by promoting aggregation is now generally recognized. While there is no longer any doubt that it increases the water-holding capacity of a soil, it does not increase the amount of available water except in the coarser textured soils. In the case of puddled clay soils, Breazeale and McGeorge (3) have shown that the puddled condition, by restricting aeration, produces anaerobic conditions and greatly slows down the decomposition of organic matter and nitrification. They found that under these conditions there is some loss of nitrogen by denitrification. Moreover, organic matter alone will not correct the puddled condition.

In this experiment the aim was to determine the effect of organic matter additions on the amount of water bound by a heavy clay soil when puddled. Pima clay was again used. After addition of varying amounts of alfalfa (ground to 60-mesh) and making the mixture up to 50 per cent moisture on the wet basis, the samples were puddled mechanically and the amount of bound water determined in the dilatometer. Although the term "puddled" is here used, it will be realized that samples containing high percentages of organic matter cannot be puddled to any appreciable extent. The mechanical manipulation in this case was to insure uniformity of moisture distribution. The samples were made up to organic matter contents ranging from 0 to 100

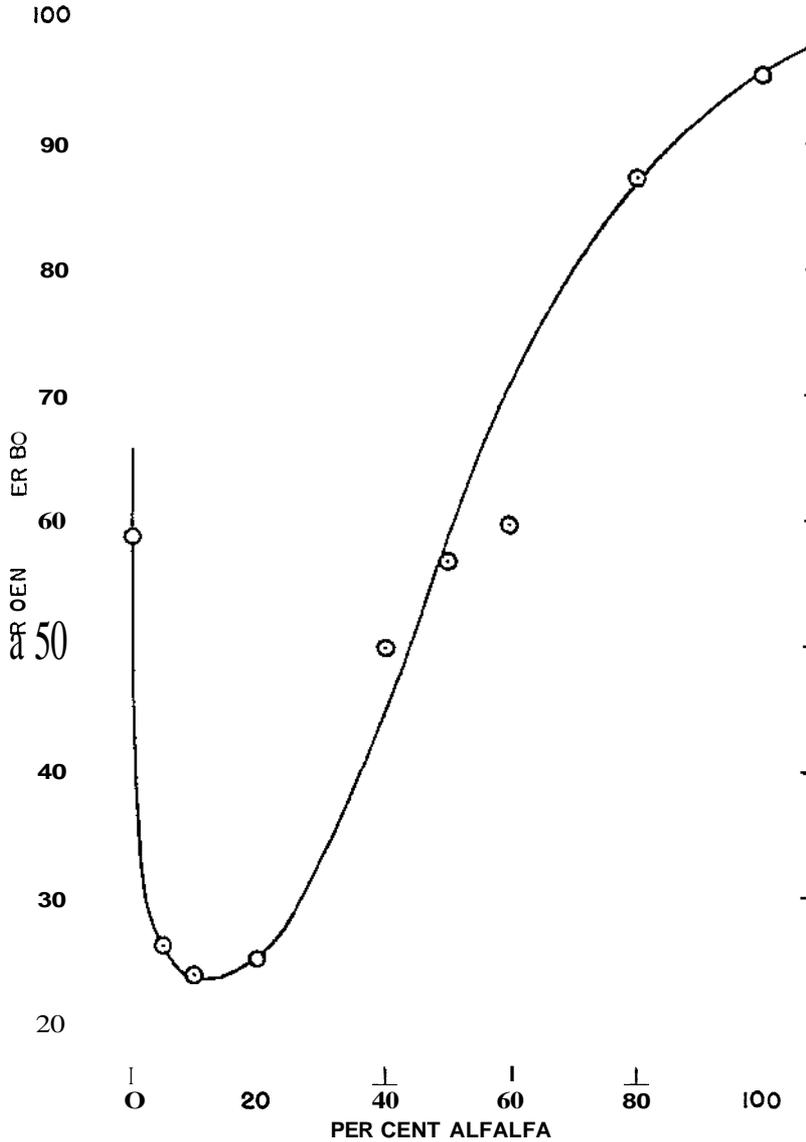


Figure 7.—Effect of alfalfa on water binding in Pima clay, (Puddling at uniform moisture content of 50 per cent.)

per cent. After puddling the samples their moisture contents were determined independently by oven drying.

The results of this experiment are shown in the graph in Figure 7.

It will be seen that small additions of organic matter decreased the amount of bound water, the curve passing through a

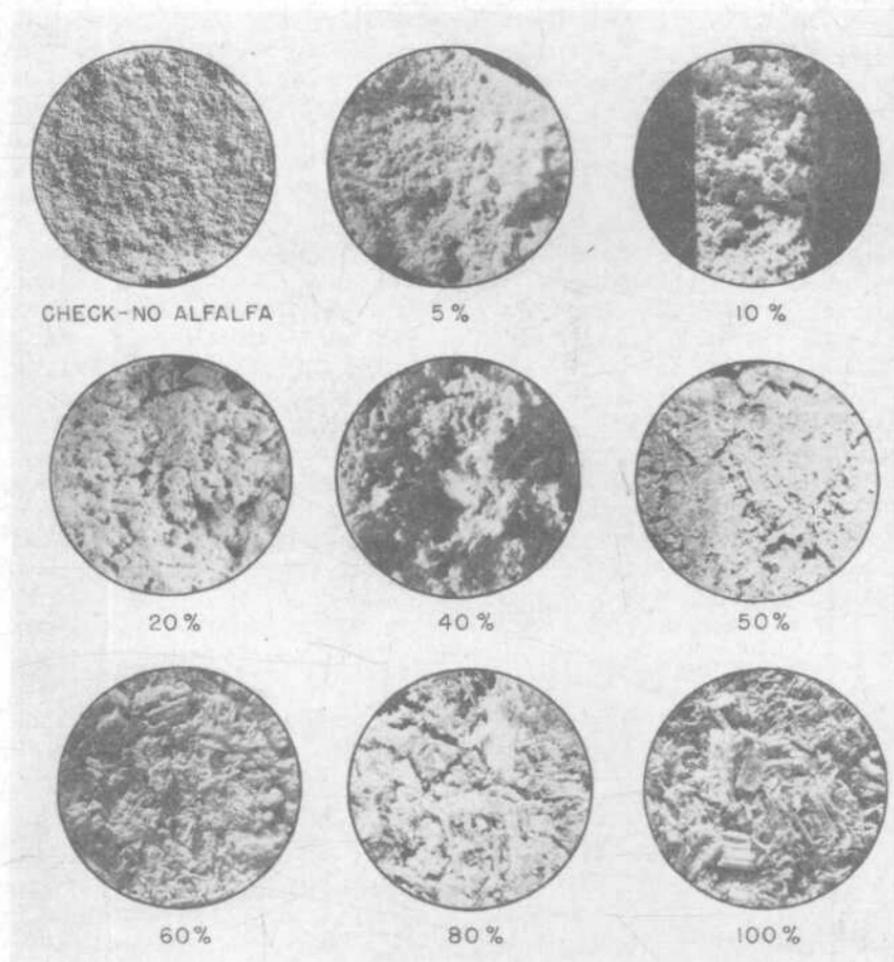


Plate I.—Structural character of Pima clay after puddling with various amounts of alfalfa meal. (Magnified 6 X on this plate.)

minimum at about 10 per cent alfalfa. Up to this point, then, the organic matter had the apparent effect of aggregating the soil and therefore breaking up the puddled condition, but it was not present in large enough quantities to bind any appreciable amount of water itself. Beyond the minimum point in the curve, the curve again rises indicating that aggregation had apparently reached its maximum, and the organic matter itself was now beginning to hold some of the moisture in bound form. Thereafter the curve continues to rise to 100 per cent of alfalfa in which about 95 per cent of the total water present was bound.

The structural character of the Pima clay after puddling with various amounts of alfalfa meal is shown in Plate I, in which samples of the nine mixtures represented in the curve of Figure 7

were photographed in section. The untreated Pima clay contained 1.21 per cent of organic matter. It will be noted that the puddled soil without alfalfa consists of a tightly compacted mass with a large number of small pore spaces. As alfalfa is added, the pores become larger and there appears to be a pronounced tendency to aggregate. At higher contents of alfalfa, the fibrous particles of the alfalfa can be observed. The samples exhibit an increasingly porous character with increasing alfalfa content.

The effect of organic matter in promoting aggregation can be ascribed to its character as a colloidal system. The clay fraction of the soil is dominantly an electronegative colloid whereas organic matter is dominantly positive depending of course on its base saturation. Under these circumstances, it is possible for mutual coagulation to occur with neutralization of the residual charge on the particles. Of interest in this connection are the results of Browning and Milam (3a) who found that treatment of unlimed Gilpin silty clay loam with alfalfa aggregated the soil producing stable aggregates. Organic materials which like alfalfa contain considerable amounts of sugars and other water-soluble organic substances are reactive and quickly produce aggregation, whereas relatively inert materials like wheat straw have little or no effect.

#### WATER BINDING BY THE MINERAL CONSTITUENTS OF SOILS

Having investigated the extent of water binding by salts in solutions at concentrations within the range found in soil solutions in soils of desert regions, and of colloids, both organic and inorganic, which are present to some extent in all soils, we shall now consider the part played by the mineral constituents of the soil in the binding of water.

For the purposes of this investigation, we shall divide the mineral constituents into three classes: (a) those whose crystal structure is such that any water bound by them can be attributed to the purely adsorptive forces arising from molecular attractions; (b) the 1:1 nonexpanding lattice type of clay mineral whose adsorbing power is due to both molecular attraction and electronic charges arising from broken lattice bonds; and (c) the 2:1 expanding lattice type of clay mineral whose adsorbing power is due in part to simple molecular attraction, in part to electric charges arising from broken lattice bonds, and to a considerable extent to isomorphous substitutions within the atomic planes of the crystal lattice.

##### **Water binding by quartz sand**

An investigation of the first of the above classes of soil minerals, of which quartz sand is a good example, was found to yield two independent sets of data, since it affords an indication of the effect of both mineral type and particle size. In this class of mineral, only surface forces are responsible for the binding of water. Hence a study of the effect of changing the surface area

per unit mass of material will yield information as to the extent of binding that occurs in the soil purely as a result of the attractive force of finely divided particles.

Quartz sand purified by treatment with acid was ground in an agate mortar and screened through a series of sieves ranging from 20-mesh (0.84 mm.) to 300-mesh (0.05 mm.). After screening, all fractions were ignited to remove completely the organic matter. In making the bound water determinations, 5-gram samples of sand were moistened with 2 grams of distilled water. The water was added to the sand in the freezing tubes by means of a hypodermic needle to insure uniform distribution of the water throughout the sample, and to prevent water droplets from adhering to the tube above the sand. Bound water was then determined by the dilatometric technique. The results so obtained on the various size fractions are assembled in Table 5.

TABLE 5.—WATER BINDING IN GROUND SEA SAND

Size of screen		Sand taken	Water taken	Water frozen	Water bound
<i>mm.</i>	<i>mesh</i>	<i>gm.</i>	<i>dm.</i>	<i>per cent</i>	<i>per cent</i>
0.84	20	5	2	100	0
0.42	40	5	2	99.48	0.52
0.25	60	5	2	87.28	2.12
0.17	80	5	2	96.72	3.18
0.15	100	5	2	96.28	3.72
0.074	200	5	2	95.21	4.79
0.05	300	5	2	94.43	5.78

The data in Table 5 show that as the particle size decreased the amount of water bound increased. The results shown graphically in Figure 8 bear out this inverse relationship. Stated conversely, the amount of water bound by a mineral such as sea sand is directly proportional to the surface area per unit of mass. It, therefore, appears that in the nonlayer lattice minerals, like quartz, which represents the linked tetrahedron type of structure within the lattice, water binding appears to be purely a surface phenomenon.

It is of interest in this connection to compare these results with those of Parker (29) who has shown that finely divided material causes a depression of freezing point of a liquid when the liquid exists in a film or capillary condition in the solid material. The specific chemical nature of the comminuted material does not enter into the phenomenon. It is not a lowering of freezing point such as one encounters with true solutions. Since Parker's results involve freezing point measurements, they are related to the dilatometric measurements of this study, since all data here reported were obtained at a constant temperature of -3 degrees C. Instead of recording the lowering of freezing point, the dilatometer measures the *amount* of solvent which fails to freeze at -3 degrees C., which amount is itself a function of the freezing point depression. For the purposes of this discussion, we re-

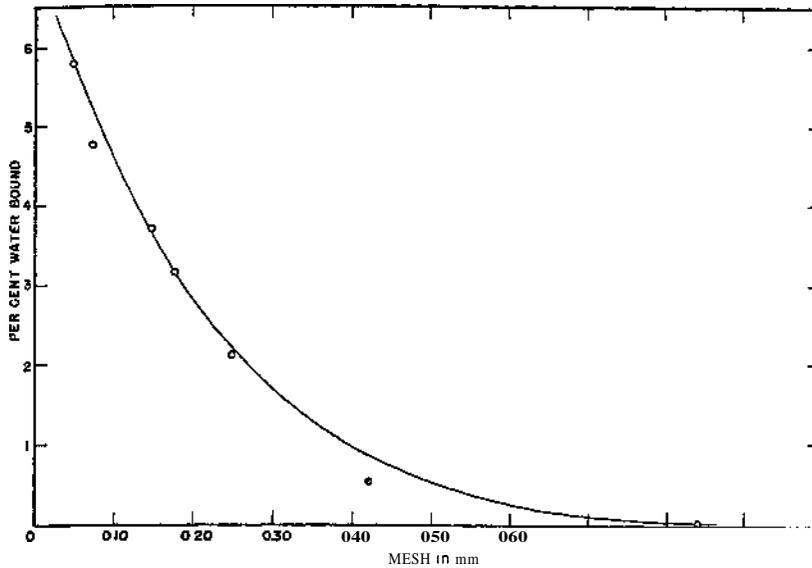


Figure 8.—Water binding in ground sea sand.

produce in Figure 9 the freezing point data of Parker obtained with finely ground silica (200-mesh).

Although Parker used a constant particle size and varied the moisture content of the sample, the effect produced by diminishing the thickness of the moisture film around the solid particles is similar to the effect observed in the dilatometric procedure. In our samples we maintained a constant total weight of water and of sand. As the particles become progressively smaller, there is a greater amount of adsorbing surface per unit mass of material, and thus the thickness of the water film about each particle is decreased. It will be noted that the curves in Figures 8 and 9 are very similar, both being hyperbolic. In Figure 9 Parker plots freezing point depression against per cent water. In Figure 8 we have plotted per cent of water bound against particle size. If the terms defining the co-ordinate axes in the two graphs are analyzed, it will be noted that the same forces of adsorption are operative in the two cases, and that they differ merely by the constants that are used in defining them. An increase in particle size increases the amount of water associated with each particle and consequently increases the amount of water capable of being frozen. A smaller mesh size increases the adsorbing surface per unit mass of material, lowers the freezing point, and thus causes a greater amount of water to be bound.

These confirmatory deductions indicate that water must be sorbed by finely divided quartz sand as a thin film, and when so sorbed, it undergoes a change in activity, which is manifested by depression in freezing point. Water so sorbed also fails to freeze

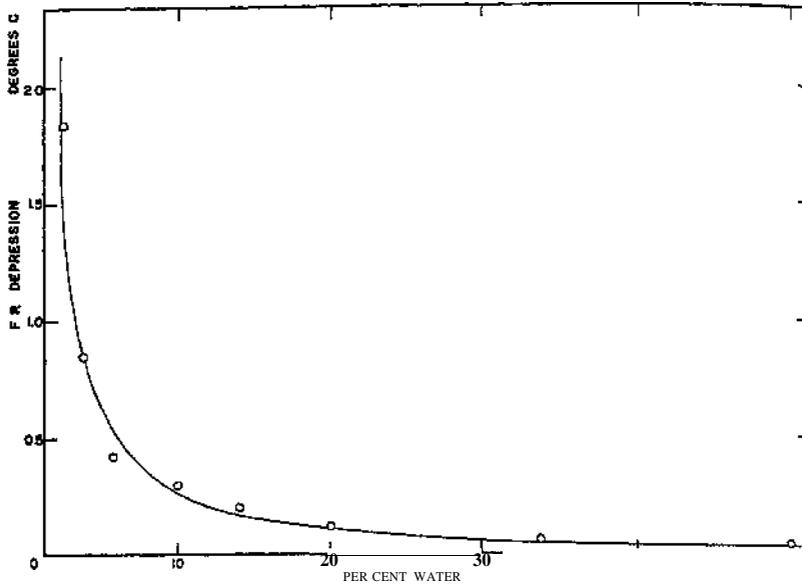


Figure 9.—Curve showing depression of freezing point of water as affected by ground sea sand (after Parker).

as determined by the dilatometer. As the water film becomes progressively thinner, the attractive forces by which it is held by the quartz particle become stronger, and bring about such changes in the physical nature of water as an increase in density and a marked decrease\* in dielectric constant (7a). This change in properties reduces the dissolving and dissociating action of water on dissolved salts, and progressively reduces the amount of water available to plants, the latter becoming zero when the pF value reaches a value of 4.2.

#### Water binding by kaolinite

Kaolinite provides an excellent example of the second class of soil mineral investigated in this study. The X-ray diffraction studies of Gruner (13) on kaolinite reveal that it is made up of plates composed of a single gibbsite and a single tetrahedral silica sheet. The kaolinite lattice does not expand with varying water content. Substitutions in the kaolinite lattice are uncommon and even impossible. In the case of magnesium substituting for aluminum which takes place easily in many minerals, such a substitution in kaolinite would distort the lattice due to difference in ionic diameter, and would render the lattice unstable. **Kaolin-**

\*T. M. Shaw, on the other hand, finds that the dielectric constant of a Miami soil increased as the soil was compacted, it being substantially a linear function of the volume-weight. The slope of the line increased with moisture content, which suggests that this effect may be due in part to a change in the dielectric constant of water itself. (Unpublished results by private communication.)

ite is characterized, in fact, by the stability of its lattice. Since, therefore, there are no replacements in the lattice which would bring about an unbalance of charge, we find kaolinite to have a low base exchange capacity and hence we should expect but a slight tendency for this mineral to bind water by reason of lattice peculiarities. Any water bound by it would be expected to be due to sorption only.

The kaolinite selected for the bound water determinations was ground to pass a 300-mesh sieve. A series of samples was puddled with moisture contents ranging between 50 and 100 per cent. The 50 per cent moisture content was selected as the lower limit since it is difficult to secure uniform moisture distribution in finely ground kaolinite at lower moisture contents. Neither is it possible to predetermine the moisture content of puddled kaolinite samples. Hence an independent moisture determination was made on a portion of each sample after puddling. The results obtained in this experiment are shown in Table 6.

TABLE 6.—WATER BINDING IN KAOLINITE

Original moisture	Wt. sample	Wt. H <sub>2</sub> O in sample	Expansion	Water frozen	Water bound
<i>per cent</i>	<i>gm.</i>	<i>gm.</i>	<i>cc.</i>	<i>per cent</i>	<i>per cent</i>
53.44	6.8413	3.6559	20.26	91.99	8.01
53.59	10.0631	5.3928	30.84	92.18	7.82
53.96	9.4100	5.0776	28.55	90.63	9.37
57.90	8.3053	4.8087	27.14	93.68	6.32
68.55	3.9004	2.6737	14.55	90.34	9.66
72.66	5.8259	4.2330	24.95	94.95	5.05
75.45	9.9213	7.4856	45.05	97.01	2.99

It is apparent from Table 6 that over the range of moisture contents studied kaolinite does not bind over 10 per cent of the total moisture with which it is puddled. In fact, there is a question whether the samples were actually puddled in the sense that it is possible to puddle a heavy clay soil. The mineral behaves peculiarly on wetting. At moisture contents above 50 per cent, a plastic mass is first formed, and further puddling reduces it to a structureless, supersaturated mass, very similar to a mixture of sand and water. Some of the water invariably separates out. If the supernatant water is removed from the apparently puddled mass, the moisture content is found to be the same regardless of the amount of water initially used.

The base exchange capacity of this kaolinite was 3.3 milliequivalents per 100 gm. Except for a slight amount of binding which might be attributed to the hydration of a few exchangeable cations present, the binding of water exhibited by kaolinite is of the same order of magnitude as that of 300-mesh quartz sand, which was 5.78 per cent as shown in Table 5.

Buehrer and Rose (4) demonstrated that alternate freezing and thawing of a puddled soil sample reduced the amount of water bound. Hence it seemed of interest to determine the effect

of such treatment on the amount of water bound by kaolinite. The results obtained showed, in fact, that the quantity of water bound was not affected by alternate freezing and thawing. These findings are in accord with those of Anderson and Edlefsen (1) who studied the volume-freezing point relationships of Aiken clay loam, a soil whose colloid fraction is known from X-ray diffraction to be dominantly kaolinitic. These authors claim that once a puddled sample of soil has been thawed, the soil returns to its original state. In the case of kaolinite this was found to be true, hence any changes in physical condition brought about by the puddling must have been reversible. There is a serious question whether all soils will return to their original granulated or aggregated state on freezing and thawing. Buehrer and Rose (4) found, for example, that in a readily aggregated soil like Clarion loam (Iowa), alternate freezing and thawing were wholly without effect. In the case of a desert soil like Pima clay, low in organic matter, there was, to be sure, a reduction in the amount of water bound, but even after six freezings and thawings, there was still about 66 per cent of its total water in an unbound state. This shows that Pima clay does not return to its initial aggregated state merely on freezing and thawing. The kaolinite samples used in this experiment did after freezing exhibit a loose, granular, almost pulverulent, form.

#### **Water binding by montmorillonite**

The final class of soil minerals studied was the 2:1 expanding lattice type in which the unit lattice consists of two silica sheets with a gibbsite sheet in between, of which montmorillonite is the typical example. These packages are stacked one above the other and are held together by water molecules which are oriented between the layer packages. The space between the packages varies with the water content, and in the limit can expand by 12 Å. per layer package. The high base exchange capacity of montmorillonite indicates the existence of a large residual electronegative charge on the lattice resulting from isomorphous substitutions. These substitutions give rise to a planar charge which is much greater in magnitude than the charge arising on the edges of the lattice due to broken bonds.

There are three sources of sorptive force in montmorillonite capable of holding water in bound form: (a) surface sorption resulting from simple molecular attraction; (b) binding of water molecules by electric charges existing at the edges of the plates as a result of broken lattice bonds; and (c) binding of water by electronic charges on the plate surfaces due to isomorphous substitutions in the atomic planes.

For the purpose of this study the writers chose a bentonite from deposits at Otay, California, ground to pass a 300-mesh sieve. It had a base capacity of 88.5 milliequivalents per 100 grams. X-ray diffraction indicated that its dominant mineral was montmorillonite.

A series of samples of this bentonite, puddled at moisture contents ranging from 35 to 95 per cent on the wet basis, was prepared for the dilatometric determinations. The wet basis was chosen for expressing the moisture content since this material is capable of sorbing so much water that at saturation it contains nearly 500 per cent of moisture when expressed on the dry basis. Care was taken during puddling to insure uniform distribution of moisture throughout the samples. A portion of each puddled sample was placed in the freezing tube of the dilatometer and a separate sample of the same material taken for the total moisture determination.

The results obtained are shown graphically in Figure 10, in which the per cent water bound is plotted against the moisture content at which the clay was puddled. The curve shows a nearly constant degree of binding of 97 per cent up to a total moisture content of 75 per cent. Throughout this moisture range the physical condition of the clay was definitely plastic and it even had the characteristics of a gel. Beyond a total moisture content of 75 per cent the clay began to become fluid and lost some of its plasticity, at the same time showing a decrease in amount of water bound. At about 83 per cent moisture a precipitous drop occurs in the amount of water bound, and the clay changes from a gel to a sol. With further dilution it becomes a suspension and the percentage of water bound approaches zero.

The phenomena here observed may be interpreted in terms of the lattice forces of montmorillonite. In the plastic or gel-like condition montmorillonite is capable of binding water between the layer packages of the expanding lattice by forces strong enough to prevent its freezing at -3 degrees C. As the moisture content of the sample is increased, the added water forces the packages further apart, thus weakening the binding forces. In passing from a gel to a sol the layer packages are no longer stacked in an orderly fashion, one above the other, but are randomly dispersed. At this stage water binding becomes a function of surface attraction of the dispersed layer packages and the hydration of exchangeable cations, in a manner similar to the behavior of quartz and kaolinite.

The manner in which water is held by montmorillonite has been investigated by Hendricks and Jefferson (15), Hendricks, Nelson, and Alexander (16), and Jackson and Hellman (17). Hendricks and Jefferson have shown from crystal structure measurements that clay mineral hydrates such as vermiculite, montmorillonite, and hydrated halloysite contain layers of water molecules joined in an hexagonal network, in which the water molecules are attached to the layer packages through hydrogen bonds, which function as pointed out in a previous bulletin (4). Successive layers of such hexagonal networks of water molecules can be built up as the moisture content increases, thus accounting for the swelling of such minerals and the increase in the (001) lattice spacing.

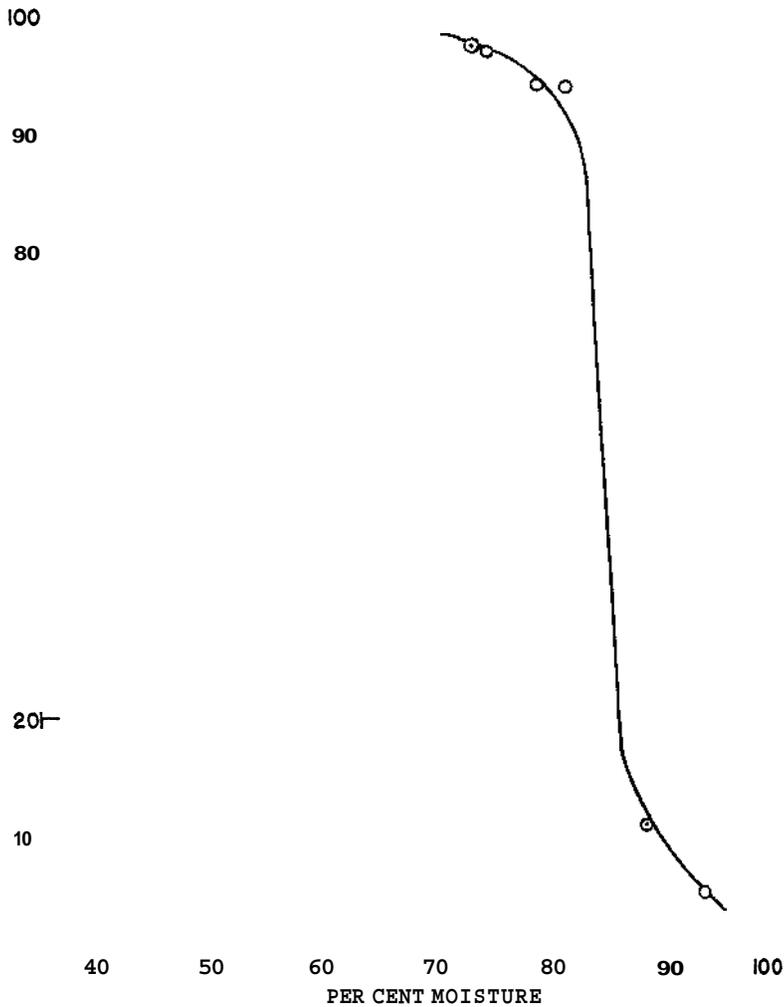


Figure 10—Water binding in bentonite clay as a function of moisture content at which samples were puddled.

Hendricks, Nelson, and Alexander (16) have shown that the exchangeable cations are located on the surfaces of the silica layers of the montmorillonite layer packages. When magnesium and calcium, for example, are the exchangeable bases, the first step in the sorption of water is to hydrate the cation with 6 molecules of water, and then a completion of the hexagonal network. The second layer of water molecules is built up on the first, and so on. In case of lithium ion, 3 molecules of water of hydration are taken up. Sodium and potassium *are not hydrated*

when present in exchangeable form in the montmorillonite lattice.

Jackson and Hellman (17) show that, by reason of its high dipole moment, water is strongly attracted to the montmorillonite layer packages, so that as the moist mineral is gradually dried, there is a continuous reduction in volume of water between the packages, resulting in pulling the packages together. The hydrated exchangeable cations, on the other hand, tend to hold the packages apart.

The imbibition of water by montmorillonite is a spontaneous process, and as such, it is conceivable that water binding as we have reported it in this study might occur without the mechanical manipulation of puddling. Such was actually found to be the case. Samples of Otay bentonite were placed in the dilatometer freezing tube, moistened with the desired amount of water, stoppered, and allowed to stand in order to swell and attain uniform moisture distribution. After three months the dilatometer expansion was determined and the amount of bound water calculated. The values were found to fall very closely on the curve of Figure 10. Puddling in such a case appears to serve merely to bring the particles closer together and to work out the air from between them. It is doubtful whether mechanical working plays any part in the entry of water into the interpackage spaces. The actual effect may be merely to hasten the attainment of moisture equilibrium and uniformity of moisture distribution.

#### RATE OF MOISTURE LOSS ON DRYING OF PUDDLED SOILS

Since water becomes bound to a greater or lesser extent on puddling, and its activity or escaping tendency thereby lowered, it seemed logical to assume that one might differentiate experimentally between free and bound water by the rate at which it is lost in drying. Puddling brings about pronounced changes in the soil: water equilibrium. If the water is held by different types of forces by the soil in a puddled state, the different forms of water should not come off with equal ease on evaporation, unless there be a transformation of bound water to free during the process. It was therefore expected that one might be able to deduce the proportions of free and bound water in a soil sample from inflections in the evaporation rate curve. Such a difference in evaporation rate for free and bound water should theoretically be observable in a puddled soil in which, due to loss of structure and increase in compaction and lower porosity, movement of moisture in the vapor phase would be greatly retarded.

An experiment was accordingly designed in which the loss of water at a given temperature could be continuously followed by weighing of the puddled sample at various time intervals without removal from the drying oven. The apparatus employed for this purpose is shown in Figure 11. The balance pan was suspended in the inner chamber of the drying oven by a platinum wire and linen thread from the arm of the balance above. In

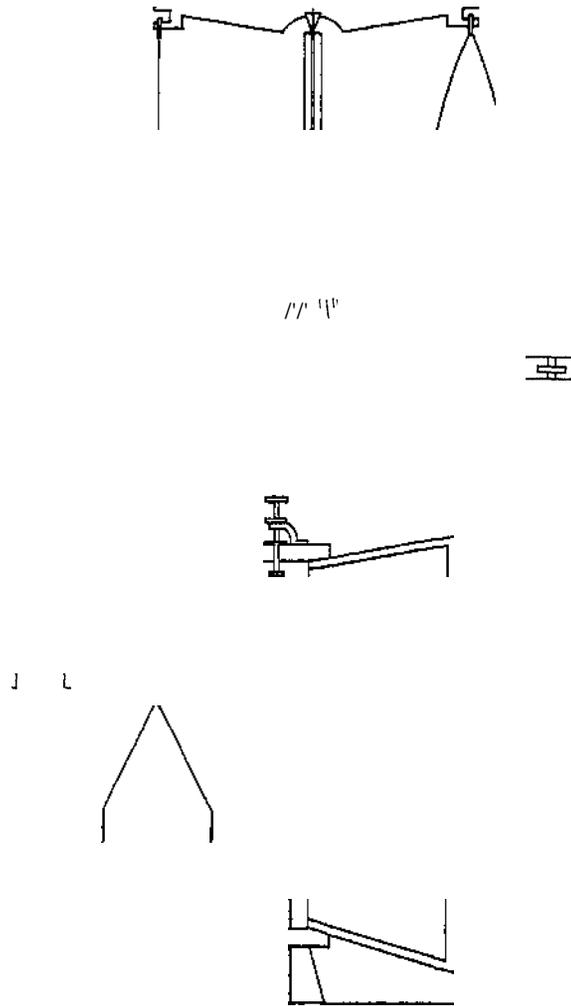


Figure 11.—Apparatus for determining the drying rate of soils,

order to reduce fluctuations of temperature and air currents to a minimum, the small chamber was installed to which was attached a copper tube connected to a humidifying apparatus. Air was slowly passed into this chamber after humidification to 10 per cent relative humidity. The drying chamber was regulated to 40 degrees C.

The puddled soil sample was put into a shallow pan or dish  $\frac{3}{16}$  inch in depth and 2% inches in diameter, levelled off with a

spatula, immediately placed on the balance pan, and its initial weight recorded. The temperature and humidity conditions were chosen to approximate as closely as possible the average conditions existing in the field. Runs were made with Prima clay, puddled at four initial moisture contents, and with Otay bentonite puddled at three different initial moisture contents. The determinations were carried out on each sample over a period of approximately twenty-four hours. Weighings must be made frequently soon after the sample is placed in the oven, since the loss of water is greatest at the start, and subsequent weighings can safely be made at greater intervals.

The results of these determinations are shown in Figures 12 and 13. The curves show the common characteristic that water evaporates from the sample at a constant rate during the initial stages of drying. As drying continues, the rate tapers off and finally becomes zero; the amount of water lost approaches a limiting value, which represents removal of all of the moisture possible under these conditions. The samples which had been puddled at a higher initial moisture content come to their limiting value more slowly but in each case the limiting value represents approximately the total amount of moisture initially taken.

The effect of tapering off of the drying rate is due to two causes: first, that as evaporation proceeds at the surface, the moisture from the interior of the sample must reach the surface either by diffusion through the soil mass or due to capillary tension through the microcapillaries; and second, a reduction in the total surface exposed, through shrinkage of the soil sample. The total shrinkage was on the average about 10 per cent of the total initial surface. We feel, however, that the second cause is less in magnitude as compared with the first, because the rate of removal of moisture is greater than the rate of reduction in the surface. In some cases the surface was increased somewhat by the sample's developing cracks as well as drawing away from the sides of the dish.

While the curves obtained do not show any striking inflections which would indicate water in different states, a correlation is nevertheless possible between the amount of moisture removed during the period of the linear evaporation rate and the amount of free water determined by the dilatometer. The results correlate quite closely, and we are inclined to conclude that the water removed during the linear evaporation period represents that portion of the moisture which is essentially "free," that is, free to move in response to the moisture gradient produced by the evaporation. The "bound" water is interpreted to be that portion of the total water held in the gel phase, from which the moisture can only be removed or brought to the surface by the slow processes of diffusion.

Several investigators have studied the rate of moisture loss from similar systems and the mechanism of drying of soils. Morgan and Hursh (24), working with Florida ceramic clays,

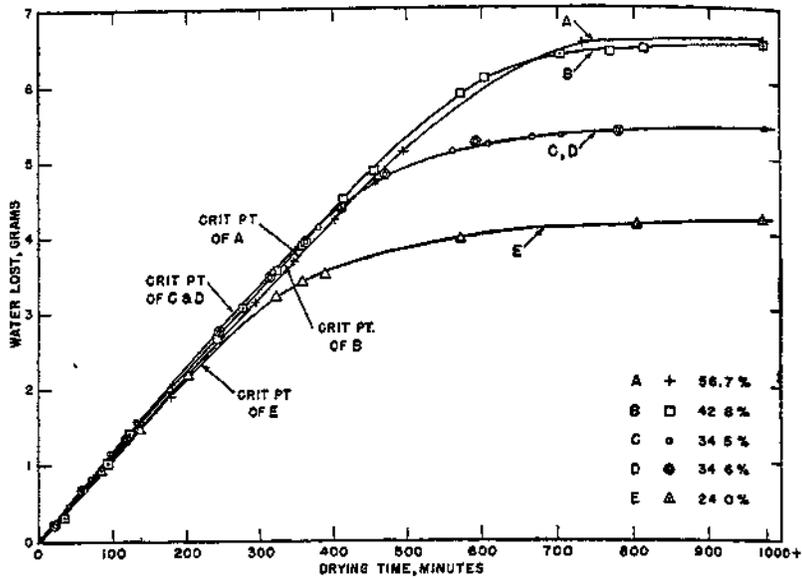


Figure 12.—Drying rate curves for Pima clay. (Percentages in lower right corner represent initial moisture contents at which samples were puddled.)

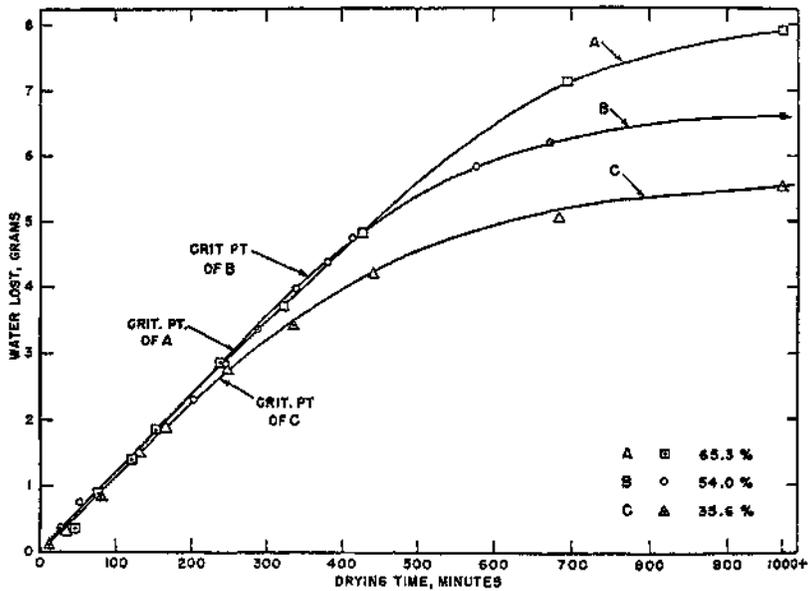


Figure 13.—Drying rate curves for puddled bentonite clay. (Percentages in lower right corner represent initial moisture contents at which samples were puddled.)

made drying tests under various conditions of temperature, relative humidity, and thickness of specimen, as well as materials of various grain sizes and various initial water contents. They found that the rate of drying is less than would be expected for evaporation from a free water surface. They advance the idea that the drying of clays takes place in two stages: an initial stage, approximately linear, during which shrinkage at the surface is completed; and the second, during which the rate of drying falls off rapidly because of increased resistance to diffusion of liquid water and of water vapor from the interior of the sample. They call the break between the linear and exponential curves the critical point, or "surface shrinkage limit." While their temperatures and humidities were higher than those used in this investigation, their drying rate curves are in general closely similar. It is possible that strict linearity during the evaporation stage below the critical point was realized because the writers employed a temperature of 40 degrees C. and 10 per cent relative humidity, as compared with 64 degrees C. and 40 per cent relative humidity used by Morgan and Hursh.

Morgan and Hursh also point out that in normal soils moisture movement is due to a continuous moisture gradient and that liquid water is present throughout the soil, but not necessarily in uniform distribution. Regions of saturation may occur side by side with regions of low moisture concentration where the system consists of widely varying pore sizes. Under such conditions there is movement of moisture both as liquid and as vapor through the pore spaces. Evaporation thus can occur at the surface without serious shrinkage. But in a puddled soil where evaporation from the surface occurs faster than replenishment of the moisture concentration from below, the drying out of the gel phase causes shrinkage and further constriction of the pores or capillaries. At this point the rate of evaporation falls *off to* an exponential function as we have found in both Pima clay and bentonite clay puddled at different initial moisture contents.

Woodruff (38) studied rates of moisture loss by evaporation from sand, sandy loams, silt loams, and clay loams. He classifies pore sizes in soils into three possible groups: (a) those with an effective radius greater than  $1.5\mu$  in which water flows as a liquid from regions of high pressure to regions of low pressure and the flow obeys the laws of capillary rise; (b) those with an effective radius between  $0.2\mu$  and  $1.5\mu$  through which water can move only as vapor and in which moisture potential adjustments are slow; and (c) those with an effective radius below  $0.2\mu$ . Such water may move through the soil as a liquid but can be extracted from the soil only as vapor. These pores are so small that their contents are affected by adsorptive pressures at the solid-liquid interface. Woodruff shows that in puddled soils of fine texture most of the pores have diameters less than  $0.2\mu$ , and that on evaporation such soils lose water from the surface until the moisture content of the profile is near the wilting point.

The evaporation rate curves of Woodruff are very closely similar to those here presented. He concludes that throughout the linear portion of the drying curve, moisture moves through the soil in the liquid phase, and the break in the curve occurs at the limiting moisture content at which liquid movement ceases. He holds that beyond this point, water movement occurs only as vapor. This limiting moisture content corresponds to the field capacity. Therefore, when the surface of the soil has become dry, and movement of liquid water ceases, further loss of water can occur only by evaporation beneath the surface. The rate of evaporation beyond the critical point is inversely proportional to the square of the thickness of the dry layer through which the water vapor must diffuse. Hence it will require *four times* as long to dry out the second inch of soil as the first inch.

In effect, then, puddling reduces the average pore size to a diameter less than  $0.2\mu$ , and thus makes it necessary for the moisture, if it moves at all, to move in the vapor phase.

### DISCUSSION

In view of the evidence that has been obtained for water binding by the different soil constituents, we are now in a position to consider the problem in an endeavor to interpret what happens to the water when a soil is puddled at a given moisture content. To do this we must keep in mind that the water will be held with forces differing in kind as well as in magnitude, and it will be oriented differently in the various soil constituents.

Let us then consider a certain amount of water added to a soil and the probable distribution that may be expected among the different constituents. We have, first of all, the sand fraction in its various sizes, even down to colloidal size. Our experiments have shown that binding in the silica system is primarily by way of adsorption. Since such adsorption usually occurs in a monomolecular layer and since a lattice of linked tetrahedra is non-expanding, the water present in the quartz fraction of a soil is not bound to a very great extent, amounting to only 5 per cent. Hence, if a soil consisted of only fine sand and colloidal silica, the great bulk of the water present would be free. This is particularly true since silica sand, even in its finest degree of subdivision, cannot be puddled in the ordinary sense. This fact is also consistent with the idea that crystals of the linked tetrahedron type, not being lamellar in structure, do not orient themselves on puddling. In comparison with the other soil constituents, the silica fraction throughout its textural range, binds water only to a negligible extent.

Passing now to the clay minerals in the soil, the 1:1 type, exemplified by kaolinite, was found to bind an amount of water less than 10 per cent. This slight increase over the amount bound by silica might be due to particle size, in view of the fact that the average size of the kaolinite particle was less than 300-mesh.

Kaolinite exhibits the typical syneresis of a thixotropic gel and indicates that binding may occur between the cleavage surfaces of the mineral and is only of temporary duration. One may expect, of course, that kaolinite should bind an amount of water somewhat greater than silica because of broken lattice bonds.

Another point of interest in this connection was the fact that when kaolinite was puddled and the puddled sample allowed to dry, it exhibited no permanently puddled structure but crumbled readily into its original physical state. Furthermore, it was found that alternate freezing and thawing had no effect on the percentage of water bound. These findings are in accord with those of Anderson and Edlefsen (1) and are further corroborated by Bodman and Day (2) who examined the freezing points of several soils and clays and concluded that puddling of the Aiken clay loam produced no effect on the freezing point depression of that soil when compared to that of the normal, unpuddled soil. Thus we may conclude that such binding as may occur in the non-expanding 1:1 lattice type clay minerals, occurs only by virtue of surface adsorption closely analogous to that which occurs in the silica system. This fact is further substantiated by the observation that a similar syneresis and thixotropic behavior was observed in the fine sand system as in the kaolinite.

The 2:1 lattice type of clay mineral, of which montmorillonite is an example, was found to exhibit a very characteristic and significant behavior. In the absence of other soil constituents and at moisture contents ordinarily existing in the field, it binds 97 per cent of the water present. With reference to actual soils dominantly montmorillonitic and low in organic matter, Buehrer and Rose (4, Table 7) found binding at the moisture equivalent to the extent of 93 per cent in the case of Pima clay, 98 per cent in Houston clay, and 90 per cent in Yolo silty clay.

With reference to the effect of neutral salts on water binding in field soils, we are inclined to the view that their effect is negligible. From the standpoint of structure, their effect is actually beneficial in that they flocculate the colloids and provide nuclei for the build-up of aggregates. Thus the amount of water bound by them is offset by the amount released through aggregation.

The peculiar effect of calcium in *decreasing* the size of soil aggregates, as reported by Peele (29a) appears to contradict the generally accepted fact that calcium is highly effective in flocculating soil colloids and as an aggregating agent. He found that adding calcium chloride or hydroxide to Cecil clay caused a marked decrease in percolation rate. Addition of calcium carbonate, however, to Iredell loam which was not readily permeable before treatment, had but little effect on the percolation rate. It is well known that addition of gypsum to a highly alkaline calcareous soil does not always result in flocculation or aggregation. The aggregating effect of lime must therefore be related in some manner to the nature of the soil colloid fraction.

The last important water-binding class of soil constituents is the organic matter. The carbohydrates and the proteins have molecular structures which make possible the addition of water molecules, either on the branches of their long chains or between the cells constituting their structures (7). This fact is shown by the tendency of these materials to swell spontaneously upon being wetted. Water must therefore enter the structure, and since the process is spontaneous, it must result in a decrease of free energy of the water, which in turn indicates a decrease in its activity. This spontaneous energy change is also indicated by the heat of wetting of these systems. Hence, it is logical to conclude that water so held is "bound."

From the standpoint of moisture binding in field soils, the action of organic colloidal materials is probably of major significance, since they act as cementing agents in the build-up of aggregates. Martin (22) indicates that as little as 0.1 per cent of polysaccharides in a soil brings about 44 to 70 per cent aggregation of the silt and clay particles as compared with 28 per cent for the control.

The organic colloids generally exist as humates in the soil. They are therefore saturated more or less with hydrogen or the various metallic cations, and the charge on the colloid is determined primarily by the exchangeable bases present. The degree of hydration, which is related to the amount of bound water held by the colloid, is also dependent upon the exchangeable bases present, chiefly sodium. These colloids are hydrated to a degree commensurate with that of a montmorillonitic clay, and their high hydration accounts for the difficulty encountered in flocculating them. When they act to aggregate the soil in the capacity of a cementing agent, the conditions must, however, be such that their charge will neutralize that on the clay and other soil minerals, as Ensminger (9) has shown in his studies on factors affecting the interaction between organic matter and montmorillonite. Once the aggregate is formed it will not be as stable as those formed by the inorganic colloidal cementing agents because of the microbial life of the soil acting to decompose the organic matter will eventually cause a breakdown of the aggregates, and produce granules. Martin (21) has found that the active aggregating material (hemicelluloselike polysaccharide) synthesized by a soil bacillus was attacked to a limited extent by fungi, but was readily destroyed by certain bacteria and actinomyces. He concludes, therefore, that it belongs to the class of microbiological aggregating agents which only temporarily contribute to increased soil aggregation.

This aggregating effect of organic matter has been studied by Peele (29b) who found that the addition of Lespedeza to Cecil clay increased the percolation rate. He points out that the beneficial effects of organic matter may be offset by the detrimental effect of lime additions. When organic matter is added to a limed soil to improve structure, it therefore appears necessary

to choose the proper proportion of lime to organic matter so as to attain the maximum amount of aggregation.

An unusual effect of the addition of manure to Pima clay has been observed by Fletcher\* who noted that it decreases both aggregation and permeability due to the formation of slimes by soil fungi. Evidently the aggregating action of organic matter is intimately related to the nature of the soil itself and the microbial flora present.

### SUMMARY

1. A comparative study has been made by the dilatometric method of the extent to which water is bound by the various classes of constituents present in soils.

2. The simple soluble salts commonly present in soils bind water to a small extent only, and the amount bound is consistent with the published values for the hydration of the common univalent and divalent cations.

3. Nonelectrolytes like glycerine and sucrose bind water in a remarkably constant proportion, the amount bound being a linear function of the concentration and indicating a constant ratio of 8 mols of water per mol of glycerine or of sucrose.

4. Agar and gelatin gels do not bind water to an appreciable extent at concentrations to which the dilatometric method is adapted. It is concluded that the formation of ice crystals expands and disrupts the gel structure, so that the water behaves essentially as free water.

5. Experiments with sand ground to various degrees of fineness showed a maximum binding of only about 5 per cent. The nature of the bound water curve suggests that the binding process is primarily one of ordinary adsorption.

6. Kaolinite exhibits water binding, syneresis, and thixotropic behavior similar to that of silica. Less than 10 per cent of the water present was bound. Since the kaolinite lattice is non-expanding, it is concluded that the water is held only by forces of sorption on the free surfaces of the lattice.

7. A bentonite clay, consisting dominantly of montmorillonite, was found to exhibit a behavior strikingly different from that of quartz and kaolinite. In the range of moisture content from 0 to 85 per cent, it was found that 97 per cent of the water failed to freeze. Beyond this moisture content, the clay suddenly changed from a gel to a sol and thereafter was able to bind only 10 per cent of the total water present. The amount of water bound at the lower moisture contents corresponds closely to the amount of water entering the expanding lattice. The high degree of binding of water is attributed to the high residual electronegative charge on the lattice as indicated by the high base exchange capacity of the bentonite (88.5 m.e. per 100 gm.).

\*Private communication.

8. Within a limited range of moisture contents, organic matter added to the soil in the form of ground alfalfa reduces the amount of water bound by a puddled soil to a minimum, beyond which further addition of organic matter causes the amount of bound water to increase. It is concluded that the decrease in water bound with addition of alfalfa up to 10 per cent, is due to a breakdown of the puddled condition and formation of aggregates. At higher percentages of organic matter, the amount of water bound again increases due to the tendency of the organic matter itself to bind water.

9. Experiments on the rate of moisture loss on drying a puddled bentonite clay and Pima clay loam showed that the free water goes off by evaporation at a linear rate and thereafter the curve tapers off in exponential form.

10. The results of this study have indicated that the chief soil constituents that are responsible for the binding of water are the expanding-lattice minerals of the colloidal clay fraction and the organic matter. These have the ability to hold the moisture in an unavailable form. Any amendments which tend to promote aggregation will reduce the amount of water bound and render it free. The importance of organic matter additions to puddled soils lies primarily in their salutary effect upon the soil structure and the formation of aggregates.

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