

LIQUID LIMIT AND ASSOCIATED SOIL
" PROPERTIES AS INFLUENCED BY HYDROCHLORIC,
SULFURIC, AND PHOSPHORIC ACIDS

by

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III. INTRODUCTION

The liquid limit test is one of the most important and frequently performed laboratory tests employed in soil mechanics. Although it is empirical in nature, it is very useful as an index to the significant properties of soils. There is thought to be a linear relationship between liquid limit and the coefficient of consolidation (Hough, 1957). If the liquid limit of a soil increases with the plasticity index¹ remaining relatively constant, its compressibility and permeability will increase, whereas the dry strength will decrease (Spangler, 1951). Some important uses of the liquid limit are the classification of fine-grained soils, the testing of uniformity of soil deposits, and the description and identification of soils.

Lambe (1953) suggests that the reason liquid limit correlates so well with many engineering properties of a soil is because it reflects the basic physical-chemical environment of soil particles; specifically, the nature and amount of water adsorbed by a soil. Because of the realization that soil chemistry is intimately associated with soil physical behavior (Michaels, 1959, Quirk and Theng, 1960, Taylor, 1959, Davidson and Demirel, 1960, Olson and Mitranovas, 1960), many chemical factors have been studied

¹Plasticity index is the liquid limit minus the plastic limit.

in relation to their influence on the soil-water system (Hsi and Clifton, 1960, Lutz and Kemper, 1959). One technique employed for such study is the determination of liquid limit after suitable chemical alterations of the soil (White, 1955). However, most of this work has dealt with the influence of cations on adsorbed soil water, with relatively little attention given to anions. Several workers (Thomas, 1960, Schofield and Samson, 1953, Krebs, Thomas, and Moore, 1960) have suggested that anions have a substantial effect on the engineering properties of some soils, particularly the acid, kaolinitic, clayey soils common in the southeastern United States. Relatively little work has been done on such soils despite their abundance, possibly because of the regional character of their distribution.

The purpose of this study is to investigate the effect of anions, in the form of acids, on the physical character of an acid kaolinitic soil, employing the technique of liquid limit determination. The results are compared to those found for contrasting soil types.

IV. THE LIQUID LIMIT TEST

In 1911 Albert Atterberg, a Swedish soil scientist, devised the liquid limit test to measure the plasticity of soils. The test was performed after pulverizing dried soil and passing it through a sieve having openings of 0.2 mm. Approximately five grams of the sieved soil was mixed with enough water to produce a slurry, which was then placed in a round-bottomed porcelain dish and spread out with a spatula so that the soil layer was slightly less than one centimeter in thickness. The layer was divided into two parts with a spatula and the dish vigorously and repeatedly hit against the palm of the hand. Additional pulverized soil was added to the slurry until, due to the shocks, the soil flowed together only in the lowest part of the groove. The water content, which was considered a measure of plasticity, was determined when the soil flowed together to a depth of one half the original thickness of the soil layer.

In order to eliminate as much personal element in the liquid limit determination as possible, Arthur Casagrande developed a liquid limit device in 1932. The design of this device has remained essentially unchanged to this date. When using this device, the liquid limit is considered to be the water content of a soil when twenty-five drops of one centimeter of a standard cup closes the bottom of an inscribed groove in the soil along a distance of $\frac{1}{2}$ inch. It was intended

that the liquid limit value, as determined by the Casagrande device, be identical to that value obtained when employing the Atterberg technique.

Casagrande also observed that a plot of water content versus the logarithm of the number of drops, called blows, of the cup usually resulted in a straight line if the number of drops was approximately between eight and forty. This line is known as a flow curve. Its definition by plotting log blows versus water content for three or four trials allows one to find the water content, or liquid limit, at twenty-five blows.

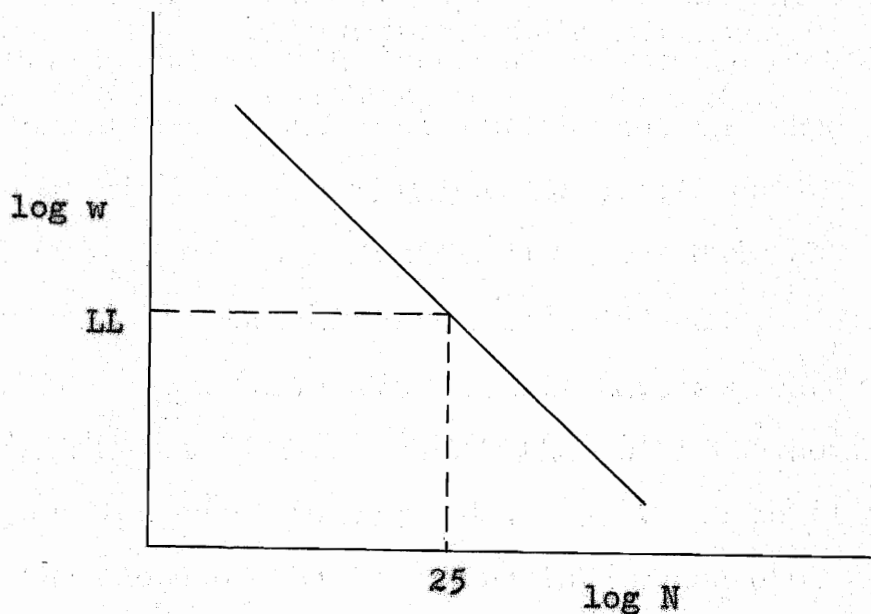
The number of blows required to close the groove is a relative measure of the shearing resistance of the soil at the corresponding water content; hence, the shearing resistance of all soils must be equal at the liquid limit (Casagrande, 1939). If two soils have identical liquid and plastic limits, but different flow indices¹, the soil with the milder flow curve usually will have a greater shearing strength at the plastic limit² than will the soil with the steeper flow curve (Casagrande, 1939). White (1955) suggests that the slope of the flow line is a measure of the

¹Flow index is the slope of the flow curve.

²The plastic limit is considered the water content below which the soil no longer behaves as a plastic material. A standard test for this procedure has also been worked out by Atterberg and Casagrande.

thixotropy of a soil (i.e. the steeper the slope, the greater the propensity of the soil to set into a gel.).

Casagrande stated, according to Eden (1960), that soils from a common geological origin might have flow curves of equal slope if the water content and number of blows were both plotted on a logarithmic scale. As a result of this statement, the U.S. Waterways Experiment Station at Vicksburg conducted 767 tests on soils from the Mississippi Valley in 1949 and concluded that all soils, regardless of their geological origin, could be treated as having constant flow indices. Hence, the following equation was proposed:



Assuming the conditions for the range of N (see Table 1) are such that a $\log w - \log N$ plot results in a straight line, then

$$y = mx + b$$

and $\log w = -m \log N + b.$

But,

$$m = \text{slope} = \tan \beta = \frac{\Delta \log w}{\Delta \log N};$$

therefore,

$$\log w = - \tan \beta \log N + b.$$

If the $\log w$ axis is shifted to the point where $\log N = 25$, then $b = \log LL$ and the equation becomes

$$\log w = - \tan \beta [\log N - \log 25] + \log LL$$

$$\log LL = \log w + \tan \beta \log \left(\frac{N}{25}\right)$$

$$\log LL = \log w \left(\frac{N}{25}\right)^{\tan \beta}$$

$$LL = w \left(\frac{N}{25}\right)^{\tan \beta}$$

where

LL = the liquid limit of the soil in percent,

w = water content, in percent corresponding to
N blows,

N = number of blows

$\tan \beta$ = slope of the flow line on a $\log w$ vs. $\log N$
plot.

Assuming that the flow curves for all soils are constant, as theorized by Casagrande and concluded by the U.S. Waterways Experiment Station, it is apparent from the above equation that only one point, as opposed to three or four,

need be determined to evaluate the liquid limit of a soil. The value of $\tan \beta$ and the range of N will, of course, vary depending upon the investigator. The results of several investigations are tabulated in Table 1.

The one-point method is particularly advantageous when a considerable number of liquid limit values must be determined. It also has the distinction of being faster than the three-point method, and is nearly as accurate. However, Bauer (1960) does not recommend the one-point method when the liquid limit is greater than 120 percent.

TABLE 1. Some Results of Several Investigations on the One-point Liquid Limit Determination

Investigator	Number of Tests and Origin of Soil	$\tan \beta$	Range of N	Conditions for Range of N
Waterways Experiment Station	767 Mississippi Valley	0.121	15 - 41 20 - 31	Classification Purposes Quantitative Correlation Purposes
Olmstead and Johnston	759 Various Points in U.S.A.	0.135	22 - 28	-----
Norman	504 Great Britain	0.092	17 - 35 20 - 30	Liquid Limit < 50 Liquid Limit Between 50 and 120
Eden	484 Canada	0.108	15 - 35	-----

V. ADSORBED SOIL WATER AND IONS

It has become customary to think of the adsorbed film, swarm, or layer of ions and water associated with soil particles, as a "double-layer". The adsorbed water and ions and the charge on the particle surface are schematically divided into two layers. Lambe (1953) described the "double-layer" by stating that "the counterions¹ constitute the 'diffuse double-layer' of the colloid; the surface charge of the colloid is the other layer of the double-layer."

Although considerable exception has been taken to this concept (Anderson and Low, 1958, Thomas, personal communication, and Aylmore and Quirk, 1959), for purposes of clarity and succinctness Lambe's schematic model of adsorbed ions and water will be employed as a frame of reference for the treatment of the results in this study.

It has been shown (Michaels, 1957, and Schofield and Samson, 1953, 1954) that the edges of the clay particle can be positively charged, and that the flat surfaces (i.e. top and bottom) of the particle are covered with negative charges. Since the ratio of surface area (negatively charged) to edge area (positively charged) is very large, the clay particle has a net negative charge. According to Lambe (1953, 1958) the net negative charge on the clay particle

¹Counterions are the ions which swarm around each soil colloid.

will attract water and cations to the clay surface, since the net electrical charge of the soil-water system must be zero. Hence, the double-layer consists of the negative charges on the surface of the clay particle and the swarm of exchangeable cations and water surrounding the particle.

The force or potential that attracts the cations and water to the clay surface is electrical in nature and diminishes with increasing distance from the particle (see Fig. 1). The curve shown in Fig. 1 is an exponential function ($\psi \sim e^{-x}$) and varies with the valence and concentration of ions (Lambe, 1953). As the valence and concentration of ions are increased, the electric potential (ψ) will decrease thus moving the curve toward the clay particle. There is, however, no definite break or termination of this force, so that there is no absolute boundary between double-layer water and pore water¹.

Lambe (1953) suggests that clay particles are attracted to one another by long range electrical forces, commonly known as "van der Waals - London forces". These forces vary inversely as a large power of the interparticle spacing; accordingly, if the clay particles are relatively far apart

¹Pore water is unaffected by, and passes freely through the soil mass (i.e. water that is unattracted by the clay particle) (Lambe, 1953).

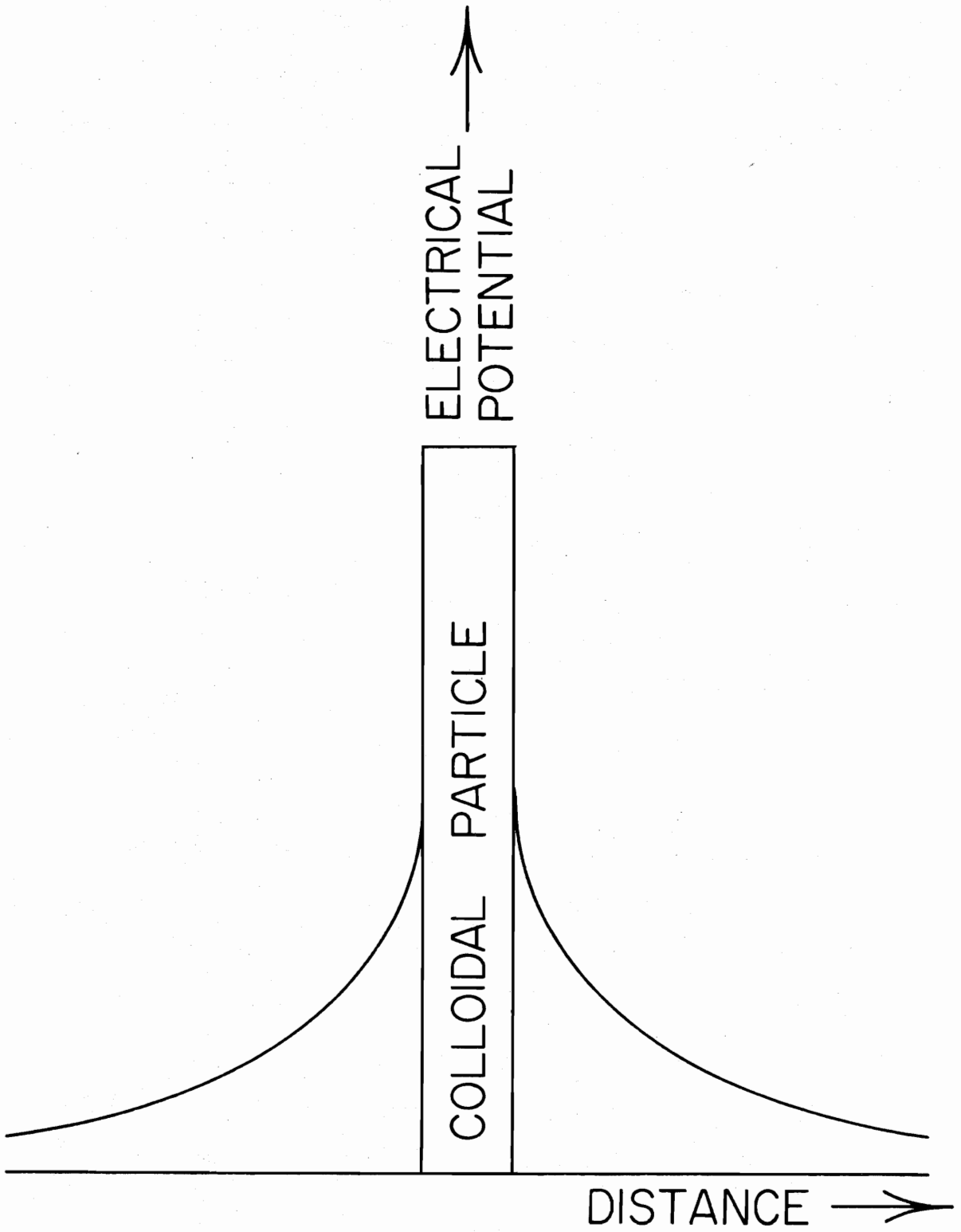


Fig. 1 Particle Potential (Lambe, 1953).

the van der Waals - London forces will be comparatively small and as the particles approach each other these forces will increase in magnitude at an accelerating rate. As two clay particles and their surrounding double-layers approach each other, a repulsive force will develop and increase as their double-layers penetrate. This repulsive force probably is an exponential function. Both the repulsive and attractive forces are shown schematically in Fig. 2.

Lambe (1953) claims that for very small interparticle distances the repulsive force will approach a finite value as the attractive force approaches infinity, and for increasing distances, the repulsive force will approach zero more rapidly than the attractive force. As a result, the net force or potential energy between two clay particles is attraction at relatively large and very small interparticle spacings, whereas an intermediate spacing probably results in repulsion. This phenomenon is shown schematically in Fig. 3.

From Fig. 3 it follows that a decrease in double-layer thickness will reduce the potential energy required to create an attraction or adherence between clay particles; such adherence is referred to as "flocculation". On the other hand, an increase in double-layer thickness would tend to increase the potential energy between particles, thus creating a tendency towards "dispersion"; a condition whereby the clay particles and their respective double-layers are relatively independent of one another. Thus,

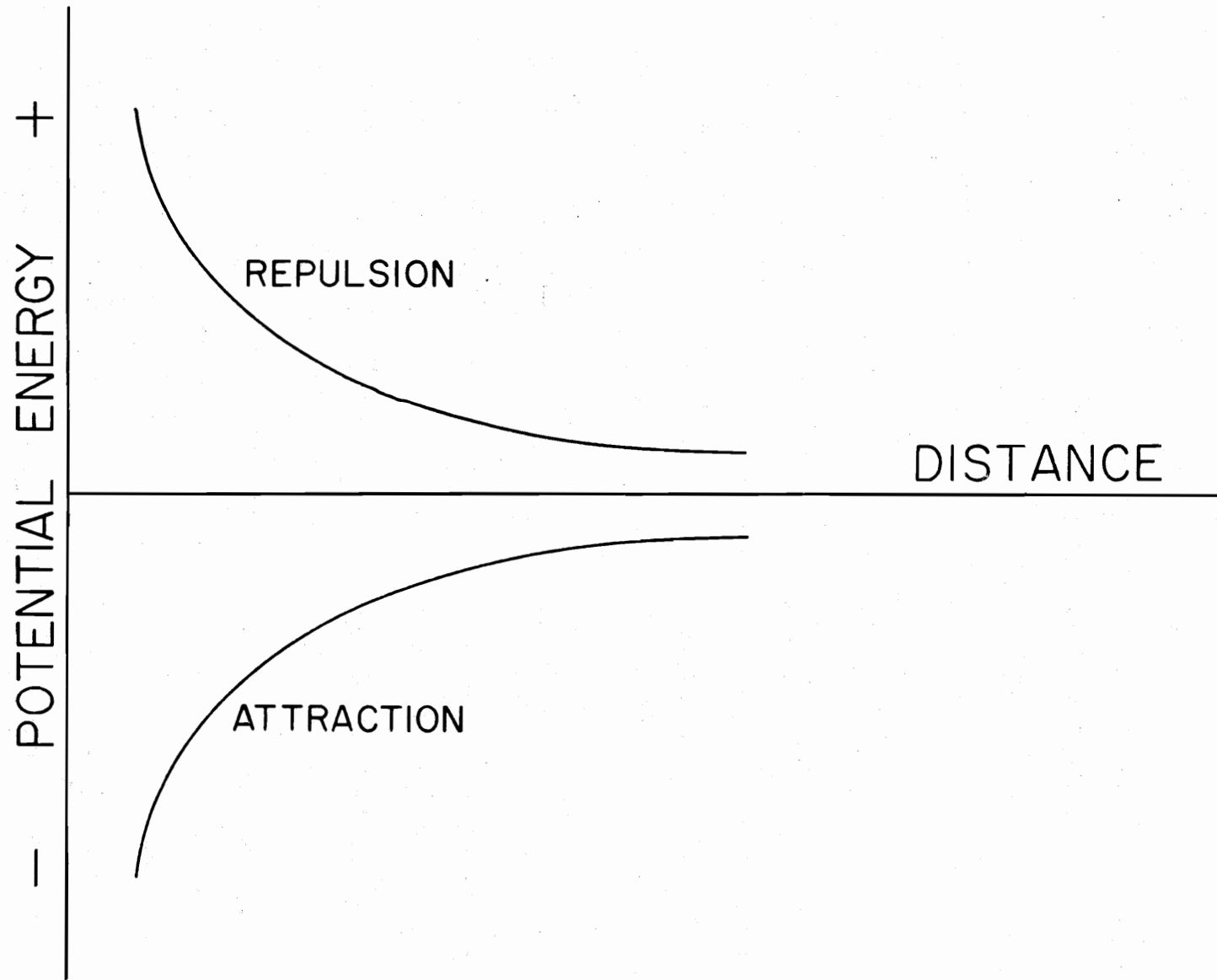


Fig. 2 Repulsive and Attractive Forces Between Clay Particles (Lambe, 1953).

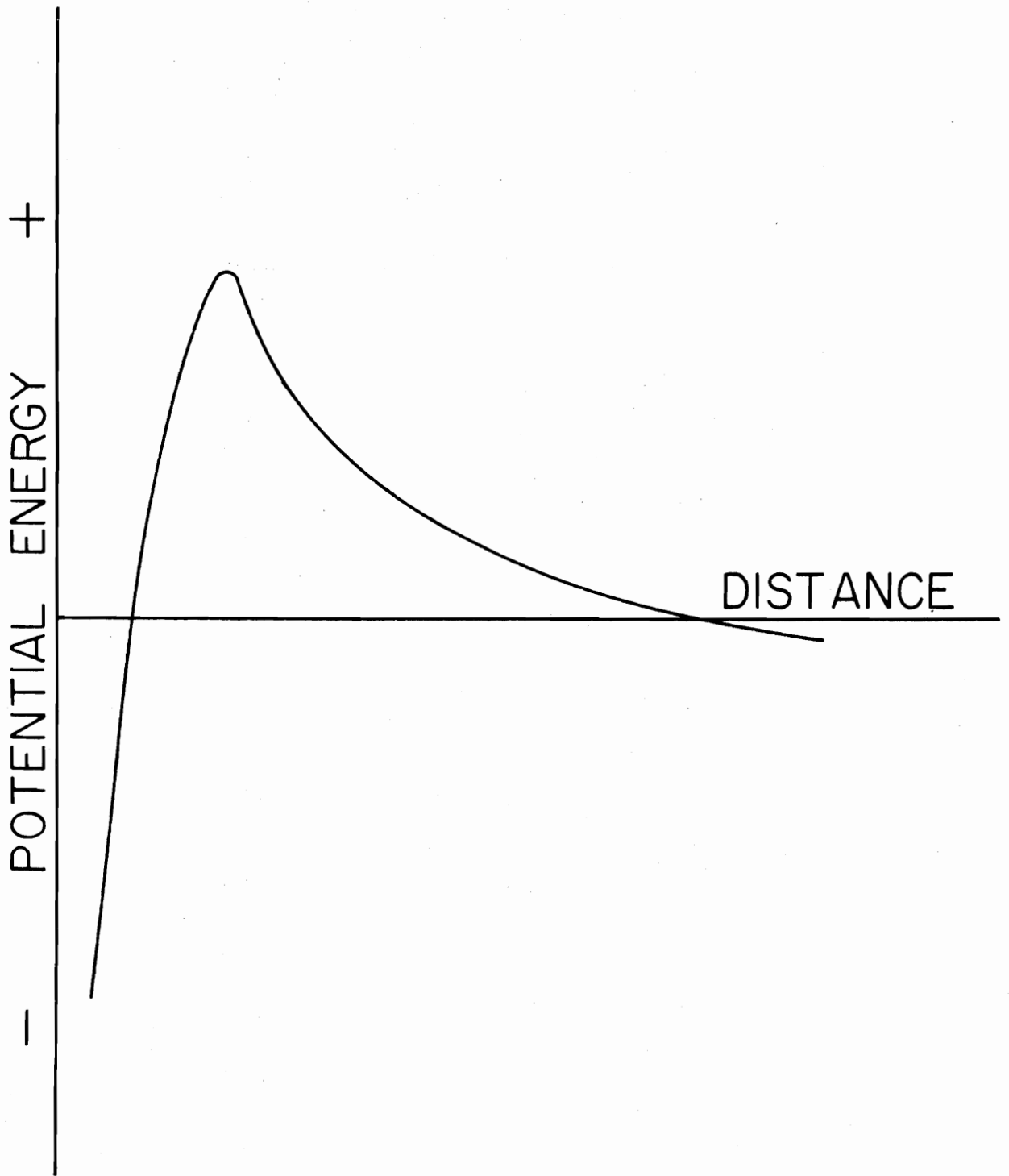


Fig. 3 Net Force or Potential Between Clay Particles (Lambe, 1953).

as the thickness of the double-layer is reduced, the tendency towards flocculation increases, whereas an increased double-layer thickness would promote dispersion. Fig. 4 illustrates the types of clay structure that result from flocculation¹ and dispersion.

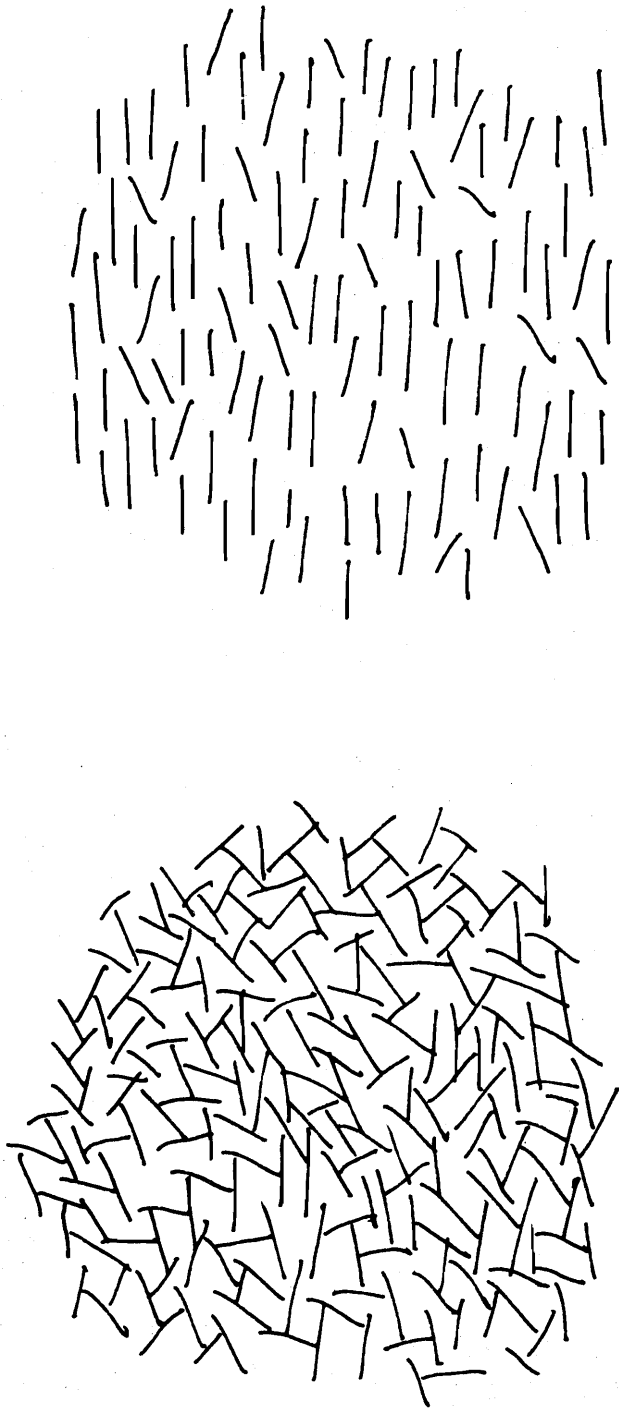
By inducing structural changes in the clay matrix, as shown in Fig. 4, double-layer thickness exerts considerable influence upon such soil properties as permeability, compressibility, and strength. Variations in the thickness of double-layer water might be obtained by altering some of the properties of the soil-water system. In terms of the Gouy-Chapman theory, flocculation can be encouraged (Lambe, 1958) by increasing:

1. Electrolyte concentration
2. Ion valence
3. Temperature

and decreasing:

1. Dielectric constant
2. Size of hydrated ion
3. pH
4. Anion adsorption.

¹Lambe (1958) recognizes that there are at least two types of flocculation as suggested by Schofield and Samson (1954). These are salt and non-salt types. To avoid the current controversy in recent literature regarding this phenomenon, no distinction will be made in this study.



FLOCCULATION DISPERSION

Fig. 4 Clay Structure

Ion valence, pH, and anion adsorption will be discussed, since they are particularly related to this study.

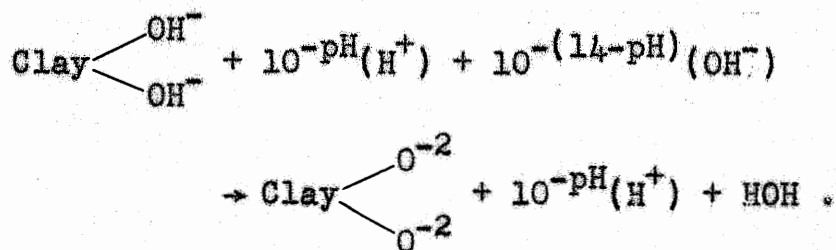
The influence of ion valence is especially important in determining the thickness of the double-layer. As mentioned previously, a clay particle has a net negative charge; thus cations are adsorbed into the double-layer to neutralize the system. The force or electric potential between the clay particle and cation is a function of the charge carried by the cation so that as the valence of the ion increases, the magnitude of force or potential between the clay particle and ion is magnified. For example, the force between Al^{+3} -ions and a clay surface is much greater than that for H^{+} -ions. Hence the Al^{+3} -ions, as opposed to H^{+} -ions, are held much more closely to the clay particle, resulting in a smaller double-layer. Also, if H^{+} -ions were adsorbed into the double-layer, three H^{+} -ions would be required to replace one Al^{+3} -ion in order to neutralize the clay-water system. This too may be a reason why the substitution of H^{+} -ions for Al^{+3} -ions increases the double-layer thickness.

Both of the above theories are controversial, some investigators favoring one and some the other. However, both are probably valid to at least some extent.

As regards pH, Lambe (1958) states: "The pH of the pore fluid affects the net negative charge on a soil particle by altering the extent of dissociation of OH groups on the edges

of the particle. High pH encourages the dissociation and increases the net charge, thus expanding the double-layer; low pH does the reverse. Lowering the pH, therefore, tends to cause flocculation and raising it tends to cause dispersion."

At a high pH, there is an abundance of OH⁻-ions (10^{-(14-pH)}) and a scarcity of H⁺-ions (10^{-pH}) contained in soil pore fluid. Therefore the OH⁻-ions of the pore fluid may tend to strip the H⁺-ions from the hydroxyl groups, which are attached to the edge of the clay particle. In effect, this will increase the net negative charge on the clay particle, thereby requiring additional adsorbed cations, an increase in double-layer thickness, and a tendency towards dispersion. This reaction is shown below:



If, on the other hand, the pH of the pore fluid is lowered, the H⁺-ions will be abundant and there will be a scarcity of OH⁻-ions. This condition may tend to discourage OH⁻ dissociation, thereby checking the decrease in net negative charge and the increase of double-layer thickness.

Again, this concept is hypothetical and although endorsed by Lambe (1958), is open to question.

"The adsorption of anions, especially polyvalent anions, increases the charge on the particles and thereby tends to cause dispersion." (Lambe, 1958). Lambe would lead one to believe that as anions are adsorbed by the clay particle, the net negative charge of the particle is increased and a greater number of cations are adsorbed into the double-layer so that its thickness increases.

In the above discussion, the thickness of the double-layer has been thought of in terms of cation adsorption, with the exception that there is a relatively small amount of anions adsorbed on the edges of the clay particle. The adsorption of the anions is thought to be due to the positive charge that occurs on the edge of the clay particle (Thiessen, 1942). However, such anion adsorption is very minor in magnitude compared to that of cations, since the ratio of positive to negative charge is very small for three-layer clay particles. This particular theoretical approach to the "double-layer theory" (i.e. adsorption of cations and exclusion of anions) is shown by the solid lines in Fig. 5.

Thomas (1960) found that the magnitude of anions adsorbed by acid, kaolinitic soils far exceeds that possible for the edges of the clay particle alone. His data suggest that in the case of such acid soils, anion adsorption is more like that shown by the dashed line of Fig. 5 rather than the hypothetical solid line of the "double-layer theory".

Clay
Surface

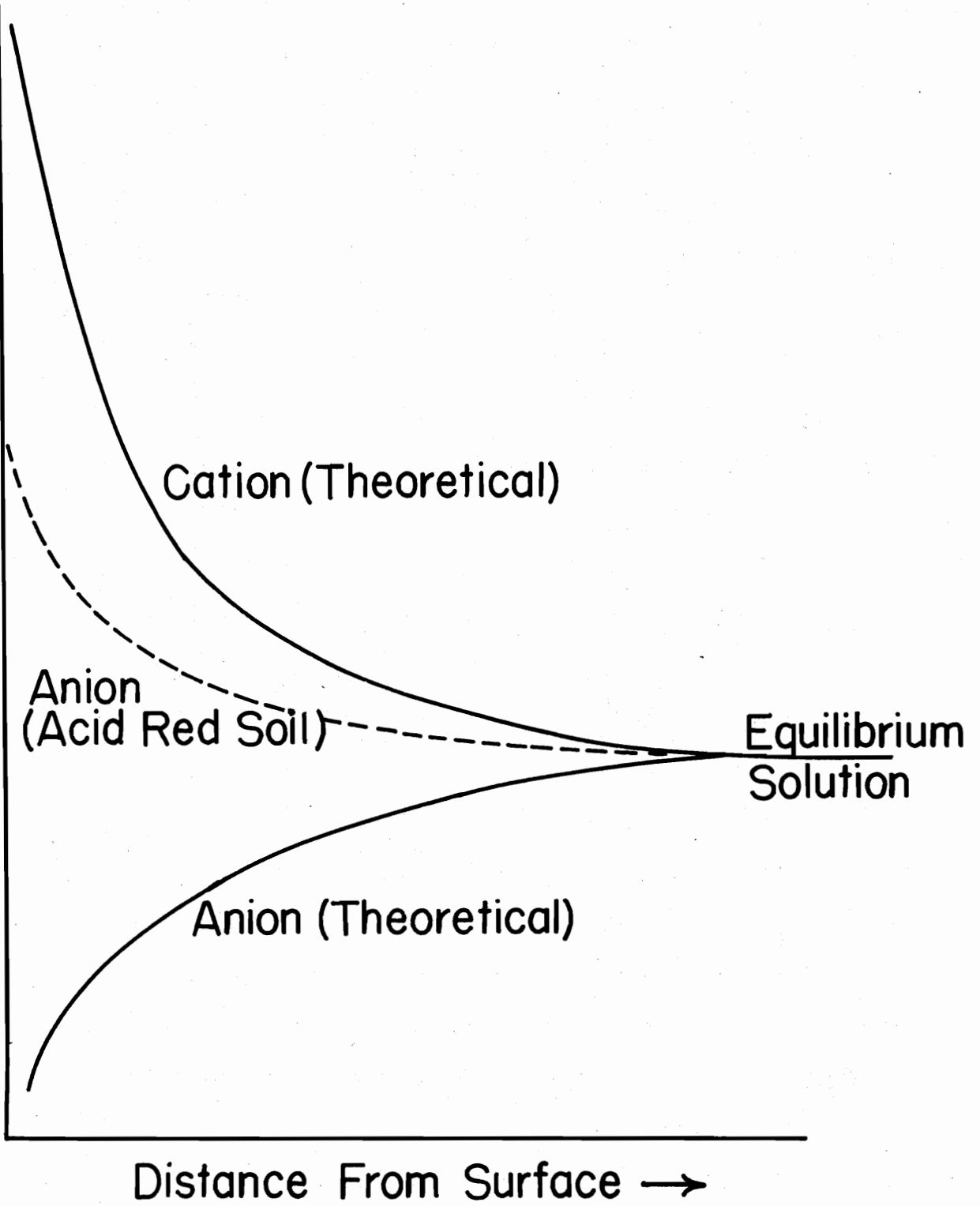


Fig. 5 Cation-Anion Adsorption
(From unpublished work by G.W. Thomas)

This indicates that anion adsorption by such soils may have an affect on their physical properties far exceeding that envisioned by Lambe, and thus led to the inception of this study.

Recently correlations have been made between the liquid limit and the double-layer thickness of fine-grained soils. Lambe (1953) suggests that liquid limit indicates the amount of water adsorbed by a soil. Thomas found a direct correlation between liquid limit and double-layer thickness for Wyoming bentonite (see Fig. 6¹). From Fig. 6 it is evident that an increase in liquid limit corresponds to an expansion in the thickness of the adsorbed water film; similarly, a decrease in liquid limit indicates a contraction of this film. On the basis of the above correlations, the liquid limit test was employed as an indicator of the so-called double-layer thickness as well as an index of soil physical properties.

¹The liquid limit values for the Na- and Ca-saturated Wyoming bentonite were taken from White (1955), and the double-layer thicknesses from unpublished work by G.W. Thomas.

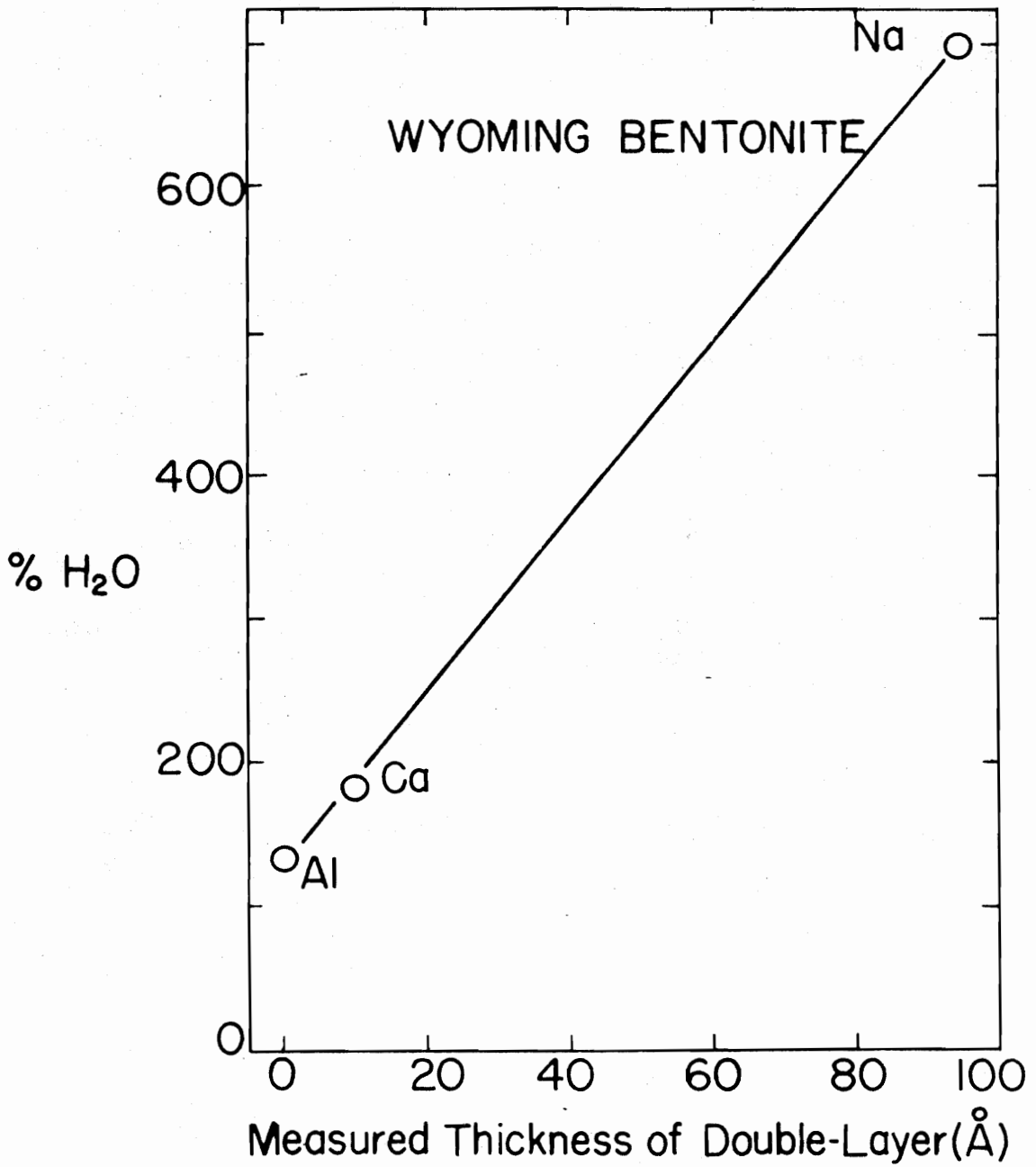


Fig. 6 Correlation Between Liquid Limit and Double-Layer Thickness (G.W. Thomas)

VI. MATERIALS AND METHOD OF PROCEDURE

Three different soil samples were used for this study. One, a residual kaolinitic soil derived from granite and with the series name Cecil, was obtained at a depth of twenty to twenty-four inches beneath the surface of the ground at Dixie, Virginia, located in the central Appalachian Piedmont. Another, a residual montmorillonitic soil derived from diabase with the series name Iredell, was taken at approximately the same depth as the Cecil at Mitchells, ^{Gadsden Co} Virginia, also in the central Appalachian Piedmont. The third, Wyoming bentonite, a montmorillonitic clay, was obtained from Upton, Wyoming.

In the natural state, the Cecil soil is primarily Al-saturated, whereas the Iredell soil is Mg- and Ca-saturated. The bentonite was pretreated with $\text{Al}(\text{Cl})_3$ and washed free of Cl with water, leaving an Al-saturated clay. Additional physical and chemical properties of these three soils are given in Table 2.

The Cecil and Iredell soils were air dried, pulverized, and passed through a No. 40 mesh sieve prior to the liquid limit determination. The bentonite was maintained in the form of a saturated paste.

Fifty grams of sieved Cecil and Iredell soil were mixed with a solution of distilled water and acid (HCl , H_2SO_4 , or H_3PO_4). The acid (H_2SO_4 or H_3PO_4) was added directly to the

HCl?

TABLE 2
CHEMICAL AND PHYSICAL PROPERTIES OF SOILS USED

Chemical and Physical Properties	Soil		
	Cecil	Iredell	Wyoming Bentonite
Exchangeable Cations ¹			
Al	3.54	0	90.00
Ca	0.10	5.20	-
Mg	0.40	11.36	-
K	0.14	0.18	-
Cation Exchange Capacity ¹	4.18	16.74	90.00
Clay Minerals ^{2,3}			
K	80	20	-
M	-	80	100
V	20	-	-
Liquid Limit	75	72	134
Plastic Limit	43	34	-
Plasticity Index	31	37	-
Flow Index	30%	24%	20%
Toughness Index	1.0	1.6	-
pH ¹	5.0	6.8	-
³ K = % Kaolinite and Halloysite, M = % Montmorillonite, V = % Dioctahedral Vermiculite with interlayer aluminum.			

¹Chemical data from unpublished work by G. W. Thomas.

²Mineralogical data for the Cecil soil from "Certain Properties of Selected Southeastern United States Soils and Mineralogical Procedures for Their Study," Virginia Agricultural Experiment Station, V.P.I., Blacksburg, Virginia.

³Mineralogical data for the Iredell soil from unpublished work by R. D. Krebs.

Wyoming bentonite, since it was previously saturated with distilled water. The specimens were cured¹, at their approximate liquid limit, from one to five days in polyethylene containers. After curing, the liquid limit values were determined as specified by ASTM (1950) with three exceptions: (1) the Harvard Type Liquid Limit device, which utilizes the micarta base and the Casagrande grooving tool, was employed; (2) the groove was cut with the cup attached to the device; and (3) the samples were oven-dried at 100° C. For each flow curve, four or five points were determined in ascending order with reference to water content, (i.e. water was always added to the soil after the determination of each point on the flow curve).

¹Curing time is the time interval from the mixing of the soil and water to the liquid limit determination.

VII. RESULTS

During the early stages of testing, there was considerable scatter of points on the flow curves. The scatter was attributed to alternate wetting and drying of the soil during each liquid limit determination. Consequently, a test was devised to evaluate this hypothesis.

Two hundred grams of air-dried Cecil soil were mixed with 160 ml. of distilled water and cured for three days. Successive points on the lower flow curve (see Fig. 7) were determined by continuously air-drying the soil, until approximately fifty blows were required to close the groove. At this point distilled water was added prior to each determination, thus resulting in a normal flow curve (i.e. correct slope and liquid limit). As shown in Fig. 7, this test resulted in two distinct flow curves; a phenomenon herein called "hysteresis". It was concluded that in order to obtain more precise flow curves, the points on each curve should be determined successively. This method was tried, and proved successful.

It was also noticed that during prolonged mixing of the moist Cecil soil, the soil appeared to gain strength even though it seemed to be well mixed (i.e. the longer the soil was spatulated, at a constant water content, the greater its strength). The gain in strength was not only apparent during initial mixing, but also after a curing time of three days.

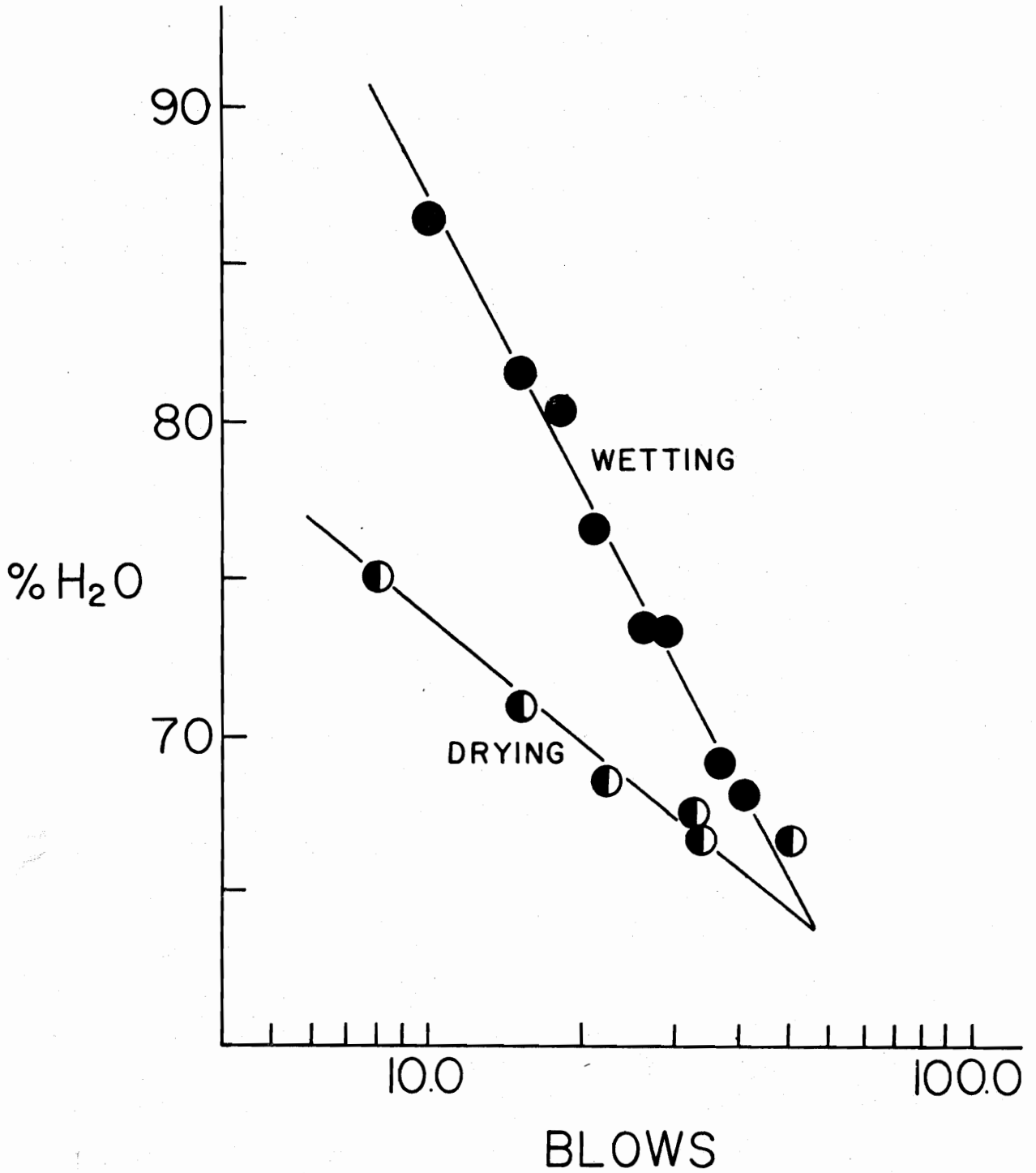


Fig. 7 "Hysteresis effect" as observed for Cecil soil

This phenomenon is illustrated by the nearly horizontal line in Fig. 8. The four points on this line were determined within one minute, at a nearly constant water content. The only treatment the soil received between determinations was further mixing. With the addition of water, after the gain in strength, the determinations progressed along the normal flow curve (Fig. 8). Both the gain in strength phenomenon and the drying of the soil are thought to have caused the hysteresis effect shown in Fig. 7.

The ability of the soil to gain in strength with prolonged mixing may be due to the breakdown of "domains" (Aylmore and Quirk, 1959) within the soil. It is thought that a number of clay particles can become clustered together in a "domain" as shown in Fig. 9. As the soil and water are mixed, it may appear to the observer that thorough mixing has occurred; however, if spatulation is continued the domains will be broken down, thus enabling the individual clay particles to adsorb more water. If the water content is held constant, the water adsorbed into the double-layer must be supplied by the pore water, thus decreasing the lubricant surrounding each domain and thereby increasing the soil strength.

In order to increase the accuracy of the liquid limit determination, the points on the flow curve should be run in successive order. Care should also be exercised during the

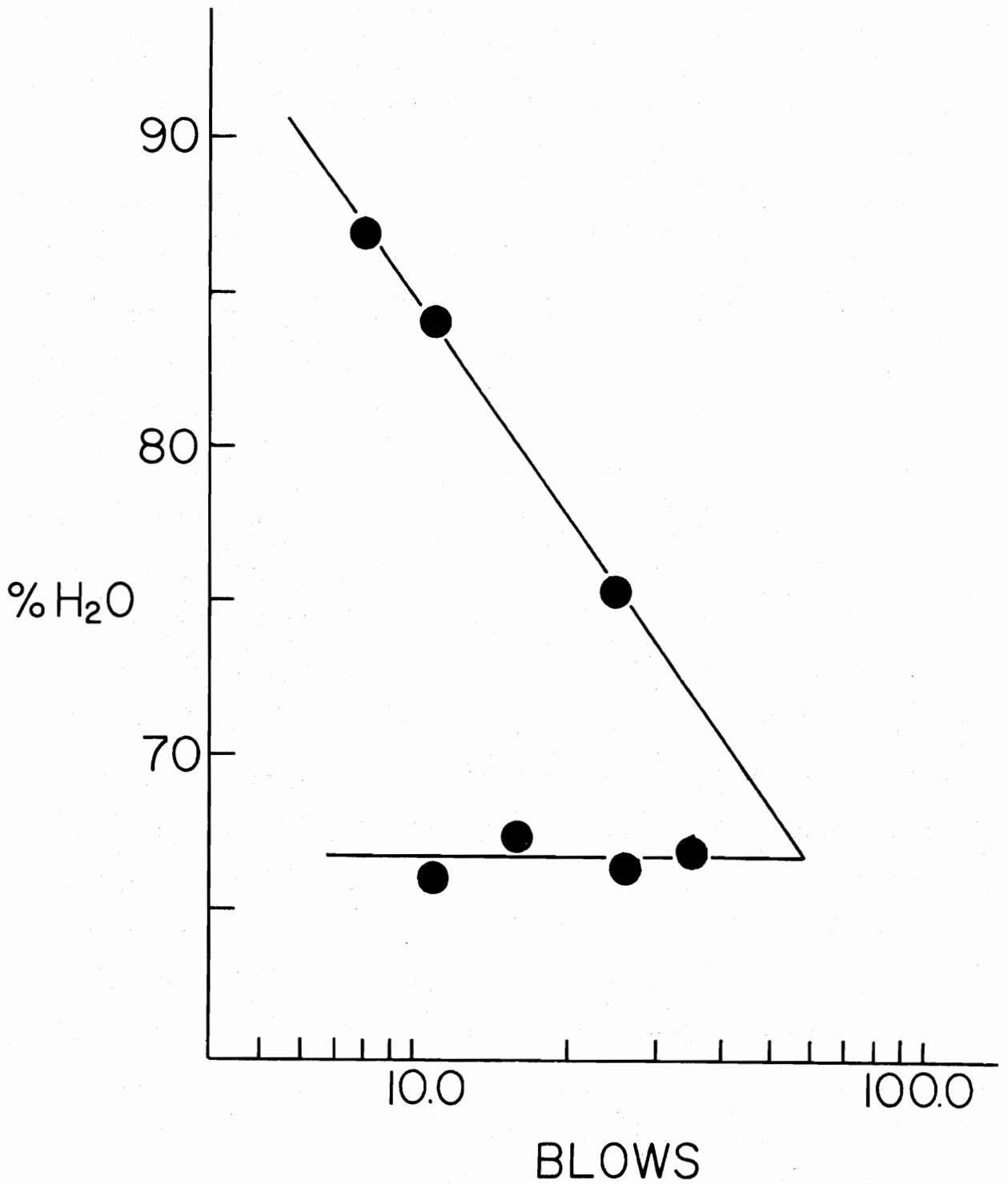


Fig. 8 Strength Gain as Observed for Cecil Soil

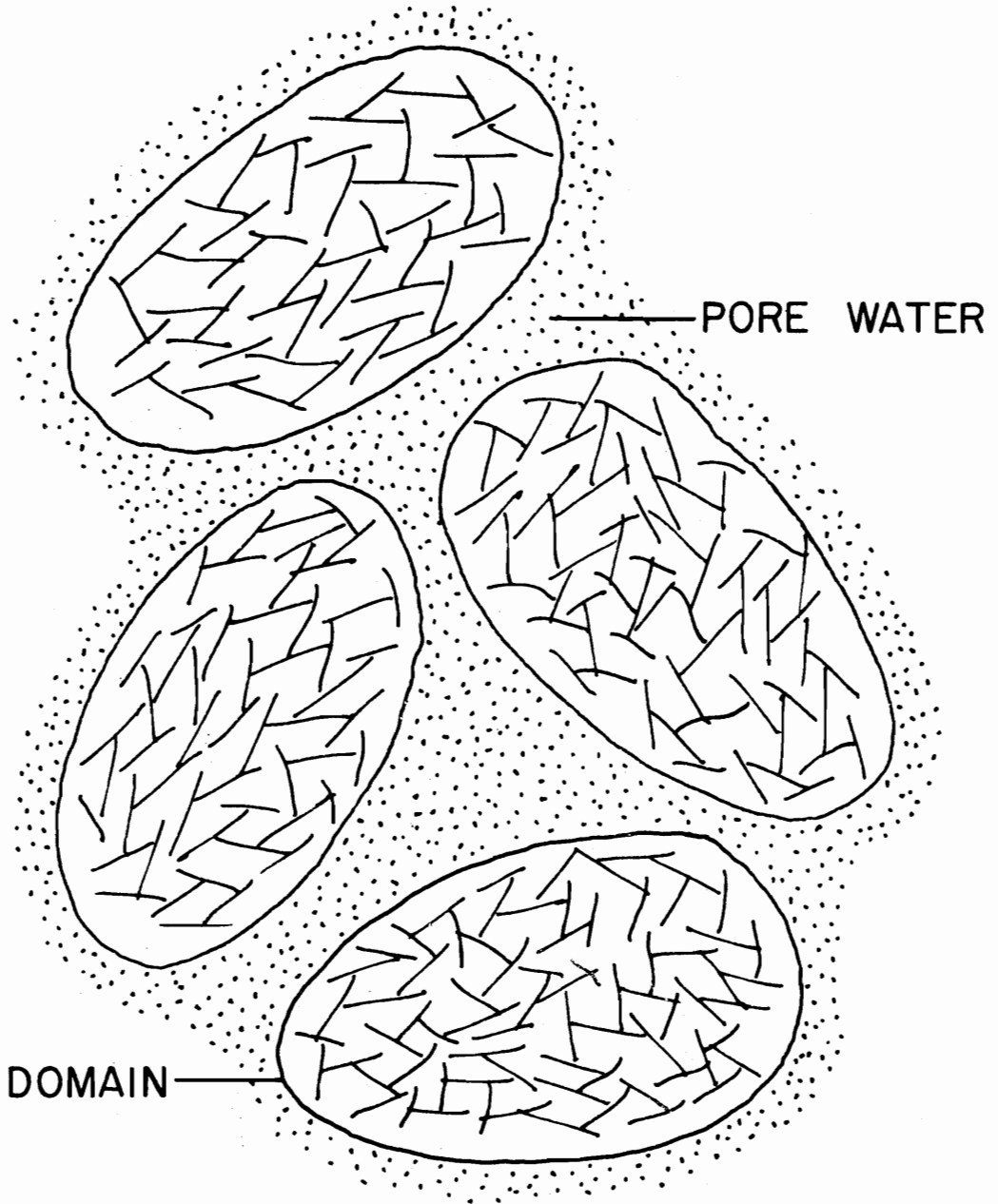


Fig. 9 Clay Domains

process of mixing to insure the complete break-down of any "domains" that may occur in the soil. It is especially important to recognize the possibility of a hysteresis or domain effect when using the one-point method in evaluating liquid limit.

As mentioned previously, the soil was cured one to five days prior to running the liquid limits. Dawson (1960) reports that curing times exceeding eight hours have a negligible effect upon liquid limit values. The curing time versus liquid limit results from this study, as shown in Table 3, lead to a similar conclusion.

Fig. 10 illustrates the effects of subsequent additions of H_2SO_4 and H_3PO_4 on the Al-saturated Wyoming bentonite. The points on the curves represent one liquid limit determination. The flow curves were well defined and had approximately the same slope. Because of this and the nearly straight line character of the acid-liquid limit curves, it is thought that the curves in Fig. 10 satisfactorily portray the influence of the addition of acids on the liquid limit of the soil.

The effects of HCl, H_2SO_4 and H_3PO_4 on the liquid limits of the Iredell soil are shown in Fig. 11. The points shown on the curves represent an average of four to five determinations. Although the curve of each run followed similar trends, there is a considerable variation from the average

TABLE 3

EFFECT OF CURING TIME ON LIQUID LIMIT

Iredell Soil							
Acid Concentrations	Curing Time in Days						
	1	2	3	5	10	20	50
5 me/100g of HCl	65	68	68	66	70	69	67
50 me/100g of HCl	70	72	74	67	70	72	72
5 me/100g of H ₂ SO ₄	71	73	71	70	72	72	73
50 me/100g of H ₂ SO ₄	74	75	74	72	75	74	75
5 me/100g of H ₃ PO ₄	68	71	72	72	73	69	72
50 me/100g of H ₃ PO ₄	68	64	67	65	67	68	77

Cecil Soil							
Acid Concentrations	Curing Time in Days						
	1	2	3	5	10	20	50
5 me/100g of HCl	72	72	74	73	77	-	77
50 me/100g of HCl	61	61	64	62	63	-	63
5 me/100g of H ₂ SO ₄	73	71	74	74	72	-	73
50 me/100g of H ₂ SO ₄	56	57	57	60	60	-	58
5 me/100g of H ₃ PO ₄	70	71	76	76	72	-	76
50 me/100g of H ₃ PO ₄	74	-	-	83	80	-	79

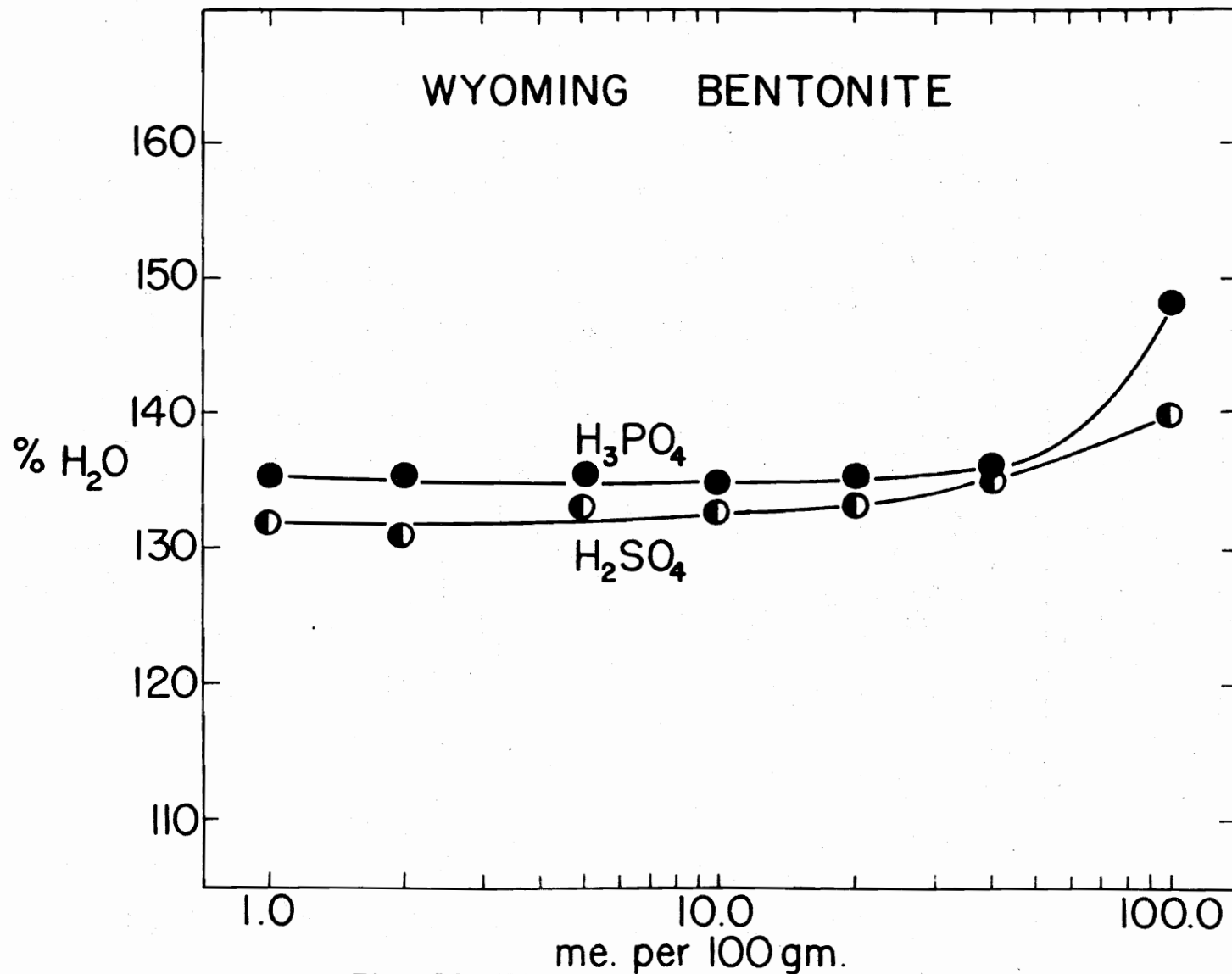


Fig. 10 Effect of H₂SO₄ and H₃PO₄ on the Liquid Limit of Wyoming Bentonite

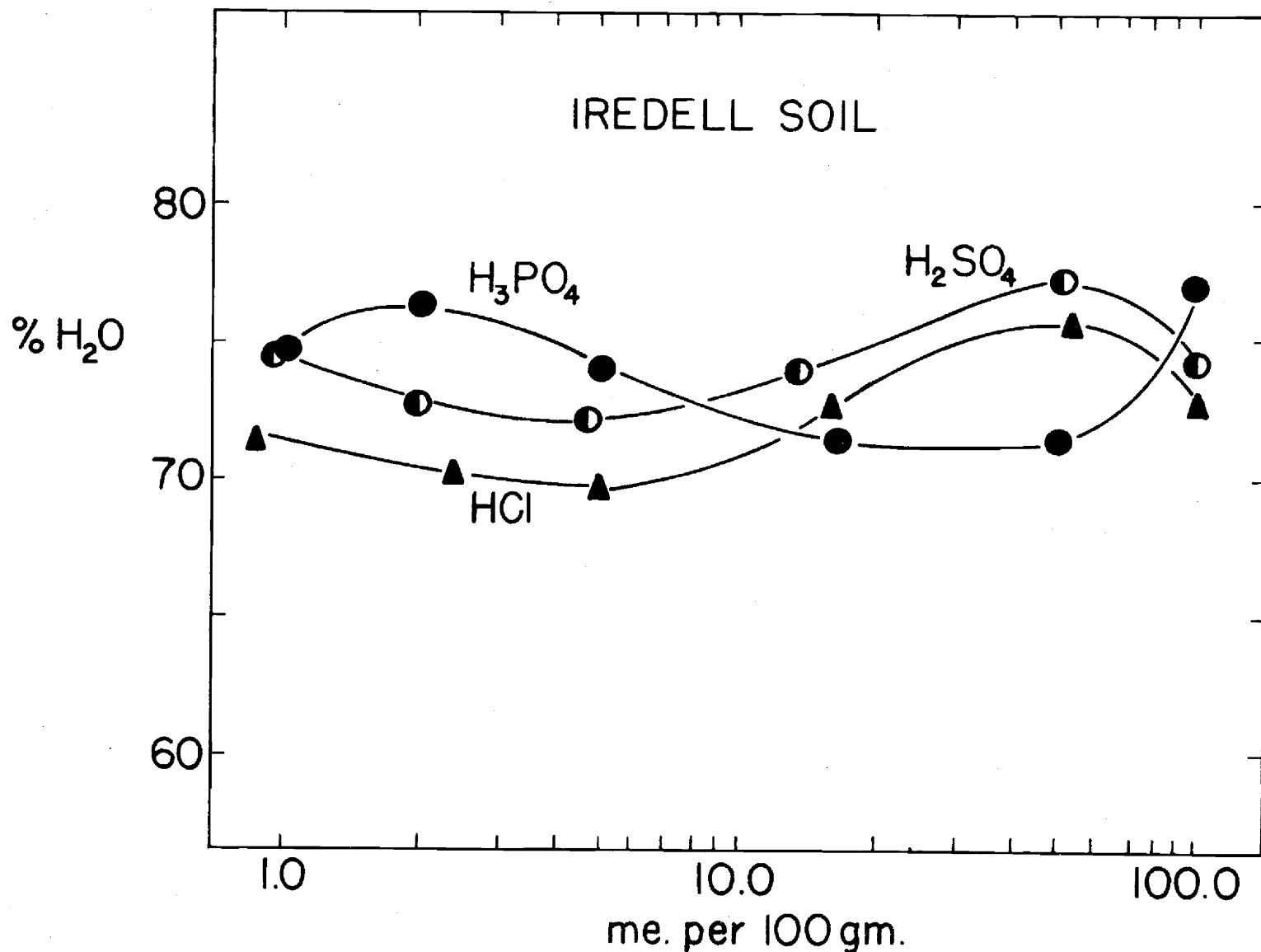


Fig. 11 Effect of HCl, H₂SO₄, and H₃PO₄ on the Liquid Limit of Iredell

with some replicate determinations. Still, the majority of the points are within $\pm 4\%$ of the average, which is within the limits of accuracy reported by Thornburn and Larson (1959). It is believed, however, that the variation in liquid limit determinations is due to the peculiarity of the Iredell soil, rather than a personal effect, as evidenced by the seemingly irregular results in Fig. 11.

The results of successive additions of HCl, H₂SO₄ and H₃PO₄ on the acid, kaolinitic, Cecil soil are shown in Fig. 12. The points represent an average of four to five determinations. Most of the replicates are within $\pm 2\%$ of the average.

For all the soils studied, the additions of acid had no observable effect on the slope of the flow curve. This suggests that the one-point determination is useful even in cases where natural or induced chemical alterations of soil occur. The error which might have occurred had the one-point determination been used in this study is shown in Table 4.

The results of each liquid limit determination made during the acid addition experiments are tabulated in the Appendix.

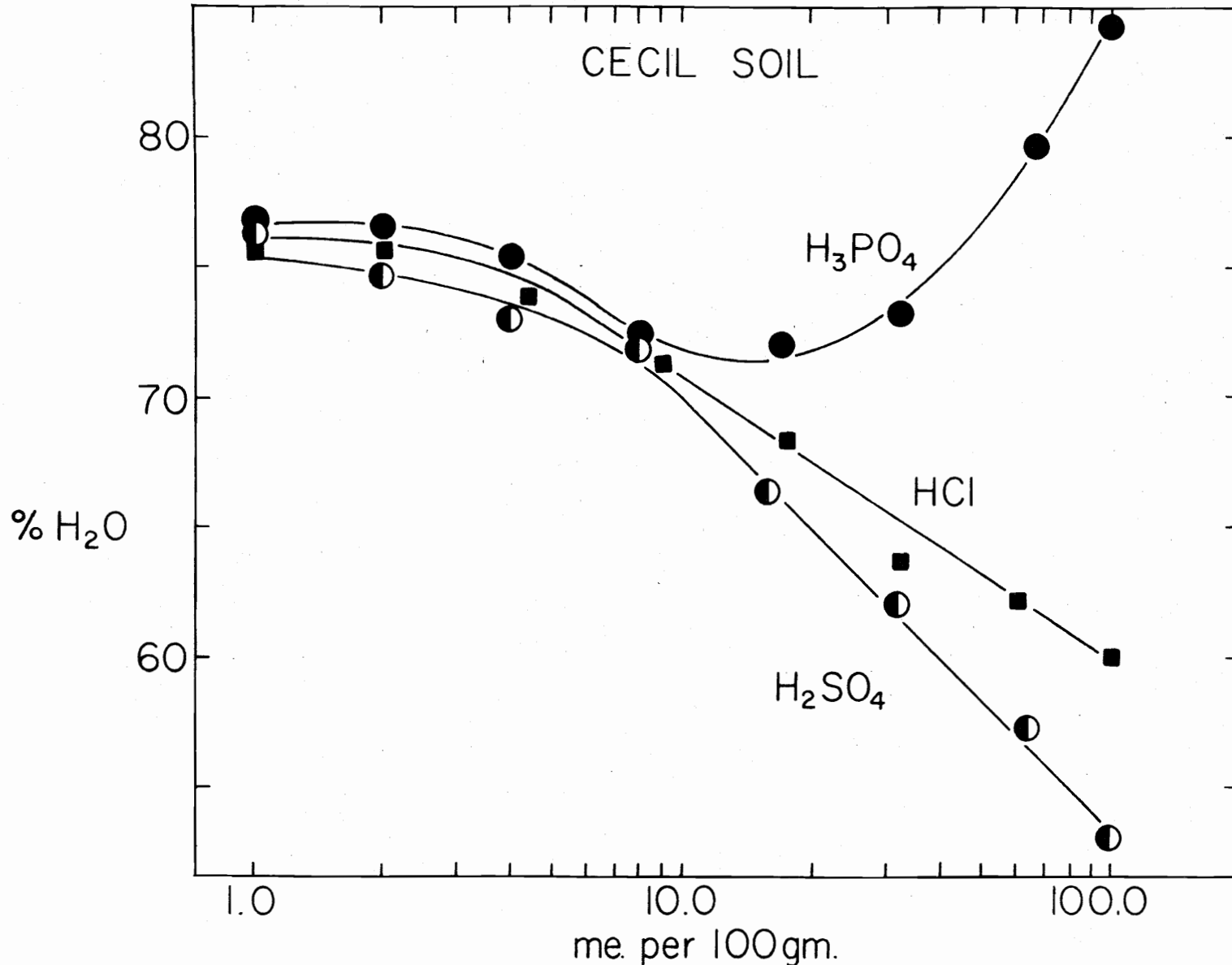


Fig. 12 Effect of HCl, H₂SO₄, and H₃PO₄ on the Liquid Limit of Cecil

TABLE 4. Comparison of One-point and Multi-point
Liquid Limit Determinations

Iredell - Liquid Limit = 72 (Multi-point Method)

One-point Method

Investigator	Liquid Limit Using w% at 20 Blows	Liquid Limit Using w% at 30 Blows
Waterways Experiment Station	72	72
Olmstead and Johnston	72	72
Norman	72	71
Eden	72	71

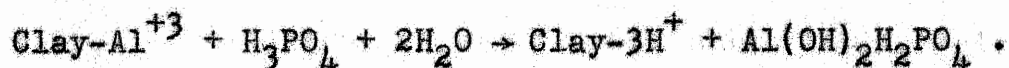
Wyoming Bentonite - Liquid Limit = 132 (Multi-point Method)

One-point Method

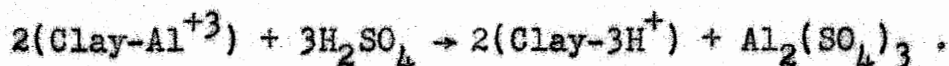
Investigator	Liquid Limit Using w% at 20 Blows	Liquid Limit Using w% at 30 Blows
Waterways Experiment Station	130	134
Olmstead and Johnston	130	134
Norman	131	133
Eden	131	133

VIII. DISCUSSION OF RESULTS

As shown above in Fig. 10, the sulfate and phosphate ions had no observable effect on the liquid limit of Wyoming bentonite except at high acid concentrations. Possibly, at the higher concentrations the hydrogen ions are replacing some of the aluminum on the exchange sites. This is particularly plausible in the case of phosphate, since there is a great tendency for aluminum and phosphate ions to react with each other, thus tending to remove the aluminum ion from exchange sites. This reaction is shown below:



A similar reaction is probably occurring between the sulfate and aluminum ions. The probable reaction is illustrated below:

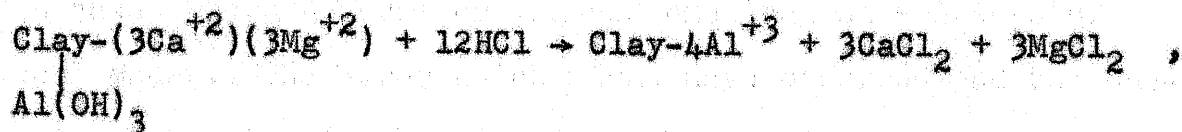


Due to the higher valence of the Al^{+3} -ion, it probably is held more tenaciously by the clay particle than the H^+ -ion. Also, since three H^+ -ions are required to replace one Al^{+3} -ion on the exchange, it follows that the substitution of H^+ for Al^{+3} may increase the double-layer thickness, thereby increasing the value of the liquid limit.

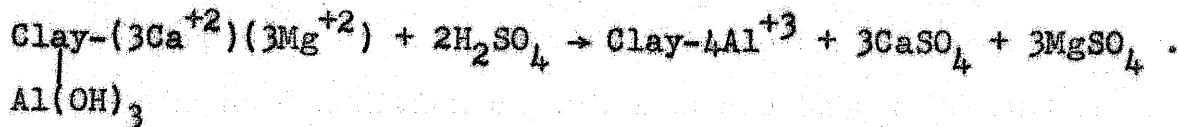
With reference to Fig. 11 it appears that the HCl and H_2SO_4 had a similar effect on the Mg^{+2} - and Ca^{+2} -saturated

Iredell soil. The initial decrease of the two curves, which presumably also represents a decrease in double-layer thickness, may be attributed to the adsorption of Al^{+3} -ions on the exchange complex. The appearance of the Al^{+3} -ions is ascribed to the partial dissolution of $Al(OH)_3$, which occurs in the clay lattice, thus resulting in the subsequent adsorption of Al^{+3} (Harward and Coleman, 1954). For every two Al^{+3} -ions adsorbed onto exchange sites, three Mg^{+2} - or Ca^{+2} -ions would be expelled. Since Al^{+3} -ions have a relatively high charge and will be held much tighter than either the Mg^{+2} - or Ca^{+2} -ions, it follows that the substitution of Al^{+3} for Mg^{+2} - or Ca^{+2} -ions may reduce the double-layer thickness. Possible chemical equations for these reactions are given below:

For hydrochloric acid,



For sulfuric acid,



Additional lowering of the pH will create high concentrations of H^+ -ions. Thus, the rise in the HCl and H_2SO_4 curves (see Fig. 11) is probably due to the replacement, by mass action, of hydrogen for calcium, magnesium, and aluminum

on the exchange complex. Due to the lower valence of the H^+ -ion, the hydrogen will be held less tightly by the clay particle than will the calcium, magnesium, or aluminum; and since a greater number of H^+ -ions will be required to neutralize the clay particle, it follows that the double-layer thickness may increase. Chemically, this is shown below:

For hydrochloric acid,



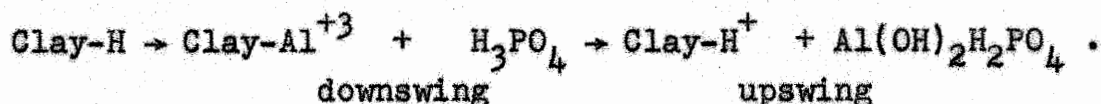
For sulfuric acid,



The final decrease of the two curves is probably due to a procedural difficulty. It is thought that water of crystallization is occurring at high concentrations of acid, thus resulting in low values of observed water content.

The H_3PO_4 curve (see Fig. 11) presents considerable difficulty in interpretation. At low acid concentrations the H_3PO_4 may be ionizing into $\text{H}^+ + \text{H}_2\text{PO}_4^-$, possibly resulting in the replacement of H^+ -ions for Ca^{+2} - and Mg^{+2} -ions. This type of replacement would tend to increase the thickness of the double-layer, thus increasing the liquid limit. The downswing of the curve might be caused by the adsorption of Al^{+3} , again released by the partial dissolution of $\text{Al}(\text{OH})_3$ in the clay lattice. The final upswing is possibly the result of an independent reaction at high concentrations of

H_3PO_4 . This reaction is probably similar to that written for the bentonite-acid upswing, whereby Al^{+3} is stripped from the exchange sites and precipitated as $Al(OH)_2H_2PO_4$. Once the Al^{+3} has been stripped from the exchange complex, it may be replaced with H^+ , thus resulting in an increased double-layer. Hence, the possible reactions are



As mentioned above, Lambe (1958) states that "the adsorption of anions, especially polyvalent anions, increases the charge on the particles and thereby tends to cause dispersion."

Table 5 shows that as the pH of a soil-water system is lowered, or the anion concentration is increased, there is virtually no effect on the net negative charge of the montmorillonitic Iredell soil, whereas there is practically a linear relationship between the decreasing pH and net negative charge for the kaolinitic Cecil soil. This decrease in net negative charge may enhance flocculation rather than dispersion.

Lambe (1958) also states that "the pH of the pore fluid affects the net negative charge on a soil particle by altering the extent of dissociation of OH groups on the

TABLE 5
Effect of pH on Net Negative Charge¹

pH	Iredell me/100g	Cecil me/100g
2.4	20.0	1.40
3.3	-	2.00
4.3	19.9	2.60
5.2	19.9	3.24
6.1	-	4.40

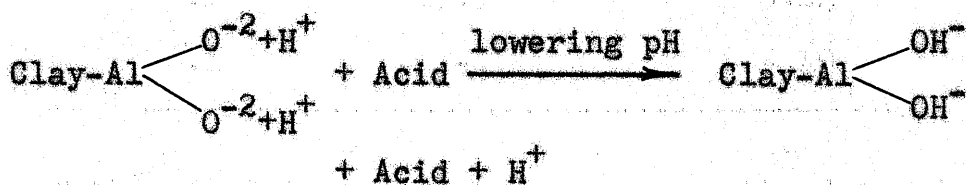
edges of the particle. High pH encourages the dissociation and increases the net charge, thus expanding the double-layer; low pH does the reverse. Lowering the pH, therefore, tends to cause flocculation and raising it tends to cause dispersion."

As mentioned above, there are at least two possibilities for decreasing the net negative charge in the kaolinitic soil. One is the creation of positive charge sites on the particle; the other, and probably the most plausible for soils containing hydroxy aluminum, such as the Cecil, is the suppression of hydrogen dissociation. At a low pH there would be an abundance of H⁺-ions ($10^{-\text{pH}}$) and a scarcity of OH⁻-ions [$10^{-(14-\text{pH})}$]; hence, the high concentration of

¹Thomas, G.W., 1956, M.S. Thesis, North Carolina State College.

H⁺-ions would tend to prevent hydrogen dissociation from hydroxyls. On the other hand, the abundance of H⁺-ions might remove the hydroxyl, which would then be replaced by the added anion. Means of lowering the net negative charge by suppression of hydrogen dissociation and hydroxyl removal are shown below:

Suppression of hydrogen dissociation



Removal of hydroxyl:

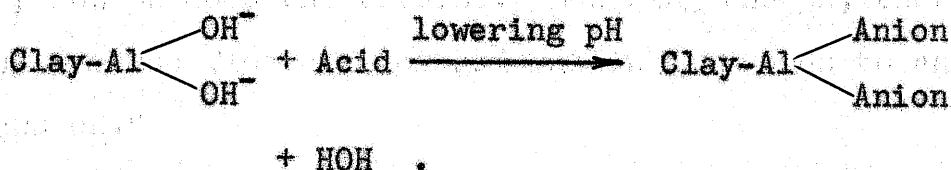
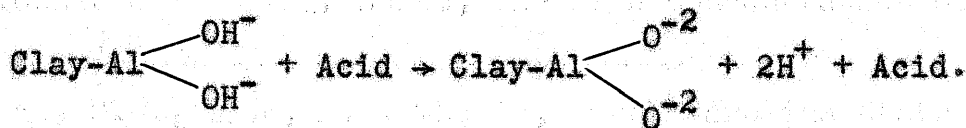


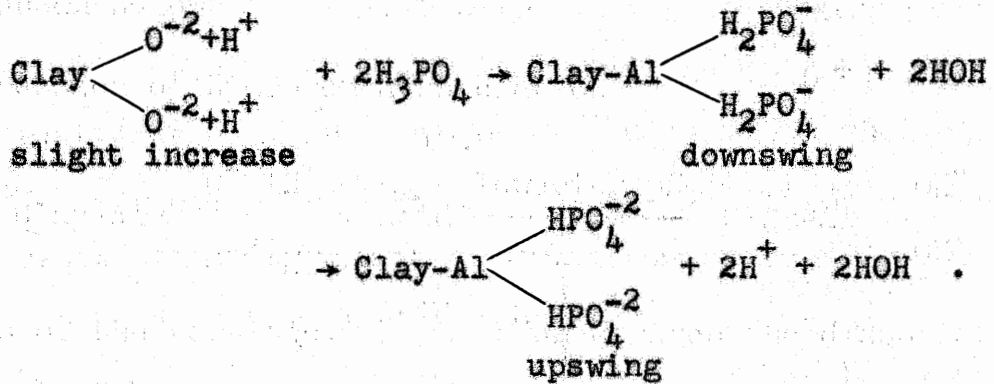
Fig. 12 indicates similar reactions occurring between the HCl and H₂SO₄, and the Cecil soil. At a relatively high pH there is probably considerable hydrogen dissociation which, in effect, results in a high net negative charge, yielding a relatively large double-layer. The probable chemical reaction is



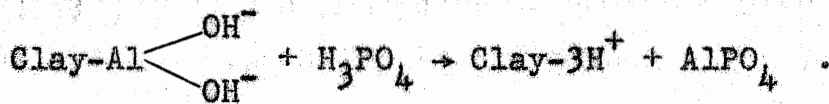
As the pH of the pore fluid is subsequently lowered, the concentration of H^+ -ions and added anions will increase. At this point either one of two, or both, reactions are possible: hydrogen dissociation is suppressed, the anions are replacing the hydroxyl groups, or both reactions are taking place simultaneously. In all probability hydrogen dissociation is being suppressed while the anions are replacing the hydroxyl groups, which in effect lowers the net negative charge on the particle. By reducing the net negative charge on a particle, less cations are required in the double-layer to neutralize the system, thus tending to decrease the double-layer thickness and liquid limit. Since the SO_4^{2-} -ions are strongly adsorbed by the soil, there will be a greater decrease in liquid limit as opposed to the Cl^- -ions, which are weakly adsorbed.

There is a possibility of three successive reactions with the H_3PO_4 and Cecil soil (see Fig. 12). At low concentrations of H_3PO_4 , there is probably a large amount of hydrogen dissociation, resulting in a relatively high net negative charge and a large double-layer thickness. As the concentration of H_3PO_4 is increased, hydrogen dissociation is depressed while H_3PO_4 is ionized to $H^+ + H_2PO_4^-$, resulting in the replacement of $H_2PO_4^-$ for some of the hydroxyl groups. This latter reaction would tend to decrease the net negative charge, thereby decreasing the double-layer. At high concentrations of H_3PO_4 , the acid is further ionizing to

H^+ + HPO_4^{-2} with HPO_4^{-2} replacing the OH groups, resulting in an increased net negative charge which will tend to create an expanded double-layer. An increase in net negative charge with addition of H_2PO_4 has often been reported (Coleman and Mehlich, 1948). The reaction for all three effects is



There is another possible explanation pertaining to the rise in liquid limit at high concentrations of H_3PO_4 . The phosphate (PO_4^{-3}) might be stripping the $Al(OH)_2^+$ from the clay particle and replacing it with H^+ -ions, hence increasing the net negative charge and expanding the double-layer. This is shown below:



The addition of HCl, H_2SO_4 , and H_3PO_4 had a considerable effect on the acid, kaolinitic, Cecil soil, whereas the Wyoming bentonite and Iredell soil were relatively unaffected. The extreme effect of the acids on the Cecil soil is thought

to be due to the mass adsorption of anions, rather than cations, onto the exchange complex (Thomas, 1960, Mattson, 1927). The adsorbed anions reduced the net negative charge on the Cecil soil, thereby tending to decrease the double-layer thickness and increasing the tendency towards flocculation. Lambe (1958), on the other hand, predicts that the adsorption of anions will increase the net negative charge and double-layer thickness, and hence tend to cause dispersion. This statement is in direct contrast with the results of this study. Although the Wyoming bentonite and Iredell did not take exception to the double-layer dicta, such common soils as the kaolinitic Cecil apparently do not follow the general hypotheses set forth by Lambe (1953, 1958).

This study shows that chemical additives can exert considerable influence on the thickness of the adsorbed water film on acid kaolinitic soils. There are additives which will increase the electrical interparticle forces or flocculate the clay particles; similarly there are chemicals which will decrease the interparticle forces, thus tending to disperse the soil. There does not appear, however, to be any universally correct criteria or hypotheses as to the effect of an additive on any given soil. In all probability the effects would depend upon such factors as the chemistry of the soil, the type of soil or clay, the chemical content of the additive, and soil structure.

The primary purpose of a chemical additive is to render an undesirable soil utile. As mentioned above, an additive will influence the interparticle forces and the double-layer thickness, which in turn will affect such soil physical properties as compressibility, permeability, soil structure, dry strength, density, and undisturbed strength.

Although it is doubtful if the full effects of additives on soil physical properties can be predetermined, some insight is acquired when the influence of these additives on soil water is evaluated.

IX. SUMMARY

Because there is evidence that an acid kaolinitic soil will adsorb a considerable amount of anions as well as cations, the effect of HCl , H_2SO_4 , and H_3PO_4 on the physical character of such a soil was investigated employing the technique of liquid limit determination. The results are compared to those found for contrasting soil types.

It was found that the various additions of HCl , H_2SO_4 , and H_3PO_4 to a montmorillonitic soil, and H_2SO_4 and H_3PO_4 to a montmorillonitic clay have a relatively insignificant influence on the liquid limit of these materials. Still, the liquid limit of a kaolinitic soil was found to be affected considerably by the addition of HCl , H_2SO_4 , and H_3PO_4 . These observed changes in liquid limit are utilized as a reference for double-layer thickness and are discussed on the basis of net negative charge and anion adsorption.

The scope of this study does not permit definite conclusions regarding the nature of the physical-chemical system that occurs in the soils studied. The results do emphasize the effects of different anions on the physical properties of some soils in contrast to others. Apparently there is a danger in attempting to use theories demonstrated to apply to montmorillonitic systems to explain the behavior of acid kaolinitic soils. Indeed, behavior predictions based on the double-layer theory in general need reevaluation

before application to kaolinitic as well as montmorillonitic soils.

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XIII. VITA

The author, the son of Mr. and Mrs. William Moore, was born on July 2, 1937, at Parkersburg, West Virginia. He attended public schools in Huntington, West Virginia, and entered Marshall College in September, 1955. In September, 1956, he transferred to Virginia Polytechnic Institute where he received a Bachelor of Science Degree in Civil Engineering.

He married the former Miss Sue Ann King of Huntington, West Virginia, on August 30, 1958.

Jack E. Moore

XIII. APPENDIX

Effect of H_2SO_4 on the Liquid Limit
of Wyoming Bentonite

Acid Concentration me/100gm	Liquid Limit 3 Day Cure
1.0	132
2.0	131
5.0	133
10.0	133
20.0	133
40.0	135
100.0	140

Effect of H_3PO_4 on the Liquid Limit
of Wyoming Bentonite

Acid Concentration me/100gm	Liquid Limit 4 Day Cure
1.0	135
2.0	135
5.0	135
10.0	133
20.0	134
40.0	135
100.0	148

Effect of HCl on the Liquid Limit of Iredell

Acid Concentration me/100gm	Liquid Limit 3 Day Cure		
	Trial 1	Trial 2	Trial 3
0.1	73		
0.2	70		
0.3	72		
0.6	70		
0.9	72		
1.0	67	69	79
1.8	69		
2.0	68	74	
3.6	70		
5.0	66	70	74
7.2	72		
10.0	75		
14.0	72		
20.0	74		
28.0	70		
50.0	76	69	84
64.0	74		
100.0	72	74	

Effect of H_2SO_4 on the Liquid Limit of Iredell

Acid Concentration me/100gm	Liquid Limit 3 Day Cure		
	Trial 1	Trial 2	Trial 3
0.1	77		
0.3	76		
0.6	72		
1.0	73	70	76
2.0	74	81	64
4.0	76		
5.0	73	68	
8.0	77		
10.0	71		
16.0	76		
20.0	72		
32.0	76		
50.0	75	80	
64.0	82		
100.0	73	80	70

Effect of H_3PO_4 on the Liquid Limit of Iredell

Acid Concentration me/100gm	Liquid Limit 3 Day Cure	
	Trial 1	Trial 2
0.1	74	
0.3	75	
0.6	74	
1.0	73	76
2.0	76	76
5.0	72	74
10.0	74	
20.0	68	72
50.0	75	74
100.0	77	

Effect of HCl on the Liquid Limit of Cecil

Acid Concentration me/100gm	Liquid Limit 1 Day Cure		Liquid Limit 3 Day Cure	
	Trial 1	Trial 2	Trial 1	Trial 2
0.5	74			
1.0	71		76	78
2.0	80		74	75
4.0			73	72
5.0	76			
8.0			70	72
10.0	72			
16.0			69	69
20.0	66			
32.0			64	64
50.0	58	65		
64.0			60	61
100.0	61		60	58

Effect of H_2SO_4 on the Liquid Limit of Cecil

Acid Concentration me/100gm	Liquid Limit 3 Day Cure		
	Trial 1	Trial 2	Trial 3
1.0	76	76	76
2.0	78	74	76
4.0	77	73	73
5.0	73		
8.0	72	72	74
16.0	66	66	
20.0	69		
32.0	62	62	
40.0	64		
64.0	56	58	
76.0	58		
100.0	52	53	53

Effect of H_3PO_4 on the Liquid Limit of Cecil

Acid Concentration me/100gm	Liquid Limit 1 Day Cure		Liquid Limit 3 Day Cure		Liquid Limit 5 Day Cure	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
1.0	71	74	74		78	
2.0	76		76	75	73	
3.0					78	
4.0			73	75		
5.0	77				78	
8.0			70	72	75	
10.0	76				70	
15.0					75	
16.0	71		70	71	72	
20.0	70				74	70
30.0					74	
32.0			71			
40.0					75	
64.0			77			
70.0					82	
100.0			81		85	87
150.0					81	82

ABSTRACT

The double-layer or adsorbed water surrounding a clay particle is thought to be comprised primarily of cations; anions being almost entirely excluded. There is evidence, however, that an acid kaolinitic soil will adsorb a considerable amount of anions as well as cations. The liquid limit test is employed on three different soil samples to evaluate this hypothesis.

The various additions of HCl, H_2SO_4 , and H_3PO_4 to a montmorillonitic soil, and H_2SO_4 and H_3PO_4 to a montmorillonitic clay had a relatively insignificant influence on the liquid limit of these soils. The liquid limit of the kaolinitic soil, however, was affected considerably by the addition of HCl, H_2SO_4 , and H_3PO_4 . The change in liquid limit results is utilized as a reference for double-layer thickness, and is discussed on the basis of net negative charge and anion adsorption.