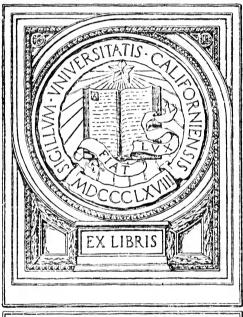# THE PHYSICAL ACTION OF LIME
ON CLAY SOILS

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF CORNELL UNIVERSITY FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY
ROBERT MIFFLIN SNYDER

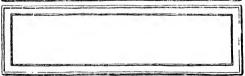*December, 1917*

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THE PHYSICAL ACTION OF LIME ON CLAY SOILS

The recent investigations in the field of soil acidity have raised anew the question of the physical action of lime on the soil. A number of physical investigations have been conducted in the past, but the recent progress in certain auxiliary subjects, as colloid chemistry, has tended to depreciate the value of much of this work, and bring new problems to the front. The question may therefore be properly considered again: What is the specific effect of each form of lime on the soil, and how great is that effect?

Our problem resolves itself into two parts: First, the selection of desirable methods, and second, their application. Let us first review the procedures available for the study of the colloidal characteristics of the soil, and determine wherein their merits and deficiencies lie. The various methods may be classified under eight distinct headings, as follows:

Methods for Estimating Soil Colloidality

Flocculation in solution.
    1. The suspension method.
Solubility of colloidal material.
    2. Fraps Ammonia Method.
    3. Van Bemmelen Acid Method.
    4. Endosmometer method.
Heat Liberation on Wetting.
    5. Pouillet-Mitscherlich Method.
Capillarity and Retentive Power.
    6. Hilgard Total Retentive Cup Method.
    7. Briggs and McLane Moisture Equivalent Method.
    8. Capillary Rise of Water.
    9. Percolation of Water.
    10. Atterberg Plasticity Method.
Adsorption.
    11. Hygroscopic Water.
    12. Dye Adsorption.
    13. Selective Adsorption of ions.
    14. Endell Histological Method.
Volume Change.
    15. Expansion Method.

Penetrability.
16. Penetration Method (Laboratory).
17. Dynamometer Method (Field).
Oxidation.
18. The Oxidation Method.

1. The Suspension Method has been used more extensively than any other. It consists essentially in making a suspension of the material in the particular solution to be tested, and observing the time required for precipitation. For a number of decades the suspension method was the only means by which the effect of ions on the stability of colloidal material could be determined. In the hands of Schulze, Bams, Picton and Linder, Bodlander, and Hardy, it was of immense assistance in the formulation of the fundamentals of colloid chemistry. The specific action of various salts, and the valence and mass relations, have been popular subjects for study. The most recent work with clay suspensions has been performed by Masoni, and by Wolkoff.

Valuable as the suspension procedure has been in the preliminary studies, the question nevertheless arises whether it should be considered a legitimate method for correctly estimating the physical effects of salts on soils. The writer is of the opinion that the precipitation of a sol by an electrolyte is of little value in gauging the action of the same salt applied to a soil under natural conditions. In a suspension the forces inhibiting the neutralization of charges are very small, while in a heavy soil the internal friction prevents the formation of the large floccules characteristic of the suspension. Probably in many heavy clays the positively changed colloidal iron remains indefinitely in approximate contiguity to the negative silicia without neutralization taking place.

A somewhat similar view regarding the inapplicability of the suspension method is held by Free. He thinks that in the soil, the tension at the liquid-vapor surface may be the determining factor in precipitation.

2. Fraps has studied the ammonia soluble inorganic soil colloids. He does not propose his method as a means by which the entire colloidal content of the soil may be measured.

3. The Van Bemmelen Method for the estimation of soil colloids consists in the determination of the material made soluble on prolonged digestion with hydrochloric and sulfuric acids. In the hands of Blanck and Dobrescu, and Vander Leeden and Schneider, the Van Bemmelen procedure has not yielded significant results. A serious criticism of the method lies in the fact that crystalloidal as well as colloidal matter may be rendered soluble.

4. The Endosmometer Method has been used by König, Hasenbäumer and Hassler for the determination of the absorbed ions in the soil. The

amount of salts released by the current bears only a very indirect relation to the amount of colloidal material.

5. The "Pouillet Effect" is another means by which the estimation of internal surface has been attempted. This method is named after C. Pouillet, who as far back as 1823 observed that finely divided substances released heat on wetting. Mitscherlich (1898) was the first to attempt the estimation of the internal surface of soils by the use of this phenomenon. Several other investigators have since then attempted similar studies. The fact that heat release in soils may be associated with a number of factors renders the Pouillet effect of doubtful value.

6. The total retentive power of the soil for water has long been used as a standard measurement. The early investigators usually allowed water to rise by capillarity in a cylinder filled with the soil, and then determined the final percentage present. Hilgard modified the procedure by using a short column of standard length, but the method still remains rather inaccurate.

The investigations of Trentler, Wollny, Blanck, and Engels indicate that calcium oxide increases the total retentive power of the soil. All these men, however, used excessive applications. The probable error in the case of Thaer's work is too high to permit the drawing of conclusions. Frear thinks that liming has no effect on the total retentive power. The writer is calling attention in each case to the instances in which limed soils have been used, for there is no better criterion as to the accuracy of a physical method, than its sensitivity to small amounts of lime.

7. The Moisture Equivalent Method of Briggs and McLane suggests itself as a possible means for estimating internal surface. Unfortunately, the probable error is so high as to probably preclude the measurement of very small lime applications. Sharp, of the California Station, is using this method at the present time in his alkali investigations.

8. The capillary rise of water in soil columns has been used by several investigators as a method for estimating soil colloidality. The usual procedure has been to place the lower end of a column of dry soil in contact with water, and record the speed and total height of ascent. Meyer, Krawkow, Gross, Blanck, and Engels have performed capillary experiments with lime treated soils. The data, considered as a whole, is inconclusive. Undoubtedly, internal surface is a factor in capillary rise, but the additional factors of surface tension and degree of compaction are exceedingly difficult to control.

9. The speed of percolation of water through soils has frequently been used as a measure of soil structure. Studies have been conducted by Vogel, Ebermeyer, Bühler, Blanck, Thaer, and Engels on the influence of lime on percolation. All agree that lime increases the ease with which water passes downward. For comparative purposes it is necessary to obtain a large volume of percolate, and this results in the removal of

salts from the sample. An objection to this procedure rests in the fact that the colloidal condition, the factor which we are measuring, depends on the salt content. A decrease in the amount of adsorbed salts results in a deflocculation of the soils. Both Mayer and Van Bemmelen noted at an early date that percolation decreased on prolonged leaching, and the same thing has been more recently noted by Hall, and by Sharp.

10. The Atterberg Plasticity Method has been proposed solely as a means of evaluating clays. It has never been applied to the estimation of internal surface. According to Kinnison, the Atterberg plasticity figure depends on too many factors to be of value.

11. The term "hygroscopic moisture" has usually been taken to mean the amount of water that a soil will absorb in order that its internal surface be covered with a film one molecule in thickness. However, there is reason to believe that the thickness of the film is greater than that stipulated by the definition. Furthermore, the slowness in reaching equilibrium, and the great effect of temperature on the final result, indicate that much of the water is present in the form of capillary water located in the interstices of the soil particles. It is more correct to speak of the phenomenon as "hygro-interstitial moisture," connoting thereby its true nature.

The early workers tested out the adsorptive power of soils for various vapors and gases. All these investigations resulted in the selection of water vapor as best suited for the purposes in hand. The hygro-interstitial investigations have been conducted according to two general types of procedure:

1. The first involves the constant passage of water vapor over or through a soil until equilibrium is reached.

2. The second requires the placing of the sample in an atmosphere whose degree of saturation is controlled, the moisture being conveyed to or from the soil by diffusion.

The classical investigations of Ammon and of von Dobeneck belong to the first type. They conducted the saturated vapor through a U-tube or some other suitable vessel containing the soil, until equilibrium had been reached. Both men were concerned with the adsorptive power of the various soil constituents, and so carefully was their work conducted, that it remains today our most valuable contribution to the subject.

One of the difficulties with the procedure was the frequency with which an abnormal condensation of water vapor occurred on the interior of the containing vessel. This led to the practice of reducing the degree of saturation of the water vapor. Heiden, for instance, employed a vapor approximately seventy-five per cent saturated, but he could not obtain valuable results. Owing to the difficulties of manipulation the subject was abandoned, and during the nineties no work was done on any phases of the question.

In 1903, Rodewald and Mitscherlich proposed a method corresponding to the second type of procedure outlined above. The soil sample, previously dried over phosphorus pentoxide, was placed in a container over ten per cent sulfuric acid until equilibrium was attained. The function of the sulfuric acid was to control the degree of humidity and prevent condensation. This method has been used by a large number of investigators. Engels, Thaer, and Czermack have found that lime, particularly calcium oxide, decreases the hygro-interstitial moisture. The amounts of lime which they used, however, were excessive.

Comparisons of the Rodenwald-Mitscherlish method with the other means of measuring internal surface have been attempted by Tadokoro, and Stremme and Aarnio. They find a good general agreement between the different methods. It should be pointed out in this connection, however, that a good general correlation is to be expected in comparing soils whose percentages of clay vary widely.

The possibility of the desiccation over phosphorus pentoxide having an influence on the colloidal material has been pointed out by Ehrenberg and Pick. They suggest that moist soil be placed in the desiccator or humidor and allowed to remain until equilibrium is obtained.

There are two main objections to the Rodewald-Mitscherlich method and its modifications:

. 1.   Too much time is consumed in waiting for equilibrium to be reached in any particular case.

2.   There is a high probable error in the method, due probably to the fact that diffusion permits only an approximation of true equilibrium conditions.

Blanck ran soils according to the Ehrenberg-Pick modification in one instance for a period considerably exceeding one hundred days, at the end of which time equilibrium had not been reached.

12.   The Dye Adsorption Method constitutes one of the standard means for determining the internal surface of soils.

Undoubtedly, there exists in the soil a great variety of colloidal substances varying in both chemical and physical condition. Four forms, namely, iron, aluminum, humus, and silica, have been generally recognized. This classification is of the crudest sort, and undoubtedly comes far from conveying an adequate conception of the variety of colloidal materials present. When we recall that the weathering processes usually increase the amount of colloidal matter, we might expect to find about as many colloids present in the soils as original rock sources. Rogers has made a review of the mineral kingdom, and finds a great number of minerals to be colloidal in nature. Many of them, we have reason to believe, exist in the soil, as, for instance, allophane, elemental carbon, opal, hematite, and limonite. Soils of volcanic origin probably contain pyrolusite and rutile.

The use of dyes in the identification of minerals has been undertaken by Pelet and Grand, Hundeshagen, Dittler and Cornu. Certain dyes are used which will be adsorbed by specific substances, and thus an attempt is made to identify the materials present. Unfortunately, it is not always possible to differentiate between the colloidal and crystalloidal matter. Furthermore, it is possible that colloids of approximately the same chemical composition may vary in their adsorptive powers for dyes. Such factors as the amount of water of hydration may quantitatively influence the results. Rohland and von Possanner find that talc and kaolin vary widely among themselves as to their adsorptive properties, and according to Bancroft, the nature of hydrous ferric oxide varies with the method of preparation.

It is possible that in the soil we have processes which tend to simplify the nature of the colloidal material. Lacroix, in a study of the decomposition products of the aluminum silicate rocks, concluded that the end product was hydrous aluminum oxide. Rohland holds the same view. In fact, it seems necessary to assume an hydrolysis of the silicates in order to explain the beneficial action following the application of calcium silicates to the soil. Whether hydrolysis takes place or not, the probabilities, nevertheless, are that in most soils we have a vast series of colloidal materials present, each varying somewhat in its qualitative and quantitative adsorptive power. It is, therefore, apparent that any dyestuff is only very roughly specific with regard to its adsorbent.

In view of the insolved nature of the subject, there has existed in the literature the greatest confusion with regard to the use of dyes on soils and the interpretation of the results obtained. However, the fact that certain dyes are adsorbed only by certain colloids when prepared in the pure state, permits our obtaining some idea as to the nature of the adsorbing material in the field. The weakness of the method consists in the fact that, owing to the variation in the properties of the colloidal matter, our evidence is circumstantial at best.

Before proceeding further, it seems necessary to discuss certain factors influencing dyestuff adsorption, and indicate their relation to soils work.

1. Nature of the dye. The opinion has existed in the soils literature that all dyes were equally valuable, as long as they were adsorbed. No idea could be more erroneous. Lyollema in 1905 found that certain dyes were specific for certain materials. The specificity of dyes has been worked out further by Rohland, and Beaumont; subject, of course, to the limitations reviewed in the preceding pages. We find that the azo dyes are adsorbed practically not at all. Rohland has tried to correlate this peculiarity of the azo dyes with certain molecular configurations. He finds safranine and indigo (the leuco indigo white?) to be specific for humus. Beaumont thinks diamine sky blue is adsorbed by colloidal aluminum. The tri-phenyl methane dyes are taken up by both humus and

silica. Methylene blue, while adsorbed slightly by humus and aluminum, is taken up in such enormous amounts by silica, that it may be rightly considered specific for the latter. The writer has found eosin to be admirably adapted for aluminum. No dye has yet been found which is satisfactory for hydrous ferric oxide. Summarizing, then, we have the following as the best suited for soils adsorption work.

Hydrous ferric oxide,—no dye.
Hydrous aluminum oxide,—eosin and diamine sky blue.
Humus,—safranine.
Silica,—methylene blue.

2. The concentration of the dye employed should be small. Within narrow limits, adsorption is a linear function of the concentration. The curve obtained by plotting the amount adsorbed against concentration ceases to be linear, however, on increasing the concentration of the dye solution. Further, the stability of the sol may be affected if the dye is too concentrated.

3. The dye should be stable irrespective of the reaction of the bath. All dyes which in alkaline solution are changed into the dye-base or leuco-base are unsuited for soils which give an alkaline filtrate on washing. Inasmuch as the great majority of soils render an aqueous solution alkaline, all colors exhibiting the above characteristics, as the tri-phenyl methane dyes, for instance, should be discarded. Unfortunately, this includes the greater portion of the colors used in the past, as crystal, methyl, and gentian violet, aniline blue, aniline green, aniline red, methyl green, malachite green, etc. Changing the reaction of the solution after adsorption is usually not sufficient to restore the color to the dye, since alkalinity may reduce the dye-base to the leuco form. Oryng, and Adams and Rosenstein have called attention to the difficulties inherent with the triphenyl methane dyes. It is not surprising that Gedroits, using crystal and methyl violet, found no relation between colloidality and adsorption.

Another potential source of error lies in the fact that alkali may unite with the dye and form a lake. This is what happens in the case of alizarine, one of the dyes recommended by Ljollema. Tadokoro, in selecting a color for his work, chose eosin, because it was stable in acid or alkaline, but he overlooked the fact that eosin is specific for hydrous aluminum oxide. We probably obtain no eosinic lake formation in the case of adsorption by soils. Too much care cannot be taken that the dye is stable under all conditions.

4. The reaction of the solution should not affect the adsorption equilibrium. In the textile industries the amount of dye taken up in any particular case is largely determined by the degree of reaction of the bath. The subject is summarized by Bancroft as follows:

The following holds for an acid dye:

a.   The dye is taken up most readily in an acid solution but may be taken up in a neutral or alkaline solution.

b.   A readily adsorbed anion decreases the amount of dye taken up.

c.   A readily adsorbed cation increases the amount of dye taken up.

The effect of the reaction on dye adsorption has been extensively studied by Bancroft, and by Pelet-Jolivet and his co-workers.   If the amount of salt in a sample of soil is large, the final equilibrium may be affected.   In order to use the dye method as a measure of internal surface, we must satisfy ourselves by preliminary experimentation that the salt is present in too small an amount to influence the degree of adsorption.   It is readily apparent that we should use small charges of soil, particularly if fertilizers have been added, for the amount of salt per unit concentration of dye increases directly with the amount of soil used.   Ruprecht and Morse in their ammonium sulfate studies, found that the amount of dye taken up by the soil was increased after fertilizer treatment.   We have no means of knowing from their work, however, whether the increase was due to the influence of the ammonium sulfate on internal surface, or whether it was the result of the changed reaction of the bath.   The effect of the added material on the adsorption equilibrium has been in the past entirely overlooked in soils work.

5.   The protective action of organic matter on colloidal material has been recognized by a number of investigators.   In running experiments on mineral colloids it is desirable to use soils as free from organic matter as possible.

13.   Selective adsorption has been used by many investigators as a means of estimating internal surface.   Heiden, Parker, and König, Hasenbäumer, and Hassler are only a few of those who have taken the adsorptive power of the soil for potassium as a measure of the internal surface involved.   The results lose their significance, however, when we recall that the soil contains a number of different kinds of colloidal material, each varying in its specificity with regard to adsorption.   Thus, Thaer finds that the potassium ion is not adsorbed by colloidal humus, and Lokolovskii observes the same thing for the ammonium radical. Daikuhara believes that the adsorption of the potassium ion is characteristic of the colloidal iron and aluminum.   The possibility of interchange of bases tends to further confuse the phenomenon.   It is, therefore, not surprising that some workers, as Tadokoro, have failed to establish an agreement in the results from selective adsorption and some of our other more valuable methods.

14.   The Histological Method for the determination of colloids in clays was proposed by Endell.   The dry clay is boiled in Canada balsam, and after cooling and hardening it is cut into small sections and colored with fuchsin.   This method has been discussed by Cornu.   Owing to the sim-

plicity of certain other procedures, the histological method has never come into general use.

15. Expansion methods are nearly as old as soil physics itself. In 1838, Schübler began work on the subject, and his investigations have been continued by Haberlandt, von Schwarz, Puchner, and Wollny. The lime studies of Thaer and Engels resulted in the conclusion that there was a slight increase in volume on liming. In all the above cases the soils were allowed to come to dryness before making final measurements. Tempany (1917) finds that in drying down, internal friction between the soil particles becomes very great. This raises the question whether measurements after drying are particularly significant. Brown and Montgomery, in a study of the dehydration of clays, finds that shrinkage is no criterion of plasticity. Furthermore, it appears just as objectionable to make measurements from a dry to a moist condition, as vice versa. R. O. E. Davis cites data from Wollny in which the latter found that a dry soil moistened with water expanded six times as much as the same soil moistened with calcium hydrate solution!

Wolff, and more recently Tadokoro, have studied the swelling exhibited by soils after being immersed in various reagents. This work is open not only to the objections already mentioned, but is also subject to the further criticism that swelling may be specific for the reagent employed. If expansion readings are made at a constant moisture content, we largely eliminate imbibitional factors, and may more correctly attribute differences to changes in soil structure.

16. The cohesion method for the investigation of soil properties was first used by Schübler, who added a gradually increasing weight to a scale pan suspended from the middle of the dry brickette to be tested. This procedure has been used by Fippin in his investigation of the effect of lime on granulation. The Schübler method has been modified by Puchner, who suspends the scale pan above the knife edge entering the soil. The Atterberg procedure is essentially the same as that of Puchner, except that the scale pan is supported by a superstructure. The penetration method has been used by Cameron and Gallagher, and by R. O. E. Davis for measuring coherence. The greater portion of their work is unconvincing because they failed to calculate the probable error of their determinations. Thaer and Engels have made penetration measurements in their work, but unfortunately the amounts of lime used were excessive.

It would seem that penetration determinations should be made at a constant moisture content for essentially the same reasons as in the case of shrinkage. On bringing to air dryness, certain cementing materials undoubtedly come into play which are not operative under ordinary conditions.

17. The Dynamometer Method consists in measuring the resistance offered to the passage of a plow through the soil. A spring is connected

with a revolving drum in such a manner as to record the traction at any particular moment. We would expect that the summations of the values obtained from various lime plats, for instance, would indicate the effect of the lime on the physical condition of the soil. Work along this line has been undertaken by Mausberg and by Noll. Unfortunately the probable error involved is so high that experiments must be carried through a long series of years before significant results are obtainable.

18. The Oxidative Power of the soil has never been used as a method for the estimation of internal surface. There seems no reason to doubt, however, that oxidation is in large part a surface phenomenon. The great ability of colloidal humus and hydrous ferric oxide to cause oxidation, as indicated by the work of Schreiner and his co-workers, would suggest that oxidation may be a specific and not a general phenomenon.

Aloin is not suited for measurements of internal surface, owing to the fact that it is catalyzed by alkalies. An aloin solution will "keep" for only a few hours because of the presence of alkali dissolved from the container. An aloin solution will keep indefinitely if a small amount of acid is added when the solution is first made. The question arises in this connection whether Schreiner and Sullivan's study of the oxidizing power of soil extracts is particularly significant.

Phenolphthalin is more satisfactory for estimating internal surface. It is convenient to read, and, unlike aloin, is very stable towards the atmosphere. One precaution to be observed, is to avoid the use of a strong alkali in bringing out the full color of the phenolphthalein before reading. In a strongly alkaline solution the phenolphthalein is converted into the colorless leuco-base. Ammonia is a very satisfactory alkali to use in this connection.

It is frequently desirable to clarify the solution with a precipitant, just prior to rendering the solution alkaline. If a soil has been rendered strongly basic by a salt treatment, the humus brought into suspension may modify the pink color to such a degree as to make a previous precipitation imperative.

DISCUSSION

In the preceding exposition we noted that the analogy between the suspension method and conditions as they actually exist in the soil, was not very close. There is no reason to doubt, however, that the fundamental phenomena involved are essentially the same, the differences being simply a matter of degree. Cameron takes the point of view that there is no basis for attributing surface action to colloids, and Gedroits holds a similar opinion, on account of the small colloidal content of any soil. On taking into consideration the large internal surface involved on even a slight subdivision of any material, however, it is found unneces-

sary to stipulate any other action to account for the surface phenomena which take place.

A consideration of the literature on the effect of lime salts on flocculation reveals an unusual amount of confusion. The relation of valence to flocculating power has long been appreciated, but unfortunately investigators are just coming to realize that the question of active masses is of equal importance. For instance, sodium salts of weak acids are flocculents or deflocculents according to the relative concentrations of precipitant and material being precipitated. This question has been discussed in detail by Given, Wolkoff, and Wiegner.

Rohland believes that on liming, the precipitating power is due to hydroxyl ions, and with calcium hydrate, the action is direct. With cases in which gypsum is applied, Rohland would assign the beneficial result to the precipitating power of the hydroxyl ions formed on the decomposition of the salt. Here again, the various colloidal materials present in the soil tend to further confuse the phenomenon. Pappada finds that the hydroxyl ion is the most powerful in the precipitation of hydrous ferric oxide. Rohland's view would hold in so far as the positive colloids are concerned, but it would not hold for the negative. A soil suspension is usually negative, but there is no ground to believe that the colloidal material in the soil is entirely precipitated by cations or other bodies positively charged.

Ehrenberg holds that the cation is the important flocculating agent. He ascribes a strong action to the calcium ion, and virtually none to the hydroxyl. Therefore calcium hydrate is the strongest flocculent of the lime salts. On increasing the strength of the acid in the salt, the precipitating action becomes less and less, until in the case of gypsum, we have practically complete antagonism. Ehrenberg's theory is better than Rohland's just in so far as it better describes the actual state of affairs. As a matter of fact, both views are extreme. A solution of the question lies in the recognition of the complex nature of the colloidal material, and the fact that flocculation is a matter of relative charges, masses, and valencies.

In past studies on the physical effect of lime on the soil, the tendency has been to make applications on a percentage basis. For example, a favorite custom has been to use one per cent of lime, and there is one instance in the literature in which one part of lime was added to four parts of soil. In view of the relation of masses to precipitation, and furthermore, the wide departure from field practice involved, the question naturally arises whether the results from such experiments are particularly significant. The work of Blanck, Thaer, and Engels, the lime studies most frequently quoted, are all open to the objection that the applications used were excessive. Unfortunately the methods available for physical studies have not been sufficiently accurate to be used in

work with comparatively small salt applications. In the present investigation, an attempt was made to obtain data from applications equal to and smaller than the lime requirement of the soil, in order to more nearly approximate field conditions.

EXPERIMENTAL STUDIES

All the soils used were of the Dunkirk silt loam series, and were obtained from two stations on the Cornell University farm. In addition, work was undertaken with samples from the lime plots on Caldwell Field. All the soils analyzed approximately the same mechanically.

TABLE I. MECHANICAL ANALYSIS OF DUNKIRK SILT LOAM SOILS

	Soil Tech. Plats and Station I	Station II
Total sands	13.9%	9.8%
Silt	67.4	71.9
Clay	18.6	18.3

Unpublished results of bulk analyses give:

TABLE II. BULK ANALYSES OF DUNKIRK SILT LOAM SOIL
(From 9 samples of Tompkins County soil)

	Surface %	Subsoil %
C. (organic carbon)	1.670	0.440
CO_2	trace	0.260
K_2O	1.740	2.110
CaO	0.430	0.830
MgO	0.450	0.690
Na_2O	1.090	1.280
N	0.186	0.082
P_2O_5	0.123	0.126

In sampling the soil in the field, care was taken to get well down below the sod line in order that organic matter be excluded as far as possible. The material was brought in to the laboratory, put through a coarse sieve, and well mixed. The soil had an acidity of 3000 pounds of calcium oxide per acre, as determined by the Veitsch method. All the limes used were 200 mesh, and pots were set up with calcium hydrate, limestone, precipitated calcium carbonate, gypsum, and precipitated calcium sulfate. In addition, studies were conducted with precipitated basic magnesium carbonate, and sodium carbonate. The limes were added in molecularly equivalent amounts, and proper corrections were made

for magnesium in the limestone (it was nearly pure), and for water of hydration. Applications were made in the equivalents of one-half, one and one-half, four and one-half, and ten tons of calcium oxide per acre, taking two and one-half million pounds as the weight of an acre— eight inches of soil. The one and one-half ton treatment exactly corresponded with the lime requirement of the soil. Into each pot was weighed the equivalent of 253 grams of oven soil. The container was given a prolonged tamping, two thicknesses of cotton gauze added, and finally a mulch of washed quartz sand placed on top to a thickness of one centimeter. Aerated distilled water was added to bring the pots up to 24 or 28 per cent water content, at which they were maintained for the remainder of the experiment. (Note: all references to water content in this treatise are on an oven dry basis.) A portion of the series were set up in triplicate; the rest in quadruplicate. The duration of the experiments was 45, 100, and 225 days. On the expiration of the required time, the mulches were removed, the soil sieved (20 mesh), dried down to 7-10 per cent, and bottled. The soils were never allowed to reach air dryness.

In the exposition on procedures for estimating internal surface, eighteen methods were examined as to their respective merits. We found that the great majority are for one reason or the other inaccurate. Six of them were used in the present investigation, namely,—

1. Penetration.
2. Expansion.
3. Total retentive power.
4. Dye adsorption.
5. Hygro-interstitial water.
6. **Oxidative power.**

EFFECT OF SALTS ON PENETRATION

The apparatus used for the measurement of penetrability was the Atterberg apparatus as improved by Prof. H. O. Buckman of Cornell University. The feature worthy of particular attention is the device for controlling the distance that the pin enters the soil. With the pin point flush with the surface of the soil, the mercury well may be set so that the metal point on top just makes contact with a similar point on the piston. The distance from this position to the surface of the mercury is constant, and represents the distance which the pin penetrates. Water is used to give the gradually increasing force to the head of the piston. On receiving the signal from the sounder, the water is stopped, and the weight in the container is determined. This value represents the penetrability of the particular soil concerned.

A series which had run for 100 days was used for the penetration determinations, and in order to avoid the results incidental to air drying,

readings were made when the moisture percentage of the soil was between 14-15 per cent. Five readings were attempted in each pot, and since the series was in triplicate, fifteen readings per treatment were obtained.

TABLE III.   PENETRATION IN GRAMS OF SOILS LIMED FOR 100 DAYS
(Each figure is the average of 15 determinations)

	Checks (no treat.)	Ca(OH)$_2$	Lime-stone	pCaCO$_3$	Gypsum	Na$_2$CO$_3$
½ T	. . . .	1148	1716	. . . .	2157	4137
P. E.	. . . .	115	39	. . . .	159	339
1½ T.	. . . .	709	1046	2374	1912	4499
P. E.	. . . .	196	37	152	182	451
4½ T.	787	392	904	2294	1832	4678
P. E.	83	29	27	117	132	534
10 T.	. . . .	306	694	. . . .	1737	3722
P. E.	. . . .	15	34	. . . .	73	387

While the probable error in some cases is rather high, nevertheless, we may draw the general conclusion that calcium hydrate decreases surface penetrability more than any of the other salts tried. One thing worthy of note is that calcium carbonate seemed to increase the value when used in small amounts. Unfortunately the question of crust formation enters in, and tends to confuse the results. There is virtually no hardening on the surface of the untreated soil, while those to which has been added a half a ton of lime per acre may form quite a tough crust, as in the case of the gypsum treatments. What our results indicate, then, is that calcium hydrate causes the formation of a less impervious crust than any other lime. If the penetration method is to be used as a measure of the internal and not the surface condition, the crust must be removed.

Penetration studies on the interior portion of the soil were attempted. Brass pins of various shapes and sizes were advanced into the soil with the ratchet of the micrometer used in connection with the expansion studies. The distance that the ratchet forced the pin into the soil was read directly on the micrometer scale. (The crust had been removed.) The results failed to show significant differences between the different salt treatments. We may therefore conclude that the influence of salt treatment is primarily on crust formation, in so far as the penetration method is a proper criterion. It cannot be used for very sensitive measurements, because it is subject to a number of uncontrolled factors.

EXPANSION STUDIES

It was evident from the preliminary discussion that we would expect flocculation and expansion to go hand in hand. Furthermore, it seemed that expansion studies should be conducted at a constant moisture con-

tent. In order to observe expansions under these conditions, a series which was running for 100 days was selected for special experimentation. Measurements were made according to a method suggested by Professor J. A. Bizzell of Cornell University. A ratchet micrometer was fastened to a standard so that the spindle head could play on a brass pin which projected three-fourths of an inch above the surface of the soil. The pin passed perpendicularly through the middle of a small brass plate, the latter resting on the soil surface. The pin was further steadied by a projection passing down into the soil. A reading was made by lowering the micrometer spindle gently in to the pin, until there was a constant "pull" on the slip of thin paper inserted between pin and spindle. This method is accurate to the hundredth of a millimeter.

In setting up the experiment, pins were placed on the one-half, one and one-half, and ten ton treatments only. The initial reading was made three hours after the pots had been brought up to weight. During the course of the experiment readings were taken from time to time; in each case, however, 24 hours after watering, inasmuch as approximately 24 hours were required to evaporate the water from the quartz mulch.

EFFECT OF TIME AND SALTS ON SOIL EXPANSIONS

(Each figure in the following data is the average of quadruplicate determinations. The values all have a negative sign, i. e., there was contraction in every case. Readings are in mm.)

Treatment	14 Days	25 Days	35 Days	45 Days	90 Days
No. treatment	1.76	2.14	2.44	3.31	3.33
P. E.	.18	.27	.25	.26	.34
Ca(OH)$_2$					
½ T	1.49	1.85	2.19	2.76	3.31
	.20	.09	.07	.09	.08
1½ T	.88	1.31	1.59	2.17	2.60
	.12	.17	.21	.14	.18
10 T	.34	.58	.79	1.22	1.39
	.03	.02	.03	.02	.03
Limestone					
½ T	1.20	1.56	1.76	2.31	2.68
	.18	.18	.15	.18	.32
1½ T	1.61	1.95	2.35	2.86	3.21
	.13	.13	.14	.15	.15
10 T	.55	.70	1.03	1.49	1.72
	.08	.10	.09	.10	.13
p. CaCO$_3$					
½ T	.98	1.50	1.84	2.44	2.96
	.15	.23	.27	.30	.49
1½ T	.86	1.35	1.76	2.33	3.03
	.07	.....	.....	.....	.....
10 T	.90	1.46	1.74	2.31	3.03
	.04	.08	.04	.04	.07
p. CaSO$_4$					
½ T	.57	1.03	1.21	1.67	1.97
	.12	.14	.12	.12	.18

EFFECT OF TIME AND SALTS ON SOIL EXPANSIONS—Continued

Treatment	14 Days	25 Days	35 Days	45 Days	90 Days.
1½ T	.71	1.33	1.55	1.89	2.20
	.11	.15	.15	.06	.09
10 T	.77	1.06	1.22	1.73	1.87
	.04	.04	.04	.06	.08
p. MgCO₃ (basic)					
½ T	.92	1.49	1.86	....	2.95
	.08	.15	.16	....	.18
1½ T	1.28	2.11	2.46	....	3.47
	.19	.17	.18	....	.25
10 T	1.73	2.05	2.26	....	3.71
	.18	.29	.25	....	.44
Na₂CO₃					
½ T	......	......	......	.89	1.19
				.13	.25
1½ T	......	......	......	.89	2.02
				.44	.51
10 T	......	......	......	3.24	3.83
				.60	.67

We see from the above data that the contraction with the calcium hydrate treatments is decidely less than with the limestone. There is not much difference between the limestone and precipitated carbonate data when small applications were employed. The limestone seemed to be superior to the precipitated carbonate, however, when large applications were used. There was less contraction with the soils to which precipitated calcium sulfate had been added than with any of the others. In this connection it should be noted that a smaller contraction than the check does not necessarily imply a greater expansion. Anything causing an abnormal solidification of the soil mass may be wrongly interpreted as an expansion. In the case of the sodium carbonate pots we probably have this action. The precipitated magnesium carbonate seems to exert no particularly striking effect.

EFFECT OF LIMING ON THE TOTAL RETENTIVE POWER

The determinations were carried out in the following manner: A soil of known moisture content was poured into a weighed Hilgard cup, in the bottom of which was a filter paper. After tamping a definite number of times the top portion was struck off with a straight-edge, and then the cup and soil weighed. Knowing the moisture content of the soil, the dry weight equivalent in the cup could be easily determined. The cup was then set into water in a thermostat so that there would just be capillary contact. After the soils had become thoroughly saturated (a matter of several hours), the cups were set aside to drain, after which they were wiped dry, and weighed. A calculation of the amount of

capillary water taken up by the soil, based on the oven dry weight, was then made.

Below are tabulated the results with treatments which had run for 100 and 225 days, respectively. Each figure in the following tables is an average of six or eight determinations.

RETENTIVE POWER OF SOILS LIMED 100 DAYS: SERIES I

Treatment	Ca(OH)$_2$	Lime-stone	p. CaCO$_3$	Gypsum	Na$_2$CO$_3$	Checks
½ T	49.1	50.1	51.6	52.8	52.2	....
P. E.	1.6	1.1	.9	.6	1.6	....
1½ T	50.5	51.5	52.0	53.4	47.6	....
P. E.	1.2	1.1	.9	1.2	.6	....
4½ T	49.0	51.0	51.6	56.2	44.5	50.3
P. E.	1.7	1.2	.9	1.1	.5	1.1
10 T	49.2	49.3	50.9	54.3	48.2	....
P. E.	1.6	2.0	1.3	.8	.8	....

RETENTIVE POWER OF SOILS LIMED 100 DAYS: SERIES II

Treatment	½ T.	1½ T.	10 T.	Checks
Ca(OH)$_2$	57.1	55.3	56.5	....
P. E.	1.0	1.0	.5	....
p. CaCO$_3$	59.3	56.9	59.3	....
P. E.	.8	.9	.3	....
Limestone	56.2	57.9	55.3	56.8
P. E.	2.34	1.6	1.9	.3
p. CaSO$_4$	54.7	57.6	54.4	....
P. E.	3.5	1.4	1.1	....
Na$_2$CO$_3$	49.6	47.1	48.0	....
P. E.	.6	.7	.4	....
M. MgCO$_3$	54.6	54.4	58.7	....
P. E.	.9	1.8	.8	....

RETENTIVE POWER OF SOILS LIMED 225 DAYS: SERIES I

Treatment	Ca(OH)$_2$	Lime-stone	p. CaCO$_3$	Gypsum	Na$_2$CO$_3$	Checks
½ T	51.3	48.3	51.9	54.1	51.0	....
P. E.	.6	1.0	.4	1.3	1.5	....
1½ T	52.1	50.2	55.1	52.8	46.7	53.1
P. E.	.5	1.6	.6	.5	1.5	.4
4½ T	50.8	52.0	56.2	52.2	47.2	....
P. E.	.5	1.2	.3	2.3	1.2	....
10 T	51.0	49.4	54.0	50.6	50.2	....
P. E.	.8	.2	.1	1.2	.1	....

It may be readily observed that none of the salts affected the total retentive power in the case of the salts run 100 days, with the exception of the sodium carbonate. With the 225 day treatment, however, we find that both calcium hydrate and limestone have caused a slight decrease in water holding capacity. The precipitated carbonate may act in just the opposite direction. The gypsum is without effect.

DYE ADSORPTION STUDIES

In the preliminary discussion, attention was called to the fact that certain factors affecting dye adsorption have been entirely overlooked in studies with soils. Perhaps the most important of these factors are, the stability of the dye, and the effect of salts on the adsorption equilibrium. There are, however, several other questions that arise in this connection:

What is the influence of the time of shaking on the adsorption equilibrium, and

Does the mechanical agitation incidental to shaking tend to destroy the flocculated condition, and hence affect the degree of adsorption?

In order to study the effect of time of shaking, adsorptions were run and terminated at regular intervals. Using two grams of Dunkirk silt loam in methylene blue, it was found that complete equilibrium was reached in from one to two hours.

The effect of mechanical agitation on adsorption was studied by adding two grams of soil to solutions in shaker bottles, the latter containing the amount of salt that would be carried over in a two gram charge of soil treated at the rate of 10 tons per acre. After shaking two hours, a few cc. of a concentrated methylene blue solution was added, and the shaking continued for five minutes longer. The results showed that final equilibrium had not been affected by the salts present, with the exception of the sodium and magnesium carbonate treatments, and in these cases we do not have to postulate any change in stability of the colloidal material, inasmuch as the solutions were very alkaline, and hence could affect the adsorption equilibrium. The subject was studied still further by running adsorptions in methylene blue, and determining whether the final result was the same irrespective of the salt present. Here again, the sodium and magnesium carbonates were found to increase adsorption somewhat.

Adsorption experiments with methylene blue were run as follows: The equivalent of 2 grams of oven soil was weighed into the shaker bottle containing 100 cc. of the dye (.25 gram per litre). After shaking two hours, the clear supernatant solution was read against a standard. The results with soils which had been limed for 100 and 225 days are as follows:

ADSORPTION OF METHYLENE BLUE BY SOILS TREATED FOR 100 DAYS
(Readings in divisions equivalent to 100 of standard)

Treatment	$Ca(OH)_2$	Lime-stone	p. $CaCO_3$	Gypsum	Checks
½ T	272	217	144	180	. . . .
1½ T	208	190	159	153	235
4½ T	153	163	112	118	. . . .
10 T	70	143	100	110	. . . .

ADSORPTION OF METHYLENE BLUE BY SOILS TREATED FOR 225 DAYS

Treatment	$Ca(OH)_2$	Lime-stone	p. $CaCO_3$	Gypsum
½ T	183	210	168	114
1½ T	162	151	163	95
4½ T	117	138	140	106
10 T	57	139	133	82

Each figure in the preceding tables is the average of triplicate determinations. While calcium hydrate decreases adsorption the most when 10 ton treatments are used, precipitated carbonate and gypsum are more efficient with slight applications.

Studies were conducted with safranine in order to observe the effect of salts in the adsorptive power of the organic matter. Preliminary experiments indicated that adsorptions could not be conducted with safranine in the presence of sodium and magnesium carbonates. The results are as follows:

ADSORPTION OF SAFRANINE BY SOILS TREATED FOR 45 DAYS

Treatment	Check	$Ca(OH)_2$	Lime-stone	p. $CaCO_3$	Gypsum
1½ T	. . . .	52	52	62	60
10 T	51	44	45	42	62

ADSORPTION OF SAFRANINE BY SOILS TREATED FOR 225 DAYS

Treatment	Check	$Ca(OH)_2$	Lime-stone	p. $CaCO_3$	Gypsum
1½ T	. . . .	47	60	61	34
10 T	51	42	61	61	34

With the soils treated for 45 days, liming seemed to decrease the adsorptive power when applied in excessive amounts. The same applies to calcium hydrate and gypsum for the 225 day treatments. On the other hand, limestone and precipitated carbonate increased the adsorptive power slightly. It may be that the analogy of internal surface does not apply to organic matter, and that the influence of salts on the adsorptive power is primarily chemical rather than physical.

Adsorption experiments were conducted with diamine sky blue and with diamine violet, both of which are specific for hydrous aluminum oxide. Unfortunately neither is stable in the presence of very much electrolyte, and experiments could be conducted with soils which had been limed not to exceed a ton and a half per acre. The tests failed to show any differences in adsorptive power. In other words, limes do not precipitate hydrous aluminum oxide when added in the equivalent of a ton and a half per acre. The writer has found eosin to be much better than either of the above dyes for the study of the adsorptive power of aluminum. Its adsorptive equilibrium is not influenced by salts present in solution in the equivalent of 10 tons per acre.

ADSORPTION OF EOSIN BY SOILS TREATED FOR 45 DAYS

Treatment	$Ca(OH)_2$	L. S.	p. $CaCO_3$	Gypsum	Na_2CO_3	Checks
1½ T........	56	58	51	45	54	54
10 T.........	45	45	40	41	48	....

ADSORPTION OF EOSIN BY SOILS TREATED FOR 225 DAYS

Treatment	$Ca(OH)_2$	L. S.	p. $CaCO_3$	Gypsum	Na_2CO_3	Checks
1½ T........	26	25	24	25	22	30
10 T.........	24	24	24	25	23	....

It seems from the above data that all limes precipitate aluminum to some degree. Probably gypsum has a stronger action in this respect than any of the others.

Taking the adsorption data as a whole, it appears that the primary effect of liming is the precipitation of the silicic acid, as indicated by the methylene blue tests. The influence of lime is noticeable, even when added in very small amounts. Indirectly, we also get a precipitation of the aluminum, and perhaps the organic matter. Any statement as to the effect on the colloidal iron will have to be deferred until a suitable dye is obtained.

HYGRO-INTERSTITIAL MOISTURE STUDIES

In view of the unsatisfactory results obtained by the Rodewald-Mitscherlich method, it seemed desirable to revert to the type of procedure used in the beginning. The writer has been fortunate in obtaining a method which is free from errors due to condensation, and is at the same time exceedingly accurate. Preliminary work with this method indicates that liming seems to have no significant effect on hygro-interstitial moisture in amounts equivalent to the lime requirements of the soil. Excessive applications decrease the value.

OXIDATION STUDIES.

The work was conducted as follows: The equivalents of four grams of soil were weighed into 8-oz. bottles, and 50 cc. of phenolphthalein solution added. After oxidation had progressed satisfactorily, the solutions were cleared of humus and suspended matter with hot alum solution, an aliquot made alkaline with ammonia, and read against a standard. The results are as follows: (Each figure is the average of three determinations. The probable error is approximately a plus or minus two).

OXIDATION OF PHENOLPHTHALEIN BY SOILS TREATED FOR 100 DAYS

Treatment	Check	Ca(OH)₂	L. S.	p. CaCO₃	p. CaSO₄	Na₂CO₃	p. MgCO₃
½ T.	75	97	87	100	76	95	82
1½ T.	......	88	72	98	58	95	71
10 T.	......	104	63	71	50	86	47

OXIDATION OF PHENOLPHTHALEIN BY SOILS TREATED FOR 225 DAYS

Treatment	Checks	Ca(OH)₂	L. S.	p. CaCO₃	Gypsum	Na₂CO₃
½ T.	....	71	62	63	46	61
1½ T.	76	82	72	72	45	53
10 T.	....	88	75	73	57	52

The data for the soil run 225 days goes just about as we would like it to go. We get the greater oxidation in soils in which we would expect the greater internal surface, and we obtain a decrease in oxidation with increasing applications of lime. The results for the soils run 100 days are not quite so satisfactory. It may be that in certain cases an exchange of bases results in the release of substances which catalyze the reaction.

STUDIES WITH PLAT SOILS

An attempt was made to determine whether differences could be observed between soils from limed and unlimed plats, using our methods for estimating internal surface. Accurate samples of the surface and subsoil were taken from plats 7007, 7008, 7207, 7208, 3611, 3612, 3613, and 3614. The seven thousand plats received a moderate application of CaO in the summer of 1915, while the three thousand plats were last limed in the summer of 1910. The soils were examined according to the total retentive power, dye adsorption, and oxidation methods. None of the results were consistent with regard to the limed and unlimed plats,—with one exception,—the oxidation results for the seven thousand plats.

OXIDATION OF PHENOLPHTHALEIN BY LIME PLAT SOILS

Soil	Description	Comparative Figure
7007	Unlimed	59.5
7008	Limed	63.0
7207	Unlimed	93.0
7208	Limed	106.0

The above figures are averages of duplicate determinations, and the probable error is less than one. We may conclude that several years time are usually sufficient to virtually obliterate all physical differences between limed and unlimed soils.

DISCUSSION

Six methods have been employed in the present investigation. We have observed that the total retentive power and penetration procedures are not particularly valuable because of the high probable error involved. The oxidation method has not been used sufficiently as a means of estimating internal surface to permit its appraisement at the present time. Expansion, hygro-interstitial moisture, and dye adsorption seem to be accurate and valuable methods. It appears to the writer that the dye method has the brightest future of all, for it permits the determination of the effect of substances in specific materials.

CONCLUSIONS

1. The penetration method is not a suitable procedure for estimating internal surface.

2. Small contraction exhibited by a salt treated soil does not necessarily imply large expansion.

3. Gypsum treated soils contracted less than any other lime treatment.

4.   Gypsum appears to be an active precipitant of silicic acid and hydrous aluminum oxide.

5.   New methods for the determination of soil expansions and hygro-interstitial water have been devised.

6.   Liming in amounts equivalent to the lime requirement of the soil has no effect on the hygro-interstitial water.

7.   Calcium hydrate is only slightly more valuable as an ameliorating agent than limestone.

8.   The physical effect of precipitated magnesium carbonate on the soil is nil.

9.   The dye adsorption method has the greatest possibilities of all methods for estimating internal surface.

10.   The primary effect of liming is on the silicic acid.

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