

UNIVERSITY OF MISSOURI

COLLEGE OF AGRICULTURE

AGRICULTURAL EXPERIMENT STATION

Research Bulletin 210

Experimental Studies on the Development of Heavy Claypans in Soils

GUY D. SMITH

(Publication Authorized May 21, 1934)



COLUMBIA, MISSOURI

JUNE, 1934

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Hans Jenny for his advice and direction in this investigation.

TABLE OF CONTENTS

	Page
Introduction	3
Definition of claypan	3
Occurrence of claypans	4
Theories of origin of claypans	6
Nature of illuvial clay particles	7
Experimental Work	7
Object and plan of the investigation	7
Preparation of soil skeleton	8
Preparation of clay sols	9
Criterion of pan formation	10
Pan formation with a Na-clay	11
Effect of electrolytes on pan formation	15
Discussion of influence of electrolytes	19
Significance of hydration	22
Role of humus	23
Role of positive colloids	24
Flocculating power of ground waters	27
Application of Experimental Results to the Theory of	
Claypan Formation	27
Process of formation in an "ideal" soil	27
Application to natural claypans	29
Summary	30
Literature Cited	31

Experimental Studies on the Development of Heavy Claypans in Soils.

GUY D. SMITH

INTRODUCTION

Soils with heavy claypans are definitely limited in their productivity under average farming conditions. In some cases, the claypans so reduce the returns from soil treatment that cropping, even under the best known systems, remains unprofitable. Furthermore, the growth of trees on these soils is so slow that in the opinion of competent foresters most of the claypan soils are not adapted to the growing of orchards or timber.

The utilization of soils with clay horizons, unfitted for cropping or forestry, also presents a serious economic problem because of the large areas they occupy. Preliminary estimates from the soils department of the Missouri College of Agriculture, and the Illinois Soil Survey, indicate that in the two States, not less than 7,500,000 acres are underlain by claypans so impervious that crop yields are limited in all but the most favorable years.

In spite of the wide distribution of claypans very little is known about their origin and nature. The following study is directed to an inquiry into the factors that are responsible for the development of claypan soils.

Definition of Claypan

The Committee on Terminology of the American Soil Survey Association^{16†} has defined a claypan as "An horizon of accumulation or a stratum of stiff impervious clay." This definition makes no distinction between those strata of clay which owe their existence to weathering processes and those which have come into being through other natural processes. A horizon of clay produced by sedimentation in stagnant water obviously has no relation to a clay horizon which has arisen in the soil as a result of the processes of clay formation and illuviation, and to apply the same name to both is confusing. It is suggested therefore that the name "illuvial claypan" be applied to those claypans which have formed in the soil as a result of weathering and illuviation. While the

* Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Arts in the Graduate School of the University of Missouri, 1934.

†Reference is by number to Literature Cited.

other types of claypan may be important from the point of view of soil formation because of the influence an impervious stratum has on the overlying soil, the study of the origin of these pans lies strictly in the field of geology. In this paper, whenever the term claypan is used, it will be understood to apply only to illuvial claypans.

Occurrence of Claypans

In the United States, soils with heavy claypans occur throughout the Mississippi Valley, the Piedmont Plateau, and in scattered portions of the arid West and Pacific Coast. In the regions covered by the Wisconsin glaciation, claypans are not yet well developed, but in regions covered by older ice sheets, they occupy very extensive areas.

In the humid parts of Europe a combination of conditions has made it impossible for heavy claypans to develop extensively enough to attract the attention of pedologists. In the more arid portions of Europe, heavy clay subsoils are of local importance in alkali soils.

In Australia, Prescott¹⁰ has described soils with claypans along the southern and eastern coasts. According to his soil map of that continent, the areas are not large.

On the other continents very little definite information is available concerning the distribution of claypans. Shaw¹³ reports them as occurring in some provinces of China, chiefly on terraces, but little is known about their extent. Shantz and Marbut¹¹ believe that conditions are favorable for claypan development in portions of the southern half of Africa but the actual occurrence is conjectural. Available literature contains too few descriptions of soils from South America to enable much to be said about that continent.

The *climatic conditions* under which claypans may be expected are, perhaps, better known. Obviously, claypans cannot occur unless conditions permit the formation of the plastic clays which concentrate to form the pan. This eliminates the possibility of claypans in podsoles or true laterites, and likewise in soils where the lack of moisture prevents clay formation. In arid regions claypans may be found anywhere that soils are subject to conditions of temporary excessive moisture, but this occurrence is always local. Brown, Rice, and Byers³ in their discussion of the claypan soils of Nebraska show that chernozems may have well developed claypans, but as the annual rainfall decreases, the pans become thin-

ner, and finally, when the rainfall is sufficiently low, they do not form. This then confines any widespread occurrence of claypans to the temperate, and possibly tropical, humid and semi-humid regions.

However, within these regions there are many mature soils in which no claypan has developed. Norton and Smith⁸ have pointed out a **topographic** and **drainage** relationship in claypan occurrence. They state that in Illinois, soils developed on rolling topography under good drainage have a thick, friable, non-plastic, silty zone of accumulation, while soils developed on level topography under poor drainage have a thick, compact, highly plastic zone of accumulation. Norton and Winters⁹ have reported the mechanical analyses of soils developed under these two sets of conditions, and two of these profiles are shown graphically in Fig. 1, A

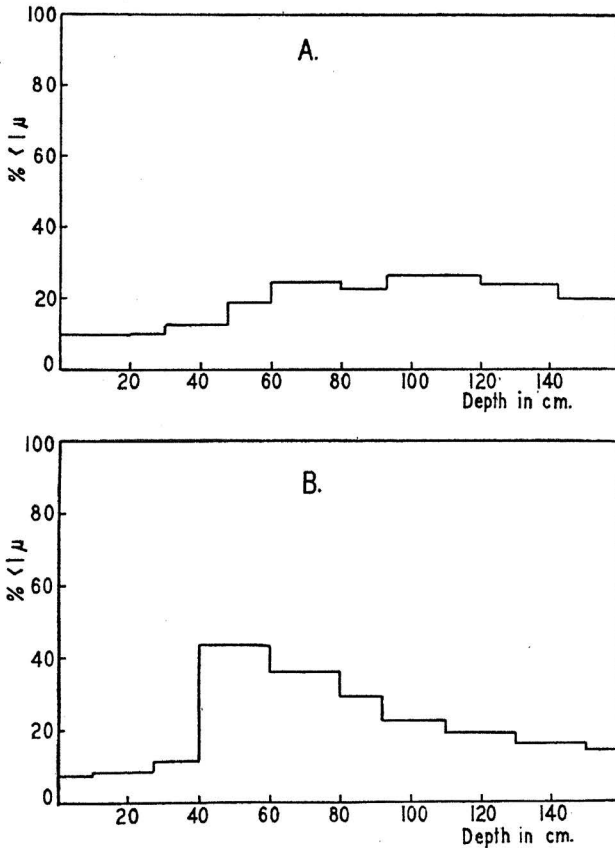


FIG. 1.—The Distribution of Clay Less Than 1 Micron in Two Profiles.
A. Well Drained. B. Poorly Drained.

and B. Fig. 1 A shows the percentage of the soil composed of particles less than one micron in equivalent diameter plotted against depth for a profile developed under good drainage. Fig. 1 B shows the same for a soil developed on flat topography and under poor drainage. This latter profile is characteristic of the heavy claypans developed throughout the Mississippi Valley from loess.

Theories of Origin of Claypans

Several attempts have been made to explain the origin of claypans. Russell and Engle¹¹ as a result of a study of the soils of Kansas and Nebraska emphasize the importance of the hydrogen ion concentration. They state that as the soil becomes leached, the surface becomes more and more acid until the clay is deflocculated. In this condition it can be carried down by percolating rain waters until a zone of higher pH is reached just above the calcareous horizon where the clay flocculates again. They state that the critical pH for lodgement of clay is near 6.5. At the time of the presentation of this paper, Bradfield brought out the point that the flocculation is not due to the hydrogen ions, but rather to the concentration of "other metallic ions" associated with various pH values.

Smith and Norton¹⁵ working in Illinois where calcareous horizons do not persist in mature soils are of the opinion that eluviation and illuviation are of minor importance under conditions of poor drainage. They believe it more reasonable to assume that most of the colloidal material is formed in place and retained because poor drainage results in conditions favoring formation and retention.

Brown, Rice, and Byers³ as a result of their study of claypan soils in Nebraska conclude that as the surface soils become acid, the clay tends to deflocculate, and moves downward until it is coagulated by the soluble calcium salts just above the carbonate layer. They believe that although there is some evidence of fractionation of the colloids, and of the presence of free ferric hydroxide or aluminum hydroxide, it is not necessary to assume that either has played a part in the development of the claypans. While this seems to be a satisfactory explanation of the claypans formed in soils with carbonate horizons, it leaves untouched the whole problem of the origin of the claypans of the humid regions where the soils are more highly leached.

Nature of Illuvial Clay Particles

The *size* of the illuvial clay particles has been studied by Bray². Working with the loessial soils of Illinois, he has divided the clay with an equivalent diameter less than one micron into three fractions, according to size. By chemical analyses, he shows that most of the particles that move in the soil are of the smallest fraction. These particles, he says, are less than .1 micron in diameter, but how much less he does not know.

Brown, Rice, and Byers³ have studied the composition of the clay fraction in the various horizons of several soils of Nebraska, and, finding a remarkable constancy in the composition of the colloid in the several horizons of any profile, have concluded that the *clay particle moves as a whole*, i. e., the different constituents of the colloidal particle move together, and not independently. Byers and Anderson⁴ reached the same conclusion in an earlier paper with regard to the soils of the Coastal Plain.

This conclusion that the clay particle moves as a whole would mean that one could isolate the finer fractions of the colloidal material from a claypan, and, after determining in the laboratory what factors would cause the clay to lodge in a bed of sand, apply the results to claypans formed in the field.

EXPERIMENTAL WORK

Object and Plan of the Investigation

Most of the literature reviewed links the formation of a claypan with the flocculation of the clay, but no experimental work to justify this viewpoint has been reported. The object of this investigation was to isolate and study in the laboratory some of the colloid chemical factors in claypan formation.

The plan of the investigation in its broad aspect was to set up an artificial soil of quartz particles of uniform size, and by passing a clay sol through this sand to study the effect on pan formation of several factors, one at a time.

The study includes the following:

1. Experiments relating to pan formation by dispersed Putnam clay in the absence of electrolytes.
2. Influence of the concentration of various electrolytes.
3. Effect of protective action of humus.
4. Role of positive iron oxide sol.

5. Significance in pan formation of dehydration of clay with alcohol.
6. Data relating to the flocculating power of natural ground waters.

Preparation of Soil Skeleton

The sand for the soil skeleton was cleaned by shaking in water to which a trace of Na_2CO_3 had been added, decanting, and washing with distilled water. This was repeated until further shaking gave no evidence of turbidity. The sand was then treated with HCl, washed with distilled water, and dried. To give particles of uniform size, the sand was separated by screening into the following groups; two groups of "coarse" sand, one composed of sand which passed a 20-mesh screen but was retained on a 40-mesh screen, and the other composed of 40 to 60 mesh grains; two groups of "medium" sand, one of 60 to 80 mesh particles, and the other of 80 to 100 mesh sand; one group of "fine" sand particles; and, one group of very fine sand. Two additional size groups were included, one of fine spherical glass beads, and the other of quartz silt.

The silt was prepared by grinding sand in a ball mill, treating with hot concentrated HCl to remove the iron fragments, washing, screening to remove the sand, and repeatedly shaking and decanting to remove the clay and finest silt particles.

Table 1 shows the sizes of the particles in these groups, and the size of the pores which each group would form, assuming spherical particles in close packing. The size of the pores is calculated on the basis of Slichter's work¹⁴, in which he shows that

Table 1.—Particle and Pore Size of Soil Skeletons.

Particle Group	Diameter of Particles	Size of Pores
Fine Beads	0.56 \pm .05 mm.	86.6 microns*
"Coarse" Sand		
20-40 mesh	0.833 to 0.385 mm.	129 to 54.3 microns
40-60 mesh	0.385 to 0.246 mm.	54.3 - 38.1 microns
"Medium" Sand		
60-80 mesh	0.246 to 0.175 mm.	38.1 - 27.2 microns
80-100 mesh	0.175 to 0.147 mm.	27.2 - 22.8 microns
Fine Sand	0.147 to 0.100 mm.	22.8 - 15.5 microns
Very Fine Sand	0.100 to 0.050 mm.	15.5 - 7.8 microns
Coarse Silt	0.050 to 0.020 mm.	7.8 - 3.1 microns

*One micron = 0.001 mm.

the pores in a system of spherical particles of uniform size in close packing are roughly triangular in cross section, and increase and decrease in size throughout their length in an orderly manner. The pore size in Table 1 is expressed as the diameter of the circle inscribed in the triangular tube at its smallest cross section. These sizes are calculated on the basis of spherical particles in close packing, and while the glass beads were truly spherical, the sand particles were angular, and approached spherical shape only in the coarser groups. The silt particles were highly angular, and although the size of the pores in this system could not be easily measured, it must have deviated widely from the calculated value.

The soil skeleton was prepared in the following way: A series of burettes with an average cross section of 12 mm. was selected, and, to retain the sand, the base of each was filled with large glass beads, .42 cm. in diameter. Five cc. of sand were placed in the burette on top of the beads, and water was forced through the system from below rapidly enough to suspend the sand. The water was then shut off and the particles allowed to settle. This gave a final separation according to size, and placed the smallest grains in the group together at the top of the sand column. The burette was struck sharply a number of times to settle and pack the sand, and was then considered ready for use. Air was never allowed to enter the pores of the column after the sand was placed in the burette.

Before the clay sol was passed through the sand, the rate of flow of water through the bed was determined. It was found that this rate depended somewhat upon the way the glass beads fitted the base of the burette, and in order to get a uniform rate of flow through different burettes, it was necessary to vary somewhat the head of water. A standard rate of flow of 5 cc. in 23 to 24 seconds was selected arbitrarily, and the head necessary to give this flow was determined empirically for each burette. Sufficient water was then passed through to be sure that the rate of flow did not change with percolation, that is, to insure stable particle arrangement. Burettes which showed a variation in the rate of percolation greater than .6 second were discarded.

Preparation of Clay Sols

A sol of 3.0% Na-Putnam clay was prepared by adding NaOH to an electrodyalized Putnam clay at the rate of 60 milliequivalents

of base per 100 grams of clay, and was shaken at intervals for several weeks to insure equilibrium. The sol was diluted to 0.3% before being passed through the sand.

When the effect of the concentration of electrolytes was to be studied, they were added to the clay in the following manner. A solution containing the desired number of milliequivalents was made up to 90 cc., and to this 10 cc. of the stock clay were added. The sol thus prepared was shaken gently in a large test tube (so that no air bubbles were formed) for 15 minutes and was passed through the sand immediately.

Criterion of Pan Formation

When the clay sol was allowed to percolate through the sand, the time required for 5 cc. of the sol to pass through grew with increasing rapidity as the pores became clogged with clay. The change in the rate of flow was selected as the best measure of pan formation. A constant rate of flow would indicate that no pan was being formed, while a decreasing rate of flow would be evidence of pan formation. With the head which gave the standard rate of flow with water, the time required to discharge 5 cc. of sol was measured with a stop watch. The flow was then interrupted while the burette was refilled to restore the original head, and the time required to discharge the second 5 cc. was observed. This procedure was repeated a sufficient number of times to give an index of the rate of pan formation. The results are reported in the tables and graphs as the relative percolation velocity.

This magnitude was calculated as follows. The time required to deliver the first 5 cc. of sol was taken as the standard and given the value of 1. Then the time required for each successive aliquot was divided by the time for the first 5 cc. Thus, when the time had doubled, the relative rate of flow would be 0.5. Since this method assigns an undue importance to the initial reading, its accuracy was checked by fitting a straight line to the first few points. When the first reading did not fall on this straight line, the intercept of the line with the ordinate was taken as the correct initial value, and the relative rate of flow calculated accordingly. When the pan formed so rapidly that only a few readings were obtained, the change was so great that the correction became unnecessary. The heavy solid lines in the graphs represent the trends, while the fine dotted lines pass through the observed values.

Pan Formation With a Sodium Clay

When a 0.3% sodium clay sol was passed through a bed of coarse sand (20-40 mesh), the rate of flow was found to decrease with time. Microscopic examination of the sol revealed the presence of relatively large particles, chiefly micro-organisms, although some may have been clay aggregates which had formed during electro dialysis and had not been completely dispersed by the addition of the sodium hydroxide. It was important to determine whether or not the pan formation as measured by the decrease in the rate of flow was entirely due to the presence of these large particles.

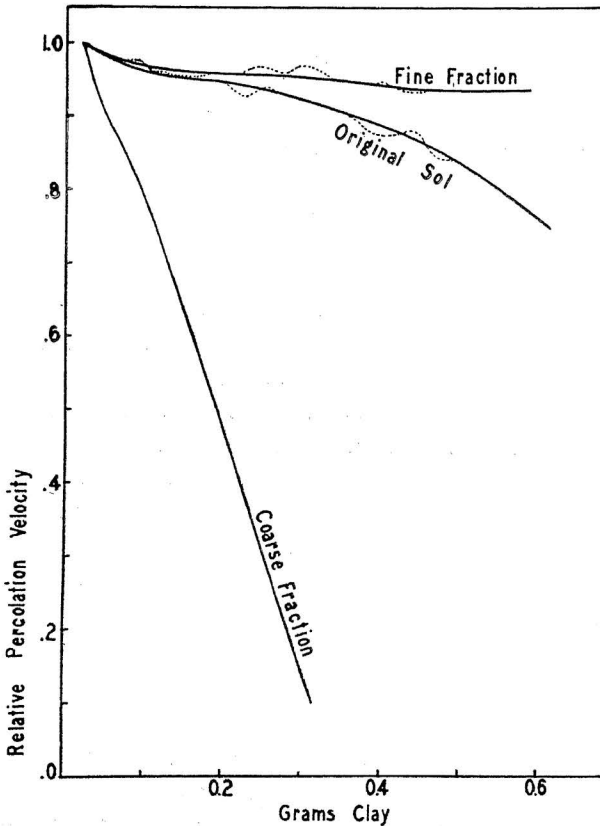


Fig. 2.—Effect of Various Clay Fractions on Pan Formation by a Sodium Putnam Clay.

Effect of Size Fractionation.—A 0.35% sodium clay was allowed to stand in a constant temperature room for one week, and at the end of that time the upper 4/5 of the sol were siphoned off, and both fractions diluted to 0.3%. The time period was sufficient to allow all clay particles larger than 0.7 microns to settle to the bot-

tom of the cylinder. Since the sol was to be passed through coarse 20-40 mesh sand, the pores of which had a diameter of about 54 microns (Table 1), this fractionation was considered ample. These sols were then run through beds of sand, and the changes in the time required to deliver 5 cc. were determined. Figure 2 shows the relative rate of flow plotted against the grams of clay passed through the sand.

To produce a given change in the percolation velocity, it required only about $1/5$ as much of the coarse clay fraction as it did of the original sol. This would indicate that the pan formation by the original sol was mainly due to the coarse fraction. However, the fine fraction reduced somewhat the rate of percolation, although the last third of the readings were constant. Apparently some of the particles were large enough to be caught in the narrower portions of the irregularly shaped pores.

Effect of Filtering Clay Sols Through Sand on Their Abilities to Form Pans.—If the sodium clay sol was passed through a bed of 20-40 mesh sand and subsequently through another one of the same pore size, the behavior in the latter was the same as that of the fine fraction in the preceding experiment (Fig. 2). A slight decrease in rate of flow was observed, but it tended to become constant. On passing through a third bed of sand, the sol again behaved in a similar manner. To determine whether this was purely a matter of particle size, the following experiment was performed. A 0.3% Na-clay sol was first passed through a bed of 20-40 mesh sand, and subsequently through a bed of 60-80 mesh sand to remove the large aggregates. This double filtered sol was then passed through a bed of 20-40 mesh sand, and the rate of flow observed. Finally, the same sol was passed through a bed of fine sand, and the changes in the rate of flow recorded. The results are shown graphically in Fig. 3.

It will be observed that after the sol had been filtered twice, (through 20-40 and 60-80 mesh sand), it was unable to change the rate of flow through the 20-40 mesh sand, but was still able to form a pan in the fine sand. The pan formation in the fine sand was slower in this case than it was with the original sol, but there can be no question but that it was actually forming one.

These two experiments indicate clearly that the pan formation with the sodium clay used was due simply to the presence of large aggregates, and after their removal no pan was formed. If pan formation were due to surface forces instead of the presence of

large particles, a sol which would not form a pan in 20-40 mesh sand would not be expected to form one in the bed of fine sand. The conclusion, then, must be that *if a Na-clay is sufficiently dispersed, it will not form a pan in a soil of sand or silt texture.* This is confirmed by another experiment in which a natural Putnam clay

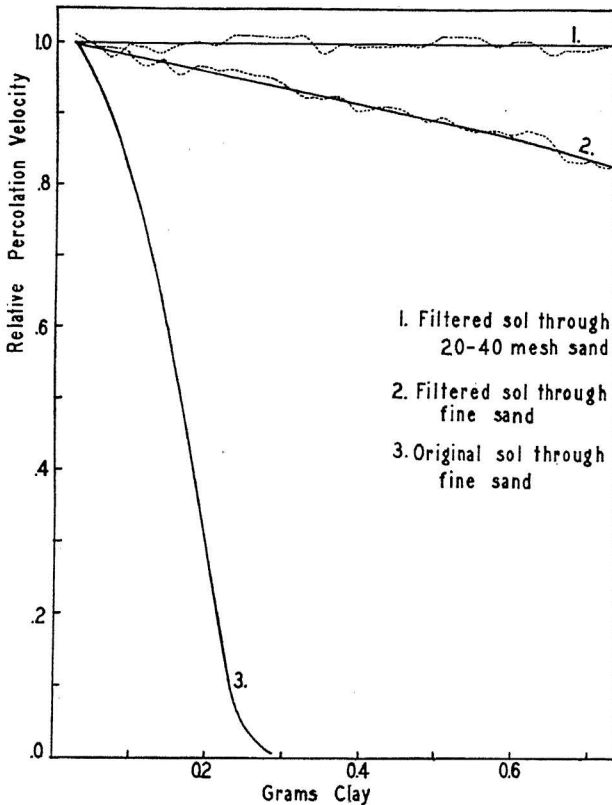


Fig. 3—Pan Formation by a Na-clay Sol Previously Filtered Through a 60-80 Mesh Sand Column.

sol was passed through a bed of 20-40 mesh sand without changing the rate of percolation.

The tendency of the Putnam clay particles to move through the sand unless mechanically caught in a small pore would indicate that the tendency for the clay in a soil profile is to move downward with the percolating ground water and to move entirely out of the solum unless some factor other than pore size is present to cause its retention.

Rate of Pan Formation in Different Sand Size-Groups.—It was mentioned previously that microscopic examination of the Na-clay indicated that it contained large aggregates. With such a clay system the rate of pan formation would be expected to increase if the size of the sand through which the sol was passing were decreased because there would be an increasing number of clay particles large enough to be caught in the pores. Particles too small to be effective in pan formation in the larger pores would be retained if the size of the passage were reduced.

To check this possibility, a separate sample of .3% Na-clay sol was passed through a bed of each of the sand size groups list-

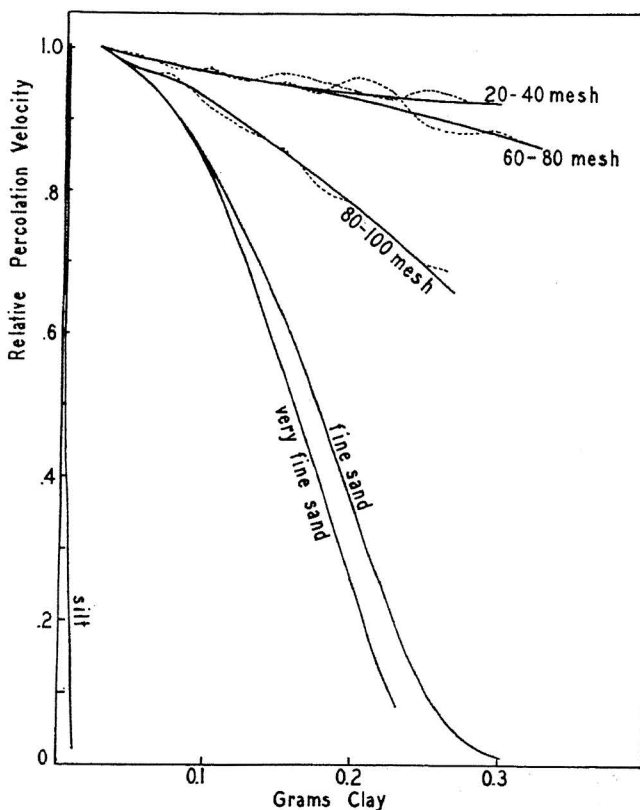


FIG. 4.—Effect of Various Sand Size Groups on Pan Formation by a Na-clay Sol.

ed in Table 1. The results are shown in Figure 4. Since the same results were obtained with the 40-60 mesh sand and the 20-40 mesh sand, the results from the former were not included in Fig. 4. This

similarity probably means that the clay particles large enough to be caught in the 40-60 mesh sand were also large enough to be caught in the 20-40 mesh sand, and consequently were equally effective. However, when the size of the sand is decreased further it is found that each decrease brings with it an increase in the rate of pan formation, which indicates that there are an additional number of particles large enough to be caught.

Experiments Relating to the Effect of Electrolytes on Pan Formation

In view of the emphasis laid on the importance of flocculation in claypan formation by various investigators, and in view of the influence of electrolytes upon the charge and state of aggregation of clay particles, it was considered important to determine the effect of various electrolytes in concentrations below and above the flocculation value. It is known that the cation of an electrolyte is most effective in bringing about the flocculation of a clay, and that the concentration of electrolytes required for flocculation decreases as the charge or valence of the cation increases. Consequently salts of four cations of different charges were selected, namely, sodium chloride (mono-valent), calcium chloride (di-valent), lanthanum nitrate (tri-valent), and thorium chloride (tetra-valent).

The concentration of each of these salts necessary to flocculate the clay was determined as follows:

Five cc. of a 3.0% Na-clay were diluted with water and varying amounts of salt solution to a total volume of 50 cc. The sol was shaken for 15 minutes in such a way that air bubbles were not formed. Then 10 cc. of this sol were diluted to 35 cc., shaken gently 50 times, and placed in a water bath at 30 degrees Centigrade. At the end of six hours, the presence or absence of flocculation was noted. The concentration of each electrolyte necessary to produce flocculation under these conditions is shown in Table 2. The concentration is expressed in terms of symmetry

Table 2.—Flocculation Values of Cations.

Cation	Flocculation Value	Flocculation Conc.
Na	17.5 S	1 F
Ca	1.4 S	1 F
La	1.0 S	1 F
Th	0.85 S	1 F

concentrations. A symmetry concentration is the number of milliequivalents of electrolyte equal to the milliequivalents of exchangeable ions adsorbed on the clay used, and will be referred to in this paper as the S concentration.

In some instances, the concentration of electrolyte will be expressed in terms of multiples of flocculation values, or F concentrations.

Effect of NaCl on Pan Formation.—NaCl was added to sodium clay in concentrations of 10, 20, 50, and 100 S. These sols were passed through beds of 20-40 mesh sand, and the changes in

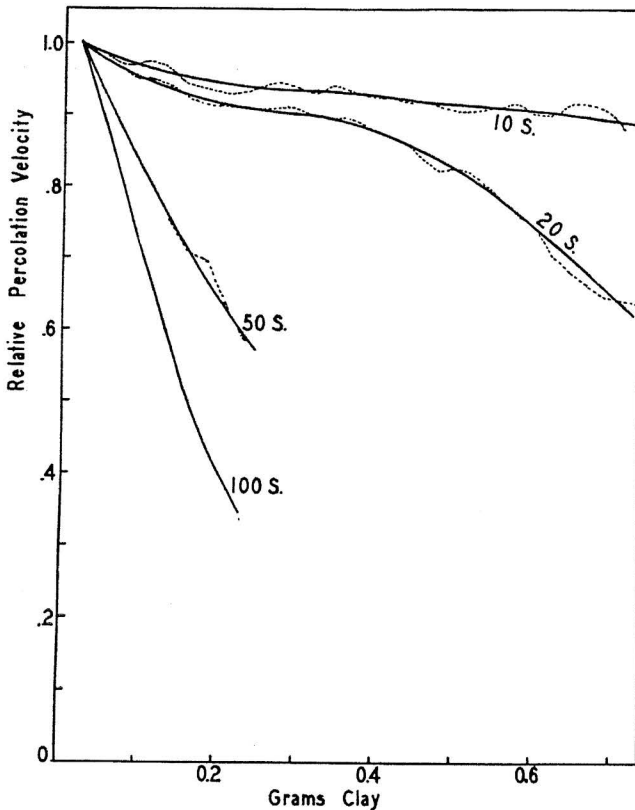


FIG. 5.—Effect of Addition of NaCl on Pan Formation by a Na-clay Sol.

the rate of percolation noted. The results are shown in Figure 5. While salt concentration below the flocculation value decreased the rate of pan formation, concentrations above the flocculation value hastened the process. (Compare Original Sol in Fig. 2 with sols shown in Fig. 5). Changes in the size of the smallest particles

would not affect pan formation unless they formed aggregates larger than the smallest diameter of the pores. Large aggregates apparently did not begin to form until the concentration of salt was raised above the flocculation value. Further discussion will be omitted until the effect of the other salts has been pointed out.

Effect of CaCl_2 .— CaCl_2 in concentrations of 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 4, 10, and 25 S was added to a series of sodium clay sols. These were percolated through beds of 20-40 mesh sand, and any changes

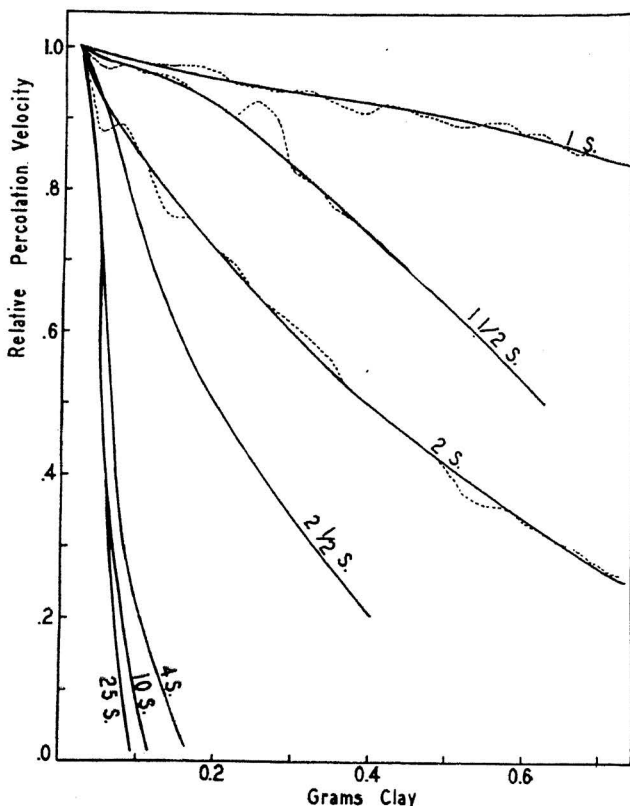


FIG. 6.—Effect of Addition of CaCl_2 on Pan Formation by Na-clay Sol.

in the rate of flow were observed. The results are shown in Figure 6. Here again, with salt concentrations below the flocculation value, the rate of pan formation was decreased slightly, and with concentrations above the flocculation value the rate of pan formation was increased. At the flocculation value, pan formation was

only slightly more rapid than it was with NaCl, but when the concentrations of CaCl_2 was increased above the flocculation value, pan formation became very much more rapid than it did when high concentrations of NaCl were added. After a concentration of 4 S CaCl_2 was reached, there was but a slight change in the rate of pan formation with increases in salt concentrations up to 25 S.

Effect of $\text{La}(\text{NO}_3)_3$.—To a series of sodium clay sols, lanthanum nitrate was added in concentrations of $\frac{1}{2}$, 1, and 2 S. These sols were passed through beds of 20-40 mesh sand, and

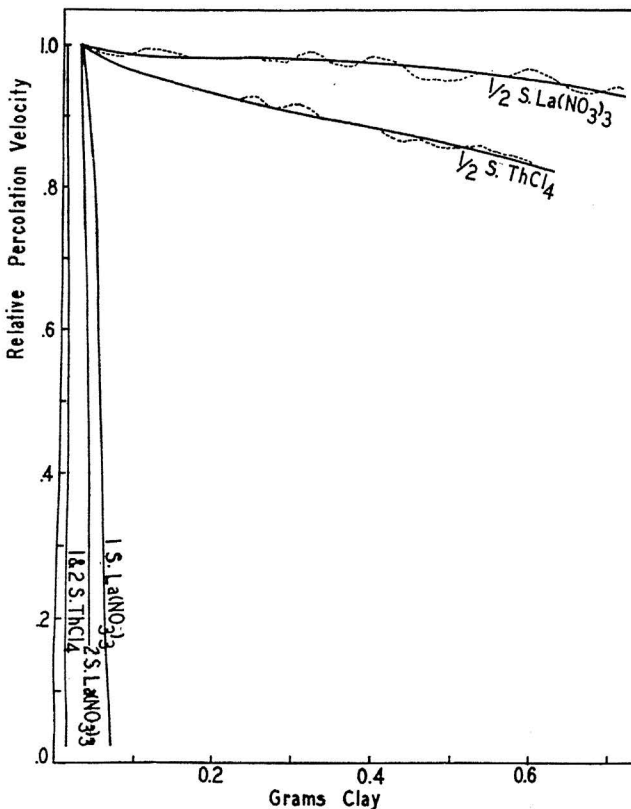


FIG 7.—Effect of Addition of $\text{La}(\text{NO}_3)_3$ and ThCl_4 on Pan Formation by a Na-clay Sol.

changes in the rate of percolation noted. The results are shown in Figure 7. Once more the addition of salt in concentrations below the flocculation value decreased the rate of pan formation, while concentrations at or above the flocculation value increased pan

formation. The flocculated sols formed pans much more rapidly than did the sols coagulated with sodium or calcium.

Effect of ThCl_4 .— ThCl_4 was added to sodium clay in concentrations of $\frac{1}{2}$, 1, and 2 S. Changes in the rate of percolation of these sols through beds of 20-40 mesh sand were noted. The results are shown in Figure 8. With the tetra-valent cation, concentrations both below and above the flocculation value have increased the rate of pan formation, and it is very rapid at about this value.

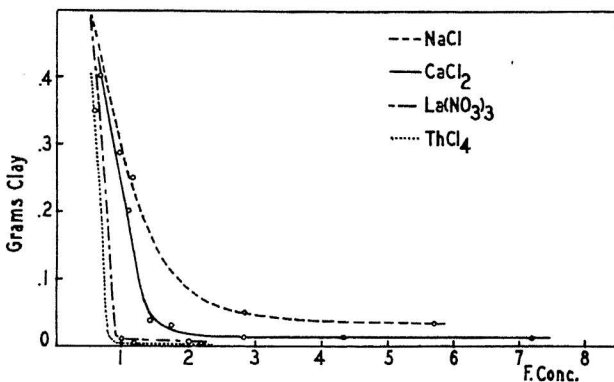


FIG. 8.—Grams of Clay Required to Reduce Percolation Velocity by 10% as a Function of Electrolyte Concentration.

General Discussion of the Role of Electrolytes

The results of these studies on the effect of electrolytes on pan formation have been summarized in Figures 8, 9, and 10. In Figure 8 the grams of clay needed to reduce the initial percolation velocity by 10% have been plotted against the salt concentration, expressed in terms of flocculation values. At the flocculation value, the effectiveness of the ions in pan formation is in the order $\text{Th} > \text{La} > \text{Ca} > \text{Na}$. The differences although becoming less pronounced persist at high concentrations.

In Figure 9, the per cent reduction of the initial percolation velocity by 0.021 gms. of clay is plotted against the S concentration of electrolytes. This figure brings out more clearly than words the tremendous differences in the effectiveness of the cations in pan formation. Traces of the polyvalent ions have much more influence than high concentrations of sodium.

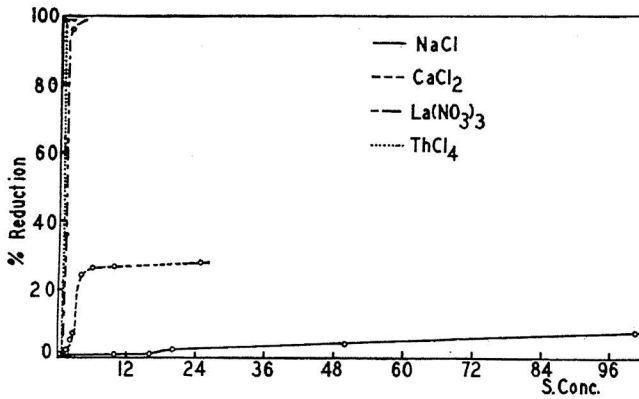


FIG. 9.—Reduction of Initial Percolation Velocity by 0.021 gms. Clay, as a Function of Electrolyte Concentration.

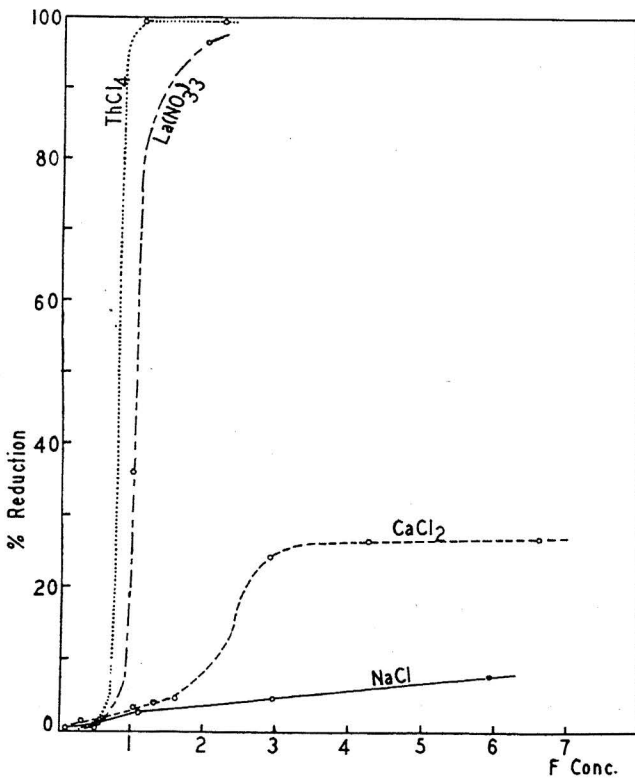


FIG. 10.—Reduction of Initial Percolation Velocity by 0.021 gms. of Clay, as a Function of Flocculation Concentration

Figure 10 shows the per cent reduction of the initial percolation velocity by 0.021 grams of clay, plotted against the concentration of electrolyte expressed in terms of flocculation values. In some ways this is a more accurate way of comparing the ions of different charge, and it will be observed that the differences in the effectiveness of the various ions are very large.

In every case the flocculation of the clay brings about an increase in the rate of pan formation. However, if the flocculation value were a measure of the effect of the various ions on particle size, and if particle size were alone responsible for pan formation, one would not expect any difference in the behavior of the various ions at or above the flocculation value. It is evident, though, that there are large differences in the effectiveness of these ions, and that the pan forming power varies directly with the charge of the ion. Furthermore, these differences persist at high electrolyte concentrations. There are several possible explanations. First, at the flocculation point the size of the aggregate formed may depend on the charge of the coagulating ion, and ions with the greatest charge may form the largest floccules. Secondly, it may be that the stability of the floccules increases with the charge on the ion. A third possibility is that the sign of the charge on the floccule is important. Putnam clay and bentonite clay⁵ become positive upon addition of Al and Th salts.

While the results show that relatively high concentrations of Ca and Na are required to bring about a rapid pan formation, it must be remembered that these experiments were performed with coarse sand. The pores in such a system are large, and high concentrations of electrolyte are needed to form large enough aggregate to close these pores. It would seem reasonable to assume that the concentration of electrolyte needed to produce a stable aggregate large enough to close a pore would depend somewhat upon the size of the pore. The smaller the pore, the lower the concentration of electrolyte that would be required. It seems fairly certain that in a soil with a silty texture, the change in the rate of pan formation brought about by flocculation would be very great, even in a system with mono-valent ions.

Effect of Removing Coagulating Salts.—Pans formed under the influence of electrolytes do not persist when the electrolytes are removed. If distilled water is passed through a pan formed with clay coagulated by CaCl_2 , for example, as the calcium is leached

out the clay disperses, and the rate of flow of the water increases. It approaches the initial value exponentially.

Significance of Hydration in Pan Formation

The differences in rate of pan formation by the sodium and calcium floccules might be caused by the high hydration of the sodium clay. The water carried by Na-clay particles might cause the floccules to be relatively unstable and allow them to break up into very small aggregates during passage through the sand. The attempt, therefore, was made to dehydrate the aggregates with alcohol to determine the effect on the rate of pan formation.

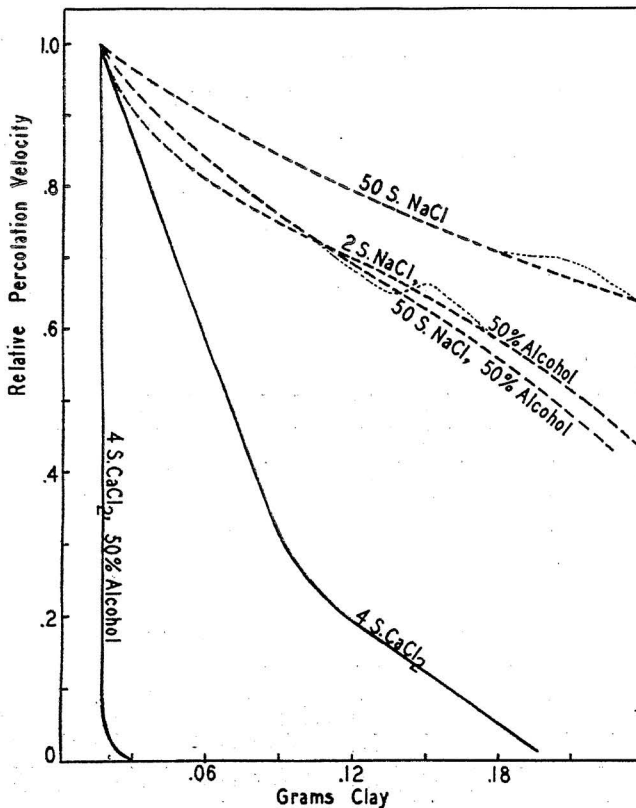


FIG. 11.—Effect of Dehydration by Alcohol on Pan Formation.

NaCl and CaCl₂ were added to systems of sodium clay in amounts equal to 2.86 times the flocculation value, which is equivalent to 50 S NaCl and 4 S CaCl₂. Alcohol was added to these systems to give them a final concentration of 0.3% clay in 50%

alcohol solution. The sols were then passed through beds of 20-40 mesh sand, and the changes in the rate of percolation observed. A sample of Na-clay with 2 S NaCl was included for comparison. The results are shown in Figure 11. Curves for similar sols without alcohol are included for comparison.

In every case the alcohol increased the rate of pan formation, but the Na ion was still not as efficient as the Ca ion in causing rapid pan formation. That the difference should persist is not surprising, because the sodium clay holds water very strongly, and probably was not as highly dehydrated as was the calcium floccule.

The changes brought about by the alcohol indicate clearly that hydration of the floccules is a factor in pan formation, in that it diminishes the rate. It is not improbable that the differences in hydration will explain, at least in part, the observed behavior of the Ca and Na aggregates.

Role of Humus in Pan Formation

When a highly hydrated type of colloid (emulsoid) is added to a suspensoid sol, such as gold or certain clays, there is a distinct tendency for the former to impart its properties to the latter. Emulsoids, not being readily coagulated by electrolytes, give stability to a suspensoid sol in the presence of amounts of salts above the flocculation value. This phenomenon is known as protective action. The organic colloids of the soil are emulsoids, and have a protective action on the inorganic colloids. To study this effect on pan formation, natural humus from a sample of muck was added to systems of sodium clay at the rates of .017 gm. and .033 gm. per gram of clay. Two times the symmetry concentration of CaCl_2 was added to each, and they were passed through beds of 20-40 mesh sand. Changes in the rate of percolation were observed, and the results are given in Figure 12. The samples with no humus and .017 grams of humus per gram of clay showed flocculation, but the other did not.

The results demonstrate that under the conditions of the experiment, the presence of humus retards pan formation. This is undoubtedly due to the protective action of these organic colloids:

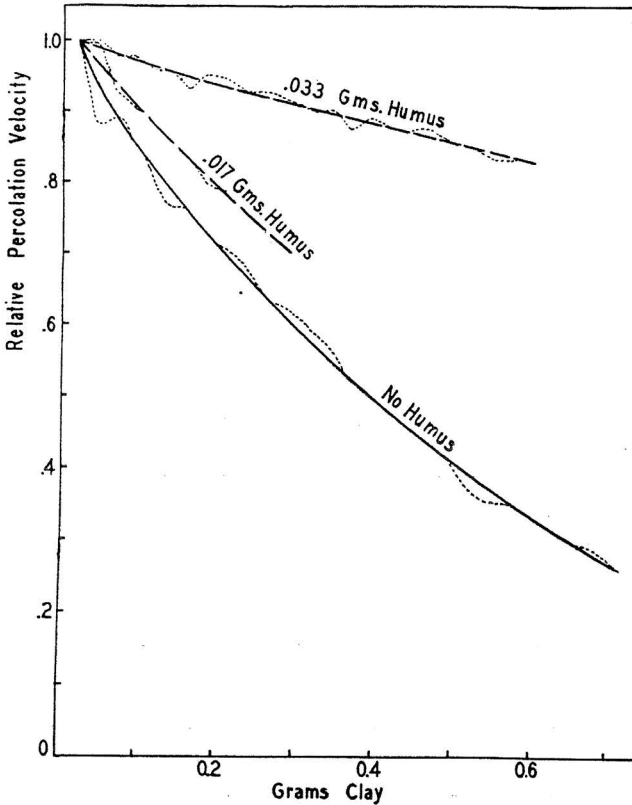


FIG. 12.—Effect on Humus on Pan Formation by a Flocculated Clay.

Role of Positive Colloids

In view of the presence of free iron and aluminum oxides or hydroxides in most soils, and in view of the tendency of these metals to form positive colloids, it was considered important to determine what role, if any, they might have in pan formation. Their frequent segregation and accumulation in claypans and in other B horizons raises the serious question of whether or not they have been active agents in the formation of these layers of accumulation.

A sol of hydrated iron oxide was prepared by hydrolysis of ferric chloride. The excess acid was neutralized with NH_4OH , and the sol was dialyzed to remove the electrolytes. The particles of this sol were small enough that on passing them through a bed

of 20-40 mesh sand, no change in the rate of percolation was observed. However, it was noticed that the sand was coated with the iron, and that this coating could not be washed off with water. This raised the question of whether or not this iron would hold clay in a similar way.

A burette was made up containing 10 cc. of fine glass beads. Ten cc. of a 0.3% Fe-sol were passed through, and the iron not held on the glass bead surface was washed out with five successive washings of 10 cc. of water. Then 10 cc. of 0.3% Na-clay were passed through this bed, and the system was rinsed with water. Iron and clay sols were alternately run through the beads in this manner, washing carefully with water each time to prevent any mixing of the free colloids, because such a mixture would flocculate out, and would tend to form a pan. The rate of flow of the sols and of the water was carefully determined.

To determine the behavior of a pure iron sol in glass beads, another burette was made up, and, after 10 cc. of the iron sol had been passed through and the beads washed, more iron was added. Iron and water were passed through the bed alternately, but no clay was added. The rate of percolation of the sol and the water was measured.

In a similar way, clay and water were alternately passed through a third bed of beads, and the rates of flow observed. Finally, equal quantities of the clay and iron sols were mixed, and the flocculated sol passed through a fourth bed of beads.

The results of these experiments are shown in Figure 13. The velocities reported are those of the wash water. When the clay sol or the iron sol alternated with water, there was no significant change in the rate of percolation, indicating that these sols themselves had no tendency to form a pan. When iron and water alternated with clay and water, a pan was formed in the following manner. After the positive iron sol had passed over the beads, a thin coat of iron was held tenaciously. When the clay came in contact with the iron, the positive iron held a thin layer of the negative clay which could not be removed by washing. The clay was able to hold a second coating of iron, while the latter in turn attracted more clay, and so on until the pores were materially reduced in size.

The charge on the soil skeleton always had the same sign as did the charge on the colloid which had been passed through last. The sign of the charge was determined by electroendosmotic flow.

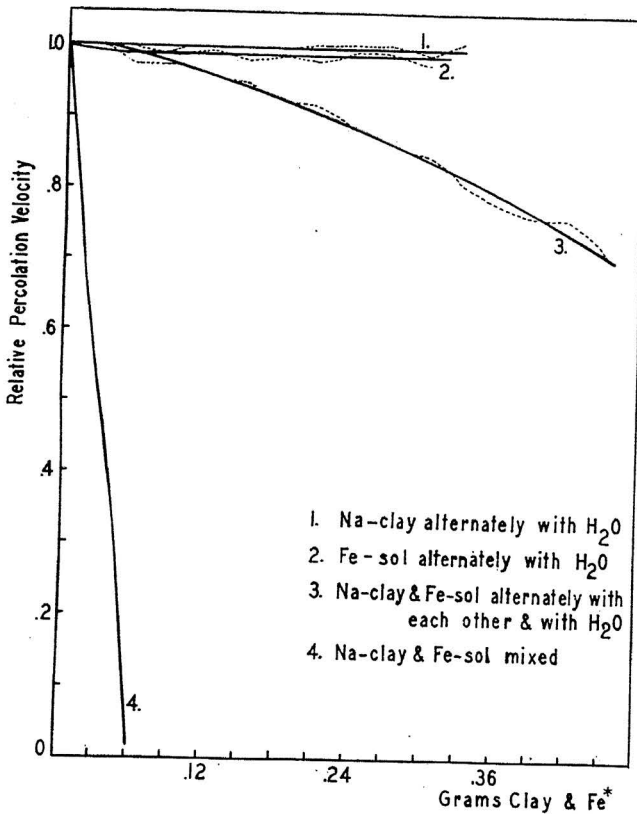


FIG. 13.—Effect of Positive Fe-sol on Pan Formation by a Na-clay
*(Fe(OH)₃xH₂O).

The original charge on the soil skeleton was negative, but after washing with an iron sol and with water, the charge was positive. Washing with a clay sol again made the skeleton negative, and it was found that the charge could be reversed as often as desired. It is very difficult to see how the sign of the charge could have been reversed unless alternate layers of clay and iron were held on the surface of the soil skeleton.

These experiments show that it is possible to form a pan in the absence of flocculated aggregates. Nor is it necessary for pan formation that the moving particles be larger than the pores, since the colloids can be held on the walls of the pores by surface forces.

The Flocculating Power of Ground Waters

In the humid portions of the Mississippi Valley, the heavy claypans are similar to those of the chernozem soils of Nebraska, as reported by Brown, Rice and Byers³, in that there is very little chemical fractionation of the colloids in the subsoil. Since the heavy chernozem subsoils have been attributed in part to the presence of calcium salts, and since Norton and Smith⁸ have shown that the heavy subsoils of Illinois form only under conditions of poor drainage, it was thought important to determine whether the ground waters, even in the absence of a lime horizon, contained enough electrolytes to flocculate a clay sol.

The attempt was made to disperse some Putnam subsoil in four samples of ground water. One was taken from a five-foot hole bored in a Putnam area near Mexico, Mo. Another sample was taken from a shallow dug well in a Putnam area near Beckemeyer, Ill. A third sample was from a shallow well in an Edina area in Shelby Co., Ill. The fourth sample was from a deep well at Columbia, Mo. Fifteen cc. of each of these water samples were placed in small test tubes with 2 grams of air dry Putnam subsoil and shaken for $\frac{1}{2}$ hour in a reciprocal shaker. They were then placed in a water bath at 30 degrees Centigrade. Clay thus dispersed in distilled water does not flocculate, but every sample, dispersed in ground water flocculated completely within a few hours. Experiments with the ground water from Mexico, Mo., showed its flocculating power to be equivalent to that of a $1/250$ N. CaCl_2 solution.

This experiment shows that ground water samples from typical claypan areas do contain a sufficient concentration of electrolyte to flocculate a clay.

APPLICATION OF EXPERIMENTAL RESULTS TO THE THEORY OF CLAYPAN FORMATION

Process of Formation in an Ideal Soil

In applying the results of these studies to natural claypans, it will be of help to first visualize pan formation in an ideal soil. Such a soil, according to Jenny⁶, is described as follows: The parent material is composed of uniform spherical particles of fine sand size. The chemical composition is that of an average of igneous rocks. The soil has a level or gently undulating topography, and

good underdrainage. The development of a claypan in this soil will be considered as it would take place under two sets of climatic conditions, one a temperate, semi-humid climate, and the other temperate and humid.

Under *semi-humid conditions*, the following events would be expected to take place. The water in the soil attacks the primary minerals, liberating the bases as hydroxides or carbonates, and forming secondary alumino-silicate clay minerals, together with small amounts of iron and aluminum oxides or hydroxides. The rain water percolating downward through the soil would remove bases from the surface, but being limited in amount would not be able to carry them out of the solum. The salts, therefore, would accumulate in the lower horizons (e. g. Carbonate horizon). When the electrolyte concentration in the surface becomes sufficiently low, the clay there will tend to disperse and move downward with the rain water until it reaches a zone where the salts have accumulated sufficiently to cause flocculation. The clay aggregates formed will be caught in the fine pores and thus begin the formation of a claypan.

Additional clay moving down through the soil would also be flocculated, or, finding the pore size restricted in the subsoil, would be filtered out. The clay in the various horizons of this ideal soil would be expected to have approximately the same chemical composition. It is very likely that the process just described represents essentially the mode of pan formation in chernozem soils as described by Brown, Rice, and Byers³.

In a *humid region*, the original parent material would not be expected to form a claypan in the same way. Continued leaching through the profile removes the flocculating electrolytes formed by hydrolysis, and the alumino silicate clays would tend to move out of the solum with the drainage waters, were it not for the fact that humid weathering produces both negative silicates and positive iron and aluminum colloids. Positive and negative colloids moving downward could flocculate each other and be filtered out, or they might be caught and held on the walls of the negative sand pores by the same forces which caused a pan to form when the glass beads were alternately washed with iron and clay sols.

If the size of the pores is gradually reduced until an effective filter is formed, any additional migrating colloids would be caught and held by sieve action. The process of pan formation just de-

scribed would result in the formation of a claypan high in sesquioxides, and the chemical composition of the clay in the different horizons would vary.

The two modes of pan formation just outlined apply to ideal soils, but nature seldom provides such simple systems. The heavy claypans found under field conditions have undoubtedly formed, for the most part, by modifications and combinations of the two ideal processes.

Application to Natural Claypans

On the basis of the experiments performed, the genesis of the heavy claypans in the poorly drained soils of Missouri, Illinois and adjacent states may be visualized as follows. The parent material was almost universally calcareous. As the rain waters percolated through the soil, the carbonates were slowly removed, and clay minerals were formed. These became dispersed in the surface before the carbonates were leached to any great depth and moved downward until they came in contact with the carbonates. In this zone they were flocculated and filtered out, filling the pores. Further leaching would reduce the electrolyte concentration below the flocculation value, and the clay would tend to disperse again, because the coagulation is partially reversible. Under these conditions, the clay would be carried out of the soil if the subjacent material were sufficiently porous. However, under conditions of poor drainage, the pores below the claypan are filled by colloidal clay, formed in place and held by the electrolytes of the stagnant ground water, so that any removal of clay is impossible.

If this is the process of claypan formation in Illinois, it explains the observation of Norton and Smith⁶ that, in Illinois, claypans form only under conditions of poor drainage. Furthermore, the contention of Leighton and MacClintock⁷ that when drainage is improved, the clay tends to be lost from a gumbotil is easily understood. Only in the absence of flocculating groundwater can the clay move out of the soil. The observation of Allen¹ that in drifts weathered under conditions of good drainage the clay minerals tend to migrate into the lower horizons lends weight to this interpretation.

It is, however, not impossible that the free iron and aluminum oxides or hydroxides have played a part in the formation of the claypans in the humid portions of this country. The evidence of chemical fractionation of the colloids in the different horizons of

the Piedmont Plateau soils as reported by Byers and Anderson⁴ would support this view.

Correlated field and laboratory studies are needed before the relative importance of the various factors in pan formation can be determined for the natural claypans.

SUMMARY

1. A method of passing clay through beds of sand has been devised which permits a quantitative measurement of pan formation.

2. Putnam clay, if sufficiently dispersed, will not form a pan in quartz sand.

3. Flocculation of a sol by electrolytes or oppositely charged colloids causes a pan to form.

4. The rate of pan formation by a flocculated clay rapidly increases with the valence of the flocculating ion.

5. The presence of protective humus decreases pan formation in so far as it decreases flocculation.

6. A pan may be formed in the absence of flocculated aggregates by building up alternate layers of positive iron and negative clay sols on the walls of the pores.

7. The ground waters from typical claypan areas in Missouri and Illinois contain sufficient electrolytes to flocculate a clay sol.

8. A theoretical discussion of claypan formation is included.

LITERATURE CITED

1. Allen, V. T. (1930) *Petrographic Studies Bearing on the Genesis and Morphology of Illinois Soils*. 2nd. Int. Cong. of Soil Science, Vol. 5, pp. 113-117.
2. Bray, R. H. (1934) *A Chemical Study of Soil Development in the Peorian Loess Region of Illinois*. Amer. Soil Survey Assn. Bul. 15.
3. Brown, I. C., Rice, T. D., Byers, H. G. (1933) *A Study of Claypan Soils* U. S. D. A. Tech. Bul. 339.
4. Byers, H. G., Anderson, M. S. (1932) *The Composition of Soil Colloids in Relation to Soil Classification*. Jour. Phys. Chem. Vol. XXXV, pp. 348-366.
5. Freundlich, H., Schmidt, O., Lindau, G. (1932) *Über die Thixotropie von Bentonit-Suspensionen* Kolloidchemische Beihefte 36:43-81.
6. Jenny, Hans. Personal communication.
7. Leighton, M. M., MacClintock, P. (1930) *Geological Aspects of the Genesis and Morphology of Illinois Soils*. 2nd. Int. Cong. of Soil Science, Vol. 5, pp. 97-111.
8. Norton, E. A., Smith, R. S. (1930) *The Influence of Topography on the Soil Profile*. Jour. Am. Soc. Agron. 22:151-162.
9. Norton, E. A., Winters, E. (1930) *Pedological Aspects of the Genesis and Morphology of Illinois Soils*. 2nd. Int. Cong. of Soil Science, Vol. 5, pp. 91-96.
10. Prescott, J. A. (1931) *The Soils of Australia in Relation to Vegetation and Climate*. Commonwealth of Australia Council for Scientific and Industrial Research, Bulletin 52.
11. Russell, J. C., Engle, E. G. (1925) *Soil Horizons in the Central Prairies*. Am. Soil Survey Assn. Bul. VI. pp. 1-18.
12. Shantz, H. L., Marbut, C. F. (1923) *The Vegetation and Soils of Africa*. Am. Geographical Soc. Research Series No. 13.
13. Shaw, C. F. (1930) *A Preliminary Field Study of the Soils of China*. 2nd. Int. Cong. of Soil Science, Vol. 5, pp. 399-424.
14. Slichter, C. S. (1898) *A Theoretical Investigation of the Motion of Ground Waters*. 19th. Ann. Rpt. U. S. Geol. Survey Part II, 301.
15. Smith, R. S., Norton, E. A. (1929) *The Structural Anatomy of the Soil Profile*. Am. Soil Survey Assn. Bul. X. pp. 35-37.
16. (1927) Report of Committee on Terminology Amer. Soil Survey Assn. Bul. VIII pp. 66-98.