

THE EFFECT OF ACIDITY ON SOME SOIL PROCESSES

by

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A. B., Tarkio College, 1934

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A THESIS

submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1941

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## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION .....	1
REVIEW OF LITERATURE .....	3
EXPERIMENTAL PROCEDURE .....	16
Soil Material Used .....	16
Treatment .....	17
Mechanical Analysis .....	18
Base Exchange Determinations .....	22
Procedure for Determining Phosphorus Fixation .....	23
DISCUSSION OF RESULTS .....	26
General .....	26
Mechanical Analysis .....	27
Base Exchange .....	29
Phosphorus Fixation .....	31
SUMMARY .....	36
CONCLUSIONS .....	37
ACKNOWLEDGMENTS .....	38
REFERENCES .....	38

## INTRODUCTION

It is general knowledge that soil acidity retards the growth of legumes and that soils of extreme acidity are generally non-productive. It is also generally accepted that liming these acid soils increases crop production.

This knowledge of increasing yields by the application of some form of lime is not new. Collings (1934) told of Pliny recording the use of some form of lime on Roman fields as early as 200-300 B. C. Weir (1936) indicated that Columella about 45 A. D. advocated soil improvement through the use of manure, green manure, chalk or marl, and ashes. Weir also stated that the Celts, who gained their greatest power in central and western Europe about 500 B. C. knew of the beneficial effects of chalk or marl on soil used for crops. Medieval farmers used chalk or marl in places but not as an extensive practice due to the general turbulence of the period. By 1600 marl or chalk was used extensively in English Agriculture and from evidence of old marl pits its use must have been introduced at a very early date, probably with the introduction of Roman culture, and was revived during the Renaissance.

Truog (1938) related that the liming of land was practiced in a few places during the colonial period but was not extensively practiced in the United States during the nineteenth century except in Pennsylvania. However, through the

pioneer efforts of Frear of Pennsylvania, Hopkins of Illinois, and Wheeler of Rhode Island, liming of acid soils has become accepted as a necessary practice by agriculturalists and essential for economic crop production, efficient soil conservation, and permanent agriculture in this country.

This interest in the use of lime on humid soils has been because of the increase in yield directly of legumes and indirectly of non-legumes. An agricultural practice gains favor because of its beneficial effects in economical production. This is evidenced by the increased use of lime in the United States as a soil amendment. Truog (1938) indicates that 6,305,426 tons of liming materials were used in 1936 as compared with 3,736,367 tons in 1929 and 1,627,057 tons in 1933. He also says this is far below the amount necessary to bring the crop land up to a satisfactory lime level and estimates that Wisconsin alone would need 15,000,000 tons to reach this level, and 1,000,000 tons annually to maintain it.

With our increased knowledge of the nature of the soil colloidal complex, ion exchange and fixation phenomena, the question arises, however, as to what effect does liming have on the soil body itself? As far as is known this question has been but little studied though its importance is recognized, for Truog (1938) indicates that the function and action of lime when applied to soils should be further studied.

The purpose of the present study was to investigate the effect of lime on the minerals composing some colluvial soil material when this material was subjected to acid treatment. The general plan was to use relatively unweathered soil material containing some free  $\text{CaCO}_3$  and leach it with solutions of varying pH and after a period of treatment compare the different samples as to amount of given separates<sup>1</sup>, base exchange capacity, and phosphorus fixation.

#### REVIEW OF LITERATURE

The literature dealing with the specific problem of the effect of lime on the soil body is very limited. For this reason it was thought best to review some papers dealing with the soil minerals themselves, and their influences on the processes whereby it was hoped to indicate changes due to the conditions of this study. In a general way this review will take the following outline: (1) The minerals which make up the soil body, (2) the possible change in character of these minerals in the soil, (3) soil factors affecting base exchange capacity, and (4) soil factors affecting phosphorus fixation.

It is an accepted fact that soils are composed of a complex mixture of mineral and organic matter, in most cases so weathered that their original properties have disappeared.

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<sup>1</sup> The soil divided into separates according to particle size determined by settling times in water.

This complexity and fineness of particle size of soils limited the early study of their mineral composition to the coarser fractions, nothing finer than the very fine sands and silts, or those particles which could be studied with the petrographic microscope and other mineralogical techniques. By these methods McCaughey and Fry (1913) identified and determined the specific gravity of 100 minerals occurring in various soils. Not all these occurred in all soils but certain ones predominated in each type depending on its parent material and the active soil forming agencies. Also Jeffries (1937) after a careful study of the very fine sand fraction of five Pennsylvania soils reported twenty-two different minerals in these sands. Some of these minerals can be identified as being primary or have the same composition as the original unweathered material and others are secondary or are the result of weathering agencies, either being partially decomposed or having formed as new minerals from constituents of the original ones. McCaughey and Fry (1913) assumed that since these minerals composed the sand and silt fractions they were also prominent constituents of the clay portion only being much finer.

The idea that the clay fraction contained large amounts of unaltered soil-forming minerals, differing from those of the silt and sand fractions only in size, was held generally by the early soil investigators, is indicated by Robinson and Holmes (1924). However this conception did not explain



base exchange phenomena as fine mechanically comminuted minerals did not exhibit this property to a great degree. To explain base exchange it was assumed some zeolite minerals were present but on investigation these could not be found. At the time of their (Robinson and Holmes) investigations, then, most soil scientists believed that the colloidal portion was of a gel-like nature resembling the artificial gels of silica, iron, and alumina.

Robinson and Holmes (1924) made chemical analyses of the colloids of 45 important soils of different texture ranges and various conditions of formation. From a study of their data and discussions the following conclusions can be drawn:

1. The colloidal fraction is probably not entirely free of common soil-forming minerals but they are present only in very small amounts in mature or old soils.

2. The silica and alumina of the colloids are not present in separate particles as they form a stable suspension (all particles having the same electrical charge).

3. The colloidal matter resists extraction of its constituents by solvents, the silica, alumina, and iron being very hard to extract with water.

4. Matter brought in solution by dilute alkali or acids was no more definite in composition than the original colloid; also the undissolved residue was no simpler in composition.

5. Stoichiometrical calculation showed that all the silica, alumina, and iron oxide could not be present as hy-

drated silicates, as kaolinite or nontronite.

These investigators thought it likely that the soil colloids were a very intimate mixture with little tendency to separate into definite compounds. They indicated the possibility of there being some, however, and that new X-ray developments would reveal their ultimate nature.

Hendricks and Fry (1930) by the use of special techniques with preparing samples for the microscope and with X-ray data came to the conclusion that the clay minerals were crystalline, and that they consisted of montmorillonite, halloysite, and ordovician bentonite (or mixture of montmorillonite and quartz). The montmorillonite exhibited marked absorption of water and swelling while halloysite showed these properties less prominently if at all.

Brown and Byers (1932) by use of chemical and X-ray data from the colloids of soils of the several great soil groups, which included eight samples from seven different profiles, decided that the mineral in the chernozems and prairie soils was predominantly montmorillonite, the podzols a mixture of montmorillonite and iron oxide, the lateritic soils a mixture of aluminum and iron oxides and partially decomposed montmorillonite. They considered mineral decomposition to be hydrolytic, the process being influenced by temperature and rainfall. They also found that the very fine colloid was of the same general character as the larger colloids.



Hendricks and Alexander (1939) used chemical, X-ray, and dehydration methods of analyses on a large number of different soil colloids and decided they were composed of three general types of minerals; the kaolinite type of four isomorphic varieties, the montmorillonite type of three varieties, and the third given the general name of "hydrous mica". This third type had previously been termed "bravaisite", "hydromica", and "illite". They also identified a few soil forming minerals in small amounts and a group, called accessory minerals, composed of hematite, goethite, titanium bearing minerals, gibbsite, and amorphous silica.

Kelly, Dore, Woodford, and Brown (1939) by use of chemical analyses, dehydration curves, optical properties and X-ray investigations, found three general types of clay minerals in California soils. These are the montmorillonite, kaolinite, and a muscovitelike type referred to as "X" mineral. They found with few exceptions that the colloid of each soil appeared to be dominated by a single type clay. Some quartz, other non-clay minerals, amorphous silica, and uncombined iron were identified also.

In Russia Sedletsii (1940b) found minerals of the montmorillonite group in solonchaks soils and those of the kaolinite group in the podzols. The study of concretions revealed montmorillonite inside and kaolinite outside, and it was concluded that under acid conditions montmorillonite will weather to kaolinite.

From this brief survey it can be stated that at the present time the soil body is considered to be a complex mixture of minerals, the coarser fractions being the "soil-forming" minerals while the colloidal is predominantly of the "clay" minerals of the three designated types, all definitely crystalline in structure. Even the uncombined oxides of iron and aluminum which occur are considered by most to be of crystalline nature.

This realization of the complexity of composition and the chemical changes that must occur in weathering brings up the question, Do mineral changes occur that can be measured during the life time of a man and what influence does the application of lime and active fertilizer elements to soils have upon their mineral characteristics? The material on this phase is slight but convincing. Volk (1933) found that in Pennsylvania where Hagerstown silt loam had received a total of 5000 pounds of KCl during 50 years, some of the K had become fixed as secondary muscovite. He also reports that the wetting and drying of clay in the presence of potassium salts make large quantities of readily soluble potassium difficultly soluble. It was found by chemical tests that lime applied to soil caused an increase in fixation of applied potassium. The mechanism by which this occurs is supposed to be:  $K_2CO_3$  is formed which dissolves colloidal silica and alumina giving a soluble product which could form muscovite. He also suggests

the presence of a colloidal alumino-silicate which combines with the soluble potassium to form muscovite.

Perkins<sup>2</sup>, making mechanical analyses of some New Jersey soils treated with limestone for a period of 25 years, found an increase in the coarser fractions over the unlimed soils. Data from similarly treated Ohio and Kansas soils show no great difference, but when compared with the New Jersey soils show a trend toward an increase in the coarser separates due to liming.

Metzger (1939) in studying some old fertility plots found that lime caused a greater retention of the phosphorus of manure than when the manure was applied alone. Also the lime and manure treatment caused an increase in the base exchange capacity. However this was lost when the soil was electrodyalized, indicating that a colloidal complex having base exchange characteristics was formed but was decomposed under an electric potential.

Sedletski (1940a) found that under laboratory conditions he could obtain montmorillonite from aluminum silicate gels, a transformation which could occur under conditions occurring in soils.

These studies would indicate that changes do occur in soil over a measurable length of time and it would seem possible that liming should influence these changes.

<sup>2</sup> Unpublished data of Dr. A. T. Perkins at the Kansas Agricultural Experiment Station, Manhattan, Kansas.

Russell (1932) related that the phenomenon of absorption by soil materials was discovered by Thompson and Way in 1850 and that Way in 1852 showed that when the ammonium ion replaced calcium in the soil it was done in equivalent amounts. Way explained the absorption on a chemical basis; the exchange of calcium for ammonium was a chemical reaction. With the introduction of the concept of colloids and their properties Van Bemmelen in 1890 concluded the replaceable basic elements were held on the surfaces of the colloidal particles by physical forces and this idea was dominant up to 1924. Since then the mechanism for "base exchange" has been in controversy though its value has been widely recognized and extensively studied. Perkins and King (1936) defined base exchange as the zeolitic-like abilities of soils to hold bases against water solution, but permit their liberation by exchange with other positively charged ions. They also indicate the base exchange capacity of a soil is a good measure of its potential fertility.

As was pointed out previously the clay minerals are definitely crystalline and Kelly, Dore, Woodford, and Brown (1931) after study by X-ray patterns of pure clay minerals, natural zeolites and colloidal soil fractions, concluded that the exchange bases are part of the crystal lattice and are true chemical compounds. When another base of higher energy of replacement or excessive amounts of one with lesser replacement energy comes in contact with the crystal, base

exchange takes place. Those clays of the montmorillonite group have high base exchange capacity and a high base content while the kaolinite type have low base content and low base exchange capacity. Kelly and Jenny (1936) studied the base exchange properties of pure minerals and some soil colloids before and after grinding. They found that kaolinite and the kaolinitic colloids increased their base exchange capacities on grinding. In the case of kaolinite and its related colloids the base exchange increase was attributed to the hydrogen ions in the crystal lattice being exposed by grinding. From their data they conclude that base exchange is a strict chemical reaction of double decomposition type.

Whitt and Bayer (1937) working with different sized Putnam clay colloid found that base exchange increased with decrease in particle size and decreased per unit of area with increase of total surface. Wagoner (1940) found essentially the same facts in his study of phosphorus fixation by several soil separates. They suggest the increase in surface area is only apparent, as the clay crystals are considered to be layers so arranged that water may enter between these layers causing the interior parts of crystals to function in base exchange while only the exterior surface is considered in determining the active surface.

Kelly (1935) clearly explained the relation of crystal structure of the various clays to their base exchange properties. He explained the low exchange power of quartz and

other anhydrous minerals to their having no active bases in their lattice structure. What capacity they do exhibit is due to oriented molecules at the exposed lattice bonds. The base exchange properties of a colloid depend upon the kind of exposed surface, which is determined by the crystal structure, and the amount of surface, which depends on particle size.

From this work it is seen that though differences in base exchange capacity may not show the presence of different minerals yet any change in crystal structure or particle size within a given soil colloid would be reflected in its base exchange capacity. It would not be known what occurred but it would be definite proof that something did happen to the colloidal complex.

The literature concerned with all the relationships of phosphorus to plants and soils is very voluminous. Benne (1937), Wagoner (1940), and Metzger and Romine (1939) have reviewed in some detail the literature concerning the conditions affecting phosphorus solubility, fixation by the soil, and its exchange for other ions.

It is well-known that in some soils plants suffer from phosphorus deficiency yet a large amount of total phosphorus is present in the soil. Also that when soluble phosphates are added as a top dressing to the soil their penetration is very slight. For example Metzger (1939) found that in soils top dressed with various phosphorus carriers for 27 years a large proportion of the total phosphorus was fixed in the



surface twelve inches and the greatest share of this was in the surface six inches. As this knowledge is widely spread and of interest to several fields of agricultural science, the mechanism whereby this phosphorus is fixed in the soil has received a great amount of study.

Wagoner (1940) after reviewing the literature concerned with this problem, summarized the evidence and decided that fixation of phosphorus can be accounted for as an anion absorption on the surface of the soil particles and by chemical reaction and precipitation both in the solution and on the surface of the colloids. Either one of these may be influenced by the reaction of the soil, temperature, ratio of soil to solution, the kind of bases associated with the colloids, the degree of base saturation, and the composition of the soil complex.

Some of these conditions may be illustrated by individual studies. Sarishvili and Bagaturiya (1936) found that in sub-tropic soils active aluminum was abundant and a direct relation existed between the amount of  $P_2O_5$  fixed and the exchangeable aluminum in the soil. Perkins, King, and Benne (1932) found that absorbed iron and aluminum on soil colloids precipitated large amounts of phosphorus; the calcium, magnesium, and hydrogen colloids intermediate amounts; and potassium and ammonium colloids small amounts. Benne, Perkins, and King (1936) found that at pH ranges below approximately 5.0, fixation was due to  $Fe^{+++}$  ion and at pH 7.6

or above, fixation was due to the  $\text{Ca}^{++}$  ion.

Mattson (1931, 1932) studied the amphoteric nature and absorption properties of prepared alumina and silica gels and found them to react differently on either side of their iso-electric points; i.e., acting as base in a more acid medium and as acid in a more basic one. This knowledge was then applied to soil colloids and it was decided that in such a colloidal aggregate the iso-electric point for the group is not a constant but varies with the different proportions and strengths of the acidic and basic materials making up the complex. This would mean that over a large pH range of soil solution some of the particles would ionize as a base and combine with anions. This is further substantiated by Mattson and Wiklander (1940) when they observed some red and brown soils of Sweden would absorb and exchange large quantities of cations and anions simultaneously at or near the pH at which equivalent amounts of anions and cations are absorbed.

Scarseth (1935) studied the retention of phosphorus by a natural alumino-silicate colloid prepared from bentonite. Portions of the colloid were saturated with hydrogen, calcium, and sodium and the retention of phosphorus by each was determined at different pH values. At pH 6.0 when saturated with  $\text{H}^+$  the colloid absorbed no phosphorus and at pH 6.0 when partly saturated with  $\text{Na}^+$  the aluminum bond of the colloid absorbed  $\text{PO}_4^{---}$  ion in place of  $\text{OH}^-$  ions. At the same pH value the amount of phosphorus was increased if calcium was

on the colloid instead of sodium, presumably one of the valences of  $\text{Ca}^{++}$  attracted the  $\text{PO}_4^{---}$  ion. At higher pH values, in accord with Mattson's idea (1931), the complex absorbs  $\text{OH}^-$  ions replacing the  $\text{PO}_4^{---}$  ion which can be precipitated by the di-valent ions of calcium. It was also found that the silicate ion would replace  $\text{PO}_4^{---}$  indicating an anion exchange similar to that of cations.

Bradfield, Searseth, and Steele (1935) studied phosphorus retention by beidellite colloids prepared from soils of Pennsylvania and Ohio. They decided phosphorus was fixed over a wide range of reactions and concentrations by three distinctly different mechanisms. From pH 2.0 to 5.0 retention was due to precipitation by iron and aluminum, from 4.5 to 7.5 by surface absorption on the colloids (anion exchange), and from 6.0 to 10.0 by di-valent cations if present. The pH limits overlap because it is believed that two mechanisms are active at the transition pH values. This is essentially the conclusion of Benne, Perkins, and King (1936) and of Wagoner (1940) who investigated phosphorus fixation by various soil separates.

Murphy (1939) found by grinding clay colloids the amount of phosphorus fixed was greatly increased. Stout (1939) in an attempt to explain the mechanism involved found that ground and electrodialyzed samples of bentonite, kaolinite, and halloysite fixed from three hundred to four hundred millimols of

phosphorus while bentonite fixed an insignificant amount.

X-ray patterns showed that the crystalline nature of kaolinite and halloysite were changed by the fixed phosphorus. It was considered that the  $\text{OH}^-$  ions on the surface of the kaolinite and halloysite were replaced by the phosphate ion. Determination of water lost in this exchange seemed to confirm this mechanism.

It would seem then that if the crystal structure of the soil minerals would be altered or a change in the condition or quantity of free iron and aluminum oxides by acid conditions and consequent applications of lime, the change should appear in the base exchange capacity and phosphorus fixing properties of the soil.

#### EXPERIMENTAL PROCEDURE

##### Soil Material Used

The material selected for this study was colluvial detritus collected at the base of a more or less disintegrated limestone ledge in Pottawatomie County, Kansas. This material had developed under about 31 inches of rainfall annually, well toward the west edge of the prairie soil zone. It was selected as it had not been subjected to pedological forces and it was hoped it would show effects of continued leaching.

## TREATMENT

Samples of 750 gm. of this screened, oven-dried material were leached by N/10  $\text{NH}_4\text{Cl}$  solutions made from distilled water and adjusted to pH 3.5, 5.5, 7.0, and 9.0 with HCl or  $\text{NH}_4\text{OH}$ . Each treatment was carried through in duplicate. The solution was applied in applications of 2480 m.l. to the amount equivalent to 100 years of rainfall at the rate of 30 inches annually. The N/10  $\text{NH}_4\text{Cl}$  was used so as to settle the colloidal fraction out in 24 hours.

The leaching was effected by placing the material in four-liter bottles, making the applications of the solutions, shaking in a mechanical shaker for 20 minutes, and allowing them to set in a constant temperature room of  $25^\circ\text{C}.$  ( $\pm 1^\circ$ ), for 24 hours when the clear solution was siphoned off. A total of 104 applications were made.

In an effort to duplicate natural drying and oxidizing conditions an attempt to filter and dry the soil was made. This proved to be too long a process and would extend the work beyond the intended period so instead, each sample was aerated with compressed air for 10 minutes once each week. Occasional pH readings were taken of the supernatant solutions. At the completion of the treatment the samples were dried down and weighed. Table 3 shows the percentage loss due to treatment. These results show that all samples lost appreciable amounts by solution, those receiving the acid solutions losing the most as

more carbonates would be removed by the acid treatments.

#### Mechanical Analysis

Separates of the soil material were made by the method reported by Perkins and King (1935). Each sample was placed in a percolating jar 20 inches long, distilled water added and the mixture stirred by a mechanical stirrer and later by a glass rod. The suspension was allowed to settle for definite lengths of time when the upper 12 inches were removed by a siphon which extended into the jar. The material in the bottom of the jars was repeatedly worked by hand to break down all aggregates and stirred with additional distilled water until all particles that would settle out in a given time had done so and the upper one foot of suspension was clear. This required 20 to 40 washings depending on the separate being removed.

The last two separates were obtained by the use of a centrifuge, the material thrown down being worked with a rod having a rubber stopper on the end as a hammer. The time necessary to run the centrifuge was calculated so that the material thrown down was one-half the particle size of the last separate obtained with the percolators. The scheme of separation and average particle diameter of each separate are given in Table 1. It also shows that as the time of sedimentation is increased six times over the previous sedimentation period, the size of the smaller particles decreases approximately one-half in diameter of the next larger separate. This agrees with the results of



Table 1. The scheme by which soil separations were made and their particle sizes.

Designation	Time particles remained in suspension in 1 ft. column of water	Time particles settled in 1 ft. of water	Average diameters (mm.)		
			pH 3.5	pH 5.5	pH 7.0
A	less than 3.33 min.	3.33 min.	.06012	.05891	.06138
B	3.33 min.	20 min.	.03062	.02979	.03063
C	20 min.	2 hours	.01275	.01254	.01247
D	2 hours	12 hours	.00547	.00599	.00570
E	12 hours	3 days	.00273	.00299	.00285
F	3 days	over 3 days	all material smaller than the E fraction		

Table 2. Results of mechanical analysis in per cents.

Separate	Controls			No. 1	No. 1B	No. 1C	No. 2A	No. 2B	No. 3A	No. 3B	No. 4	No. 4A
	No. 1	No. 1B	No. 1C									
A	8.26	10.27	10.61	9.67	10.38	10.63	11.07	10.09	10.07	10.06	10.01	
B	21.38	20.64	21.13	21.62	21.22	21.23	20.51	19.84	19.96	20.77	19.98	
C	10.29	10.32	13.13	12.74	12.68	12.86	11.91*	13.71	12.71	11.34	11.64	
D	9.15	8.49	7.42	6.44	7.28	6.82	6.85*	9.60*	8.37	10.22	12.13	
E	6.92	7.01	7.14	7.66	7.20	7.13	6.48*	7.78*	7.53	8.36	9.63	
F	33.86	33.62	36.53	36.15	35.63	34.10	32.36*	37.30*	35.31	31.72	33.67	

Sample No. 1A was lost and was replaced by Nos. 1B and 1C.

\* Indicates that the samples were accidentally mixed.

Perkins and King (1936). The average diameters were determined by measuring 500 particles with a microscope using an ocular micrometer. The microscope was also used to see that all aggregates were broken up.

These analyses were made quantitatively so care was taken to see that each sample was handled in the same way. The separation was done at a temperature of 25°C. Each separate when obtained was oven-dried and weighed to one decimal place. The smallest or F separate, was washed with 85 per cent ethyl alcohol to remove excess  $\text{CaCl}_2$  and finally dried from 95 per cent alcohol. The first drying from 95 per cent alcohol left hard fragments but it was found that if this material was wetted with 95 per cent alcohol and redried several times these fragments broke down into small pieces that could be easily pulverized in a mortar if desired. Table 2 gives the results of the mechanical analysis in per cents and Table 4 gives a summary of the same data.

Table 3. Per cent lost by treatment (averages).

Control	pH 3.5	pH 5.5	pH 7.0	pH 9.0
None	5.79	5.08	4.90	4.07

Table 4. Summary of separates (average per cents).

Separate	Control	pH 3.5	pH 5.5	pH 7.0	pH 9.0
A	9.26	10.33	10.85	10.08	10.04
B	21.01	21.34	20.87	19.90	20.37
C	10.30	12.85	12.86**	13.21	11.49
D	8.82	7.05	6.83	8.37**	11.17
E	6.86	7.33	7.13**	7.58**	8.99
F	<u>33.74</u>	<u>35.44</u>	<u>34.10**</u>	<u>35.31**</u>	<u>32.79</u>
Totals	89.99	94.34	92.64	94.45	94.85
Less values from	0	5.79	5.08	4.90	4.07
Table 3	<u>89.99</u>	<u>88.55</u>	<u>87.56</u>	<u>89.55</u>	<u>90.78</u>

\*\* Data from one sample only, duplicates of pH 5.5 and 7.0 were accidentally mixed.

#### Base Exchange Determinations

The base exchange capacities of the separates were determined by the method used by Perkins and King (1935). Five grams of each separate were leached with neutral normal  $\text{NH}_4\text{Cl}$  until the filtrate gave no test for calcium or had been leached 30 to 40 times with 10 cc. portions of  $\text{NH}_4\text{Cl}$ . It was found that some of the coarser separates contained free  $\text{CaCO}_3$  so that even after 40 applications a test for calcium was obtained. The E and F separates did not filter rapidly, so these were washed by decantation. After removing all the absorbed calcium the coarser samples were washed with distilled water

and the finer ones with 85 per cent alcohol until a negative test for chloride was obtained. Separates E and F were washed by use of the centrifuge due to their slow filtering on funnels.

The absorbed  $\text{NH}_4^+$  was determined by freeing the  $\text{NH}_3$  by  $\text{MgO}$  and distilling into standard acid. Table 5 gives the averages of the base exchange capacities of the various separates.

Table 5. Base exchange by soil separates milliequivalents per 100 gm. soil.

Separate	Control	pH 5.5	pH 5.5	pH 7.0	pH 9.0
A	0.57	0.43	0.14	0.14	0.21
B	0.43	0.43	0.43	0.64	0.43
C	1.00	1.94	1.43	0.72	0.72
D	3.86	4.98	3.00	2.43	1.53
E	29.31	36.18	30.39	29.10	31.67
F	57.77	54.91	51.34	54.77	54.70

#### Procedure for Determining Phosphorus Fixation

The data for phosphorus fixation were acquired after the procedure used by Wagoner (1940) in which the amount of fixation was assumed to be the difference in amount of phosphorus in the solution applied and in the extract after it had been in contact with the soil for 24 hours. Twenty-gram samples of each separate were taken and the phosphorus applied in 50 m. l. of solution, a soil-solution ratio of 1 - 2 $\frac{1}{2}$ . The solutions were prepared by dissolving  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  in  $\text{CO}_2$  free distilled water in

equivalent amounts ranging from 2500 lbs. to 60,000 lbs. per 2,000,000 lbs. of soil.

The mixtures of separate and solutions were made in 500 m. l. centrifuge bottles and agitated at 25°C. in a constant temperature room by rotating end over end at the rate of six revolutions per minute. At the end of 24 hours the samples were removed, centrifuged for one hour and the clear supernatant solution removed by pipette. This extract was not filtered through clay filters as it was found that centrifuging for one hour gave as good comparative results as filtering and was much faster.

The amount of phosphorus in the extract was determined by the Deniges coeruleomolybdate method as adapted by Atkins (1923). The color comparisons between a standard and the unknown soil extract were made by a Dubosq colorimeter. Table 7 gives the rate of application and amount of fixation by each separate. Table 6 gives the fixation of the whole untreated soil given various applications of phosphorus.



Table 6. Phosphorus fixation by whole untreated soil.

Application lbs./acre	Dilution of Soil Extract	Concentration of Extract ppm	Per cent phos- phorus fixed
100#	25-250	0.873	92.82
200#	25-250	1.119	95.39
500#	10-250	5.167	91.48
1000#	5-250	18.42	84.82
2500#	3-250	83.99	72.31

Table 7. Phosphorus fixation by separates, per cent of  $P_2O_5$  added.

Fraction	Application lbs./acre	Control	pH 3.5	pH 5.5	pH 7.0	pH 9.0
A	2500#	21.45	16.64	26.13	30.13	23.55
B	2500#	28.07	25.09	20.52	23.22	24.28
C	2500#	37.32	37.12	40.04	33.60	33.66
D	2500#	70.73	76.41	82.19	65.76	71.46
E	4000#	88.27	93.50	94.11	94.90	93.03
F	10000#	96.74	97.53	96.81	96.99	96.46
F	20000#	93.64	94.24	94.97	95.20	94.49
F	60000#	81.83	81.73	79.28	79.85	79.81

## DISCUSSION OF RESULTS

## General

It was the plan at the beginning of this study to subject the soil material to the equivalent of 50 years of rainfall as it was hoped that by that time the treated soil would have acquired the pH of the solution applied. At the end of this period of treatment the pH values for the 3.5, 5.5, 7.0, and 9.0 treated soils were respectively 7.62, 7.77, 7.3, and 8.95. Because of this it was decided to continue the experiment up to the equivalent of 100 years of rainfall. At the end of this second period the pH values were, listing in same order as above, 7.51, 7.70, 7.75, 8.94. The pH determinations were made with a quinhydrone electrode.

This failure to reduce the pH values perceptibly was due to excessive amounts of free  $\text{CaCO}_3$  occurring in the samples. However, due to the time factor it was decided to stop the treatments and make a mechanical analysis of the samples.

The percentage loss for each sample due to treatment is given in Table 3. This shows that more material was lost by the more acid treatment which is what would be expected since there was so much  $\text{CaCO}_3$  present. It would seem that though the acid solutions increased the solution of solid material, the increase is not great when compared with the solution effect of the non-acid solutions.

### Mechanical Analysis

The data for the mechanical analyses of the various samples are presented in Tables 2 and 4 and represented graphically by Fig. 1. A study of Tables 2 and 4 will show that the control samples lost more by solution effects during mechanical analysis than the treated samples. However, the per centage of each fraction of the treated samples was calculated from the dry weight of material after treatment as 100 per cent. If from the totals of the per cents of each separate of a given sample is subtracted the per cent of loss of that sample due to treatment we get values more nearly comparative. This shows that the loss of material was due primarily to solvent action during mechanical analysis. However this calculation shows that the acid treatment removed an average of 1.93 per cent from the samples receiving the acid solutions.

A study of Fig. 1 shows that there are trends, if not significant differences, between the per cents of a given separate from samples receiving different treatment. The curves for the A, B, and C separates probably do not show differences beyond experimental error but the curve for the D separate shows a decrease due to acid treatment, no difference for pH 7.0, but a decided increase for pH 9.0. The curve for the E separate shows only an increase of pH 9.0, and the F separate a decrease at pH 5.5 and again at pH 9.0. From this it would indicate that a break or abrupt change in soil properties occurs at the size of

- A - Curve for A separate
- B - Curve for B separate
- C - Curve for C separate
- D - Curve for D separate
- E - Curve for E separate
- F - Curve for F separate
- G - Curve for sum of per cents of each separate.

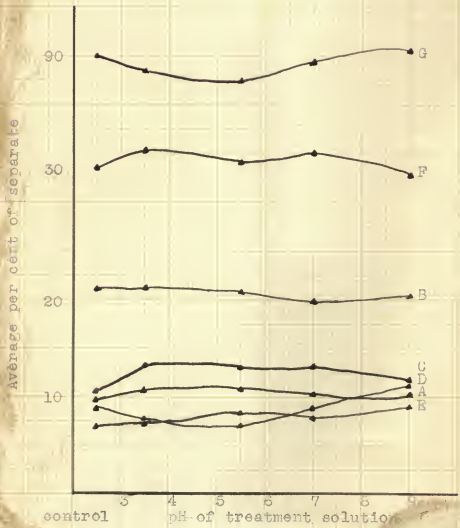


Fig. 1. Per cent of separates due to different treatment.

the D separate. Wagoner (1940) found identically the same thing. Further discussion of this study will indicate further confirmations of this observation. It is to be noted that when the amount of the C and E separates increased at pH 9.0, the F separate decreased in a proportionate amount so that the sum of the per cents of the separates at pH 9.0 compare favorably with the other samples except those receiving solutions of pH 5.5.

The curves for the various separates tend toward minima at pH 5.5, especially that of the D separate. No explanation is offered for this unless some particular unknown soil constituent is especially soluble at pH 5.5.

#### Base Exchange

Figure 2 represents graphically the base exchange data presented in Table 5. The base exchange capacity for the A and B separates are insignificant and perhaps the data for the C separate also, except a trend is indicated which is definitely revealed by the D separate, the point at which the soil properties definitely change. The acid treatment indicates an increase in base exchange, and alkalin treatments seem to decrease it. The same trend is seen in the E separate, the sample receiving a solution of pH 3.5 having an appreciably greater exchange capacity, that receiving pH 5.5 only slightly more, pH 7.0 about the same, and pH 9.0 a slight increase over the control samples. The F fraction shows a minimum at pH 5.5. It is possible that some relationship exists between base exchange and quantity of

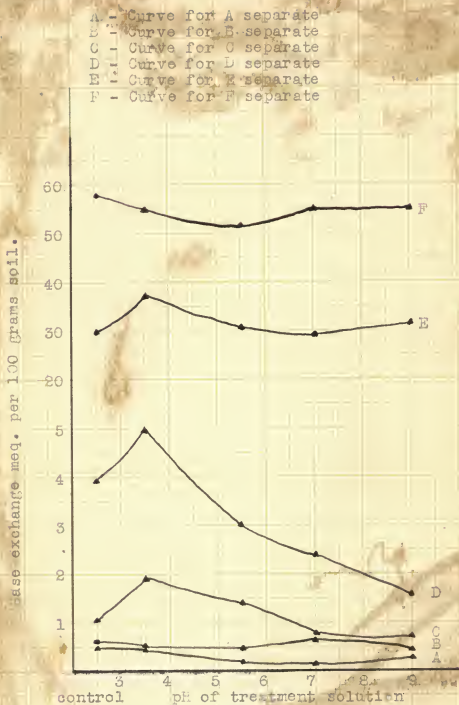


Fig. 2. Base exchange capacity due to different treatment.



separate (see Fig. 1).

In these determinations the organic matter was not removed and since the base exchange capacity of organic matter is relatively high a small difference in amount in any one separate would be magnified in the base exchange capacity of the soil. It was noted during the course of the determinations some of the filtrate became colored and in a few cases black, due to dissolved organic matter. It is believed that if the pH of the treated soil could have been brought lower by the treatment more comparative results would have been obtained.

#### Phosphorus Fixation

Phosphorus fixation determinations were also made in an effort to indicate any change of properties of the mineral content of the samples. The data are very erratic and no doubt, solvent effects other than that due to the acid applied, and errors in analyses especially where small amounts of phosphorus were fixed though large applications were made, obscured to some extent the effects of the applied acid. Especially does this seem true when the solvent action due to mechanical analysis was about 10 per cent and the action of the acid about 1.93 per cent. However, some trends can be noted and some previous indications confirmed by a study of the phosphorus fixation data as shown in Table 7 and Fig. 3.

It is understood that the pH values plotted as ordinates are the values of the treatment solution and not the pH of the

- A - A separate 2500# per acre
- B - B separate 2500# per acre
- C - C separate 2500# per acre
- D - D separate 2500# per acre
- E - E separate 4000# per acre
- F - F separate 10000# per acre
- F' - F' separate 20000# per acre
- F'' - F'' separate 60000# per acre

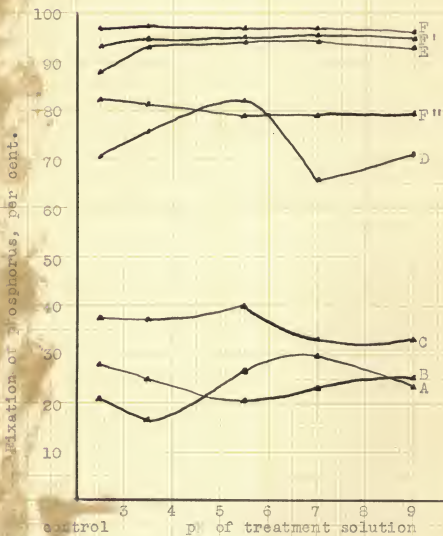


Fig. 3. Phosphorus fixation due to different treatment.

final solution withdrawn from the samples when treatment was stopped, nor is it the pH at which phosphorus fixation was determined. It is probable that this last mentioned pH was near 7.0 in the case of the A, B, C, and D separates, because some  $\text{CaCO}_3$  was present in appreciable amounts in the A, B, and C separates and in lesser amounts in the D. What influence this  $\text{CaCO}_3$  had on phosphorus fixation is not known as no pH determinations were made but it probably had some as Benne, Perkins, and King (1936) found that  $\text{CaCO}_3$  in a dilute solution of  $\text{H}_3\text{PO}_4$  would begin to precipitate phosphorus near pH 6.59.

A study of Fig. 3 indicates however, that for the A, B, and C separates fixation decreased at pH 5.5 while the D separate shows a large increase in fixation, another indication of the abrupt change in properties between the C and D separates. The rapid upward swing of the A curve at pH 5.5 and 7.0 may be due to the large excess of  $\text{CaCO}_3$  in this separate. As to why the B curve swings down through the pH 5.5, 7.0, and 9.0 points no explanation can be given. The A, C, and D fractions show increasing amounts of fixation at the pH 5.5 treatment. Why this should be is not known, but it may have some relationship with the fact that the entire sample receiving the pH 5.5 treatment apparently lost more by solution due to this treatment (see Fig. 1). The whole D curve shows more variation than either of the others. This may be due to the nature of this separate under different treatments. As has been previously pointed out this separate shows a great change in properties as compared

with the coarser ones.

The curve for the E separate indicates an increase at pH 3.5 and 5.5 as does the D curve and shows that acid treatment probably affects this separate in about the same manner as the D separate though not to as great a degree.

The three F curves are of interest primarily in showing the extent to which this separate will fix phosphorus. In Fig. 4 the milligrams of  $P_2O_5$  absorbed by one gram of soil is plotted against applications of  $P_2O_5$  expressed in milligrams. This graph shows the quantity absorbed is nearly a straight line function of the quantity applied. Apparently the F separate has a very large capacity for phosphorus fixation under the conditions of the experiment.

In an effort to determine the cause of such extensive fixation by the F separate the following pH values were taken: that of the phosphorus solution applied, that of the extract, and that of an equal amount of distilled water agitated with an equal quantity of the separate. These pH values were as follows: phosphorus solution 3.28, soil extract 4.72, and applied water 6.13. It was thought that since calcium chloride was used to settle out this fraction that some residual salt might precipitate some phosphorus but from the findings of Benne, Perkins, and King (1936) the pH would have to be at least 5.5 before this would occur. Since the pH of the phosphorus solution was 3.28 and that of the extract was 4.72  $Ca^{++}$  would not precipitate  $PO_4^{---}$ . This large fixing capacity is undoubtedly due to iron

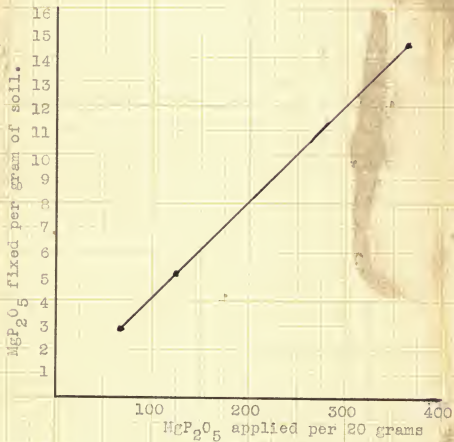


Fig. 4. Phosphorus fixation by F separate.

and aluminum of the separate made active by the high acidity of the solution.

#### SUMMARY

Duplicate samples of colluvial soil material were treated with solutions of pH 3.5, 5.5, 7.0, and 9.0 in amounts equivalent to 100 years of rainfall under Kansas conditions. Mechanical analyses by sedimentation methods were made of these samples and of a pair of untreated controls. Sedimentation times were chosen so that the diameter of each succeeding separate was one-half the size of the preceding one. In this manner six separates were collected and compared as to amount, base exchange capacity, and phosphorus fixation. Base exchange capacity was determined by leaching the material with neutral normal  $\text{NH}_4\text{Cl}$  until free from  $\text{Ca}^{++}$  and then washing with distilled water or 85 per cent alcohol until free of chloride. The absorbed  $\text{NH}_4^+$  was removed by  $\text{MgO}$  and distilled into standard acid. Phosphorus fixation was determined by treating portions of each separate with calculated quantities of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  in a soil solution ratio of 1:2 $\frac{1}{2}$ , agitating for 24 hours in a constant temperature room, centrifuging and testing the extract for phosphorus. The difference between the phosphorus in the extract and that of the applied solution was considered to be the amount fixed by the soil.

It was found that though a large amount of material was lost by solution the pH of the treated soil stayed above 7.0



and consequently not much change in properties due to the treatment was noted.

#### CONCLUSIONS

1. The experimental soil material contained excessive amounts of  $\text{CaCO}_3$  so that treatment with a solution of pH 3.5 had but little effect on the pH of the soil. Consequently only limited results were obtained due to treatment.

2. The amount of the C and E separates increased and the F separate decreased due to treatment with solutions of pH 9.0.

3. The C separate increased and the D separate decreased in small amounts because of treatment with solution of pH 3.5.

4. The D and F separates showed a decrease at pH 5.5 with no separate showing an increase at this pH value, indicating the possible presence of a soil constituent that is soluble at this pH.

5. Base exchange trends only were found, the general ones being an increase due to treatments of solutions of pH 3.5 and a decrease due to alkaline solution.

6. Phosphorus fixation was increased in the D and E separates by acid treatment and probably decreased in the B and C separates.

7. Physical and chemical properties changed abruptly with the D separate.

8. The F separate fixed large amounts of phosphorus, its capacity probably exceeding the solubility of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

## ACKNOWLEDGMENTS

Indebtedness is expressed to Dr. A. T. Perkins, major instructor, for help in planning and conducting this study; and to Dr. W. H. Metzger of the Department of Agronomy for his interest and helpful suggestions.

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