

**THE PHYSICAL
ACTION OF LIME
ON CLAY SOILS**

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The physical action of lime on clay soils by Robert Mifflin Snyder

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ROBERT MIFFLIN SNYDER

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A THESIS

**PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
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DOCTOR OF PHILOSOPHY

BY

ROBERT MIFFLIN SNYDER

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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 Colloidalilty

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.

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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 charged 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 Thær'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 colloidalty. 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, Thær, 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 Rodewald-Mitscherlich 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.