

PHOSPHORUS FIXATION BY SOIL SEPARATES

by

CHARLES EDWARD WAGONER

B. S., McPherson College, 1933

---

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

1940

Doc-  
ment  
LD  
2668  
.74  
1940  
W31  
C.2

## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION .....	1
REVIEW OF LITERATURE .....	2
EXPERIMENTAL PROCEDURE .....	17
Soil and Sand Used in the Experiment .....	17
Mechanical Analysis .....	17
Chemical Analysis .....	24
Procedure for Determining Phosphorus Fixation .....	24
Preparation and Use of the Clay Filters .....	27
RESULTS OF PHOSPHORUS FIXATION .....	28
DISCUSSION OF RESULTS .....	40
SUMMARY .....	46
CONCLUSIONS .....	47
ACKNOWLEDGMENTS .....	48
REFERENCES .....	48

## INTRODUCTION

When soluble phosphates are added to the soil, portions of them combine with it. This phenomenon has been generally called phosphorus fixation, or the fixation of phosphorus by the soil. Phosphorus fixation is an especially fitting term, as pointed out by Murphy (1939), because it implies no specific mechanism by which the soil removes a portion of the phosphorus from the soil solution. The ability of the soil to fix phosphorus is highly advantageous, as has been shown by Crawley (1902) and Roszmann (1927), as the phosphorus that is fixed, is not easily leached from the soil by rain or irrigation. On the other hand conditions may exist in the soil such that essentially all of the phosphorus is fixed, thereby leaving none for the crops.

Because of the latter condition, the mechanisms causing phosphorus fixation as well as the factors influencing them have formed the basis of much research. The literature reporting the results of the research on phosphorus fixation is at times confusing and in some instances quite contradictory. This is apparently due to the different methods of investigation, as well as the diverse nature of the many soils and artificial media used.

In the literature pertaining to phosphorus fixation it

was found that major emphasis has been placed upon each of several mechanisms of phosphorus fixation by different investigators. It seemed likely that the mechanisms causing phosphorus fixation were closely related, or perhaps operating simultaneously. It therefore seemed advisable to make a study of phosphorus fixation and attempt to correlate the mechanisms involved.

The two main mechanisms involved as condensed from the review of the literature are phosphorus fixation due to chemical precipitation forming more or less insoluble compounds, and fixation caused by the adsorption of anions at the soil-solution interphase.

#### REVIEW OF LITERATURE

A complete review of the voluminous literature pertaining to phosphorus fixation would require considerably more time than it is possible to give in the relatively short period of developing a thesis. This review covers some of the papers that pertain to mechanisms of phosphorus fixation and factors influencing phosphorus fixation.

Phosphorus fixation is not a newly recognized phenomenon for Crawley (1902) stated that it had been known for a long time that when soluble phosphates were added to the soil they became fixed. Crawley (1902) determined how

evenly the phosphorus fertilizer was distributed after it had been fixed by the soil, by adding fertilizer and then irrigating at various times afterward. When he irrigated immediately after the application of the fertilizer, he found that practically all of it was retained within the first six inches. When he waited fifteen hours before irrigating, he found that practically all of the phosphorus was retained in the first three inches. Roszmann (1927) also observed that the fixation was such that it was not greatly affected by percolating water.

The reaction of the soil has been found to be somewhat of a controlling factor of phosphorus fixation. It had been observed by farmers and agronomists that acid soils were generally in need of phosphorus. Whitson and Stoddard (1906), after making a study of the deficiency of phosphorus in acid soils, drew the conclusion that acid soils were in need of phosphates, and that it would be possible by testing the soil with litmus paper, to determine if the soil was in need or would need in the immediate future a phosphate fertilizer. Burgess (1923) determined the "active" aluminum in twenty-five acid, mineral soils of the United States and obtained a direct correlation between the hydrogen ion concentration and the active aluminum. As the active aluminum readily combined with phosphorus, he showed that the

reaction of the soil was a factor of phosphorus fixation. Miller (1928) worked with hydrated alumina and found that the capacity of the hydrated alumina to retain phosphorus was greatest between pH 3 to 4.5, the precipitate was  $\text{AlPO}_4$ . On the addition of alkali to increase the pH, the  $\text{AlPO}_4$  was changed in composition and at pH values above 7.5 the precipitated alumina dissolved as soluble aluminates were formed. He also stated that hydrated ferric oxide retained phosphorus similar to hydrated alumina. Benne (1937) based his idea of phosphorus fixation upon the work of Gaarder, Teakle, Patton, and others. He accounted for phosphorus fixation over a wide pH range as follows. At pH values between 2 and 3, the iron brought into solution precipitates with the phosphorus. At pH values between 3 and 4, the dissolved aluminum exerts its maximum precipitating effect with the phosphorus. At pH 5 the precipitating effect of the iron and aluminum decreases. As the pH is raised above 5 the precipitating effect of the iron and aluminum continually decreases and the precipitation of phosphorus by calcium ions increases. Thus, at pH values of 7 the phosphorus is fixed by the calcium ions. Bradfield, Scarseth, and Steele (1935) agree with Benne (1937) on the precipitation of phosphorus at the high and low pH values. However, they account for the phosphorus fixed between pH values of 4.5 to 7 by

stating that the phosphorus was fixed on the surfaces of the clay particles. Whereas Benne (1937) would have a gradual decrease in phosphorus fixation by the iron and aluminum and a gradual increased fixation by calcium as the pH changed from 4.5 to 7. Bradfield, Scarsoth, and Steele (1935) apparently ascribe a more abrupt change of insoluble iron and aluminum hydroxides to soluble forms and thus carry the fixing power over the pH range 4.5 to 7 by assuming it to be an adsorption phenomenon.

According to Heck (1933) the fixed phosphorus may be regarded as falling in three groups: (1) readily available as  $\text{Ca}_3(\text{PO}_4)_2$ ; (2) moderately available as  $\text{AlPO}_4$ ; or (3) difficultly available as  $\text{FePO}_4$ ,  $\text{Al}_2(\text{OH})_3\text{PO}_4$ , and  $\text{Fe}(\text{OH})_3\text{PO}_4$ . Nemes (1930) observed that soils with adequate calcium contained more available  $\text{P}_2\text{O}_5$  than soils deficient in calcium. Askinazi and Yarusov (1926) reported that a soil which had  $\text{P}_2\text{O}_5$  as its minimum factor was not in need of phosphorus fertilization after nine years of liming. Wityn (1926) reported that acid soils often contain more  $\text{P}_2\text{O}_5$  than neutral or productive soils, only it is less available, and that liming increased the solubility of the phosphates by changing them to calcium phosphates. Perkins, King, and Benne (1932) treated portions of a soil with Al, Fe, H, Mg, Ca,  $\text{NH}_4$ , and K. They found that applications of  $\text{CaCO}_3$  decreased

the fixing capacity of the Al, Fe, and Mg treated soils and increased the fixing capacity of the  $\text{NH}_4$ , H, Ca, and K treated soils. They reported that more soluble phosphates were formed by the addition of  $\text{CaCO}_3$  to the Al, Fe, and Mg treated soils, thus decreasing the fixing capacity. A more insoluble calcium phosphate was formed by the addition of  $\text{CaCO}_3$  to the H,  $\text{NH}_4$ , Ca, and K treated soils than was already present, thus increasing their fixing capacity. The results of these experiments would indicate the necessity of having a good supply of lime in the soil to help keep the phosphate in an available form.

As to the effect of increased temperature upon phosphorus fixation Ford (1933) found that a prolonged heating of soils at  $185^\circ \text{C}$ . reduced the fixing capacities of the soils. He believed the decrease in the fixing capacity to be due chiefly to the dehydration of goethite<sup>1</sup> which produced hematite, as he had found that goethite fixed phosphorus and hematite did not.

Peterson (1911) found a decrease in the fixing power by oxidizing the organic matter of the soil with hydrogen peroxide. The amount of phosphorus fixed by oxidizing the organic matter was less than the amount fixed after the soil had been heated to  $200^\circ \text{C}$ . Doughty (1935) also found that

---

<sup>1</sup> Limonite.

the oxidation of the organic matter with hydrogen peroxide decreased the power of the soil to fix phosphorus. He stated that the decrease in the fixing capacity of the soil was because the phosphorus that was in the organic matter became fixed by the soil when it was liberated from the organic matter during oxidation, thus reducing the fixing capacity of the soil. Doughty (1935) further stated that when peat was heated to 800° C. for two hours the fixing capacity was not destroyed, but when heated at 900° C. for two hours there was a complete loss of fixing power. He attributed the complete loss of fixing power when the peat was heated to 900° to the reaction of ferric phosphate with lime to form calcium phosphate. Doughty (1935) believed that the soil organic matter had only a minor role, if any, in the fixation of phosphorus.

The ratio of the soil to the solution during agitation has been pointed out by Fraps (1922) and Hibbard (1935) to be a factor influencing phosphorus fixation. Fraps (1922) stated that the percent of fixation decreased 54 percent from a soil:solution ratio of 1:10, to a ratio of 1:20. The soil:solution ratios that have been used in phosphorus fixation research have varied considerably.

The length of time of agitation or of exposing the soil to the phosphate solution is another factor that is quite

important in phosphorus fixation. Fraps (1922), Searceth and Tidmore (1934), Hibbard (1935), Davis (1935), Murphy (1939) and others have indicated that fixation increases as time of agitation increases. Murphy (1939) and Searceth and Tidmore (1935) have placed particular attention on the large amount of phosphorus that is fixed immediately as the soil and the phosphate solution are mixed.

The kind of bases adsorbed by the soil have been shown by Perkins, King, and Benne (1932) and Ravikovitch (1939) to be a factor effecting phosphorus fixation. Perkins, King and Benne (1932) found the effectiveness of the various exchangeable cations on fixing phosphorus, to be in the following arrangement:  $Al > (Fe \text{ and } Mg) > H > Ca > K > NH_4$ . Ravikovitch (1939) found the effectiveness of various cations to fix phosphorus in a slightly different arrangement:  $Ca > Mg > H > NH_4 > Na$ .

Beck (1934b) reported that the degree of base saturation was a factor effecting phosphorus fixation. He observed that soils which had their exchangeable bases removed, fixed more phosphorus and that the increase was somewhat in proportion to the amount of bases removed.

The review thus far has chiefly dealt with the factors that influence phosphorus fixation. The remainder of the review will be concerned largely with the mechanisms by

which phosphorus fixation supposedly takes place. The literature is confusing as to the terms used to designate these mechanisms, and much overlapping of terms is encountered.

Bradfield, Searseth, and Steele (1935) contend that there are three distinct mechanisms of phosphorus fixation: (1) from pH values 2 to 5 the phosphorus is fixed by the iron and aluminum; (2) from pH values 4.5 to 7 the phosphorus is fixed on the surface of the clay particles; and (3) between pH values 6 to 10, if divalent cations are present, the phosphorus is fixed by them. Davis (1935) divides the possible mechanisms into four groups, namely, (1) precipitation of phosphorus with the cations in the soil solution; (2) precipitation by double decomposition of relatively insoluble soil minerals to form insoluble phosphates; (3) adsorption at the soil-solution interface; and (4) absorbed by the soil minerals to form complex systems with the iron and aluminum on the surfaces of the particles. He called the last two mechanisms sorption, and the first two chemical precipitation. Metzger<sup>2</sup> divides the mechanisms into two groups, which he designates as absorption and adsorption. Under absorption he would consider all precipitation which would include the first two and last mechanisms

<sup>2</sup> Unpublished work by Dr. W. H. Metzger at the Kansas Agricultural Experiment Station, Manhattan, Kansas.

of Davis, namely, precipitation with free cations in the soil, precipitation caused by double decomposition, and the precipitation on the surfaces of the soil particles due to the active iron and aluminum there. Under adsorption he considered only the phosphate anions which seemed to be fixed on the surface of the particles.

From these three recent papers, it is obvious that there are two main mechanisms by which phosphorus is fixed. One would include all chemical precipitation whether it be in the solution or on the surface of the particles; the second, a surface phenomenon.

Fraps (1910) treated soils with potassium phosphate in a 1:10 ratio for five hours. He obtained a direct relationship between the increasing fixation of phosphorus and the increasing  $R_2O_3$  content of the soils used. The direct relationship between the  $R_2O_3$  content and the fixing capacity of a soil, as was found by Fraps, has been verified to some extent by most all of the investigators on phosphorus fixation. Toth (1937) found that the adsorption of  $P_2O_5$  from Cecil clay which contained 12.38 percent free iron oxide was reduced from .370 to .205 m.e. per gm., when the free iron oxides were removed. Romine and Metzger (1939) removed the  $R_2O_3$  by a weak extraction reagent from different

<sup>3</sup> Sesquioxides which include iron and aluminum oxides in the soil.

horizons of the soil and found that the fixing capacity varied directly with the  $\text{Fe}_2\text{O}_3$  content as extracted by the reagent. Metzger<sup>4</sup> continued, working in the pH range where Bradfield, Seacrest, and Steele (1935) contend the fixation was accounted for by surface adsorption. Metzger removed the free iron oxides from a number of soils of field conditions. He reported a decrease from 20 to 94 percent of phosphorus fixation for those samples which had their oxides removed. Metzger concluded that fixation by iron and aluminum accounts for a large part of the fixing capacity of slightly acid soils under field condition.

As the soil is such a complex system, some investigators have resorted to artificial media in the study of phosphorus fixation. Ellett and Hill (1909) agitated one gram of a number of salts with a solution of mono-calcium phosphate. They reported the salts fixed from 4.4 to 55 percent of the phosphorus added and in the following order:  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Al}_2(\text{OH})_6$ ,  $\text{Fe}_2(\text{OH})_6$ ,  $\text{FeCO}_3$ , and  $\text{Fe}_2\text{O}_3$ . They also stated that the phosphorus combined with the iron and aluminum hydroxides was in the most unavailable form and that by adding lime to the iron and aluminum hydroxides the fixation of the phosphoric acid was not so great. Rostworowski and Wiegner (1912) prepared a potassium permanganate from an

---

<sup>4</sup> Unpublished work by Dr. W. H. Metzger.

artificial gel containing potassium, calcium, aluminum, and silicon dioxide. They intended to determine if the  $P_2O_5$  absorbed in the soil was in part an adsorption phenomenon depending upon zeolites, instead of a chemical precipitation. They found that the potassium permanganate had normal power of exchanging bases, but it absorbed only small amounts of  $P_2O_5$ . Gordon and Starkey prepared hydrogels<sup>5</sup> of silica, alumina, and iron as pure as possible. Samples of these gels were shaken with solutions of different salts until equilibrium was attained. They reported that iron and aluminum colloids influence adsorption more than silica colloids, as the silica gels showed small adsorption as compared to the iron and aluminum gels. They also stated that the iron and aluminum gels attained equilibrium slower than the silica gel. Wiley and Gordon (1922) in a continuation of the previous experiment used pure silica hydrogels and hydrosols<sup>6</sup> to find what power silica had to hold negative ions. They found that the nitrate and sulfate radicals were practically not adsorbed at all by the colloidal silica and the phosphate radicle was slightly adsorbed by the hydrogel. The third paper continuing the work, Lichtenwalner, Flenner, and Gordon (1922) used ferric and

---

<sup>5</sup> A jelly consisting of water and a colloidal substance.

<sup>6</sup> An aqueous colloidal suspension.

aluminum hydrogels. Solutions of different salts were added and agitated with these gels. They reported that the phosphate ions were adsorbed more than the sulfate ions, and both of these were adsorbed more than the nitrate ions. The results of the experiments using artificial media show that phosphates are fixed by colloidal solutions and that the fixation is materially increased when iron and aluminum is present in the composition of the media.

Since the colloidal portion of the soil is the most active in fixing phosphorus, in the more recent years considerable attention has been placed on phosphorus fixation as related particularly to particle size. Murphy (1939), working with clays, stated that by grinding a clay loam for nine days in a ball mill the phosphorus fixed was nearly tripled and continued grinding increased the fixation. He found that not all of the clays fixed as much phosphorus as did kaolinite, but he believed their presence in soils were a contributing factor to phosphorus fixation. He also stated that the type of clay minerals in a soil determined to a large extent its phosphorus fixing capacity. Hibbard (1935) stated that if the composition of the soil complex was inert like quartz, there would be little fixing power, but if the soil complex was composed of reactive substances like kaolin or mica, the fixing power would be greater.

If then the particles of the soil have the ability to fix phosphorus and the phosphorus was not chemically combined with any material on the surface of the particle, there had to be some mechanism offered by which the  $\text{PO}_4$  anions were held to the soil particle.

It has been reported by Kappen and Bollenbeck (1925), Gile and Smith (1925), and Scarsoth (1935) that an addition of silica to a soil releases some of the phosphorus, therefore assuming that there is a replacement of  $\text{PO}_4$  anions by  $\text{SiO}_4$  anions. Mattson (1931), Ravikovitch (1934), Scarsoth (1935), and Pugh (1936) state also that the OH anions replace the  $\text{PO}_4$  anions. The anions are believed to be held to the surface by two aluminum valences and the exchange is believed to be somewhat similar to base exchange. Pugh (1936) believed that the hydroxyl ion displaces  $\text{SiO}_3$  and the  $\text{PO}_4$  ions in equivalent amounts. Bradfield, Scarsoth and Steele (1935) also believed that quantitative anion exchange is possible.

Mattson (1927, 1931, 1932) and Mattson and Gustafsson (1937) in a series of papers on "The Laws of Soil Colloidal Behavior" have elucidated the physico-chemical relationship between the soil colloid and the adsorbed anions. The relationship is primarily due to the amphoteric nature of the soil colloids. The soil material possesses amphoteric

properties, thus combining with both anions and cations. Which of these combinations dominate depends upon the iso-electric<sup>7</sup> point of the soil particles. By amphoteric property is meant the ability of a substance, which when placed in a medium, which is more acid than its iso-electric point, to ionize as a base and combine with anions. If the medium is more alkaline than the iso-electric point, the material will ionize as an acid and combine with cations. It is generally assumed that the alumino-silicate particle is so composed that it is predominantly acid. When the acid residue of the particle is strong the base part would be weak, so the iso-electric point would be on the acid side. Thus, when the alumino-silicate is in a medium, which is more alkaline than its iso-electric point, it would ionize as an acid and combine with cations. This has been the chief evidence offered by those who say that the alumino-silicate of the soil complex can not adsorb anions. Matteson (1931, 1932) however pointed out that the strength of the acidic and basic portions of the ampholytoid<sup>8</sup> vary considerably, depending upon the relative proportion and strength of

---

<sup>7</sup> The iso-electric point is where the dissociation of the negative ions is in equilibrium with the dissociation of the positive ions.

<sup>8</sup> A colloid which can act either as an acid or as a base depending upon its environment.

1

the reacting acidic and basic materials. Therefore the iso-electric point is not constant but varies due to the different proportions and strengths of the acidic and basic materials of the ampholytoid. In a colloidal aggregate there could be most any relationship between the acidic and basic portions of individual particles so that some of the particles would have an iso-electric point allowing them to ionize as a base, and would therefore combine with anions. Mattson (1932) also stated that in a climate of heavy rainfall the amphoteric colloids had a tendency to alter their composition so that their iso-electric point would coincide with that of the prevailing solution. That would occur chiefly in laterite soils. As a result of the electrochemical relationships thus established, Mattson and Karlsson (1936) propose two types of surface adsorption. The anions are held in the micellar structure, or in an electrically charged sphere about the micelle balancing the positive charge, and these are called "colloid bound" and "saloid bound", respectively.

The review of the literature may be summed up as follows. Phosphorus fixation has been accounted for by anion adsorption on the surface of the particles, and by chemical precipitation both in the solution and on the surface of the particles. Phosphorus fixation is effected by other

factors including the pH of the soil, temperature, ratio of the soil to the solution, length of time of agitation, the kind of bases associated with the colloids, the degree of base saturation, and the composition of the soil complex.

### EXPERIMENTAL PROCEDURE

#### Soil and Sand Used in the Experiments

The Wabash soil used was an alluvial soil developed from Prairie soils. The upper six inches was obtained, which is a dark colored soil, containing slightly over 30 percent clay. No free lime is present in the soil. The Ottawa sand used was a white sand free of iron. It was ground so that after the mechanical analysis there would be separates of similar size to those of the Wabash soil.

#### Mechanical Analysis

Separates<sup>9</sup> of the Wabash soil were obtained by the method of sedimentation as reported by Perkins and King (1935). A portion of the soil was placed in percolators<sup>10</sup>, 20 inches long, distilled water was added, and the mixture stirred well by a mechanical stirrer. The suspension was

---

<sup>9</sup> The soil was divided into six separates according to particle size.

<sup>10</sup> Elongated jars used for the sedimentation.

allowed to settle for a definite length of time, at the end of which the top 12 inches was withdrawn by a syphon which extended into the suspension. Table 1 shows the scheme by which the separations were made. The soil in the bottom of the percolators was repeatedly worked by hand in order to separate all of the aggregates. The sample of soil was continually stirred and allowed to settle for the specified time until all of the particles that would settle one foot in the given time had done so, as was indicated by the clearness of the suspension. This took from 20 to 30 washings for each separate. The last two separates were divided by the use of a centrifuge in order to hasten the work.

The time necessary to run the centrifuge was calculated so that the resulting smallest separate would be one-half the diameter of the next largest separate in order to approximate the results obtained by the sedimentation in the percolators.

The average diameter of each separate was determined by measuring 1000 particles with a microscope, using an ocular micrometer. The microscope was also used to determine if all of the aggregates were completely separated.

Table 1 gives the average diameter of the separates. It also shows that as the time of sedimentation is increased

six times over the previous sedimentation period, the size of the smaller particle decreases approximately one-half in diameter of the next larger separate. This agrees with the results of Perkins and King (1936).

Table 1. The scheme by which the Wabash separates were made.

Designation of separates	Time particles remained in suspension in one foot column of water	Time particles settled in one foot of water	Average diameter mm.
A	less than 3.33 min.	3.33 min.	.06
B	3.33 min.	20 min.	.034
C	20 min.	2 hrs.	.016
D	2 hrs.	12 hrs.	.006
E	12 hrs.	3 days	.003
F	3 days	over 3 days	less than .003

Table 2 gives some calculated data for the Wabash separates showing how the surface area and the number of particles per gram of separates increase as the particles become smaller.

Table 2. Data for the Wabash separates.

Designation of separates	A	B	C	D	E	F <sup>11</sup>
Radius in mm.	.03	.017	.008	.003	.0015	less than .0015
Percent of the entire soil	13.01	32.12	10.25	6.8	6.79	30.93
Particles per gm. (millions)	3.3	18.6	177.6	3375	27000	217000 or more
Surface per gm. of separate (sq. cm.)	382	670	1420	3815	7640	15350 or more

<sup>11</sup>

.00075 mm. was used as the radius of the F separate in the subsequent calculations.

The Ottawa sand was divided into four separates by sedimentation in the percolators. The data for the Ottawa sand are given in Table 3.

Table 3. Data for the Ottawa sand.

Designation of separates	Bs	Cs	Ds	Es
Radius in mm.	.013	.0054	.002	less than .002
Surface per gm. of separate (Sq. cm.)	970	2100	5725	11,450 or more

A portion of each of the Wabash separates was then subdivided into two fractions.<sup>12</sup> The fractions consisted of those minerals with a specific gravity heavier than 2.62 and those less than 2.62. The fractionation was made by centrifuging small amounts of the separate in a solution of bromoform-carbon-tetrachloride. The specific gravity of the bromoform solution was adjusted to 2.62 each time before it was used. After placing the soil and the bromoform solution in a centrifuge tube, the soil was thoroughly stirred and then centrifuged. The soil material that came to the top after the first centrifuging was stirred again and the entire content was centrifuged again. The material that came to the top after the second centrifuging was decanted onto a filter. More bromoform solution was added to the tube and the material that had settled was stirred loose and thoroughly dispersed and then centrifuged for the third time. After centrifuging each small sample three times, the soil material that came to the top and that which remained in suspension was separated from that which settled in the bromoform solution. The minerals heavier than specific gravity 2.62 are designated by a plus sign following the capital letter that designates the separate and the light minerals have a minus sign following the capital letter.

---

<sup>12</sup> On a specific gravity basis.

By this fractionation the heavy minerals contain the quartz group and the light minerals contain the feldspar group, as classified by Jeffries (1937).

Table 4 shows that as the particle size became smaller, the amount of heavy minerals decreased and that there was only a trace of heavy minerals in the entire clay portion of the soil. It was assumed that either there were no heavy minerals in the clay portion or that these particles were associated with a film of water about them so that they would not exert their true weight in the bromoform solution.

Table 4. Data for the Wabash fractions.

Fraction	Weight gms.	Percent of separate	Ratio of the light to the heavy minerals
A-	860	63.4	1.14
A+	490	46.6	
B-	650	54.3	1.18
B+	548	45.7	
C-	510	63.7	1.75
C+	290	36.3	
D-	885	98.91	88.5
D+	9.8	1.09	
E+	trace	----	----
F+	0	----	----

In an effort to rid the clay particles of adsorbed water two methods were employed. First, portions of the two

smallest separates E and F were saturated with the bromoform solution and placed in a desiccator which was then evacuated. After this treatment the separates were centrifuged with the bromoform solution and still no heavy minerals were obtained. The second method was to attempt to dehydrate the clay particles with absolute alcohol and anhydrous ether. Portions of the E and F separates were twice shaken and centrifuged with 80 percent ethenol, twice with 95 percent ethenol, twice with absolute alcohol, and once with anhydrous ether. The separates were dried from the ether by drawing air through a calcium chloride tube and through the centrifuge bottles containing the separates. After this treatment there were still no heavy minerals obtained when the separates were centrifuged with the bromoform solution. It was concluded that either the clay particles still held water, or that these secondary minerals formed were all of less specific gravity than 2.62.

It is of interest to notice that there is a break between the C and D separates in several of the tables. Table 1 shows that the average diameter of the D separate is less than half of the C separate. Table 4 shows there is a decided difference in the ratio of the light to the heavy minerals between the C and D separates. And, in Table 5 there is a break between the C and D separates in the

chemical analysis. The  $\text{SiO}_2$  goes from 85.41 percent in the C to 70.33 percent in the D, and the  $\text{R}_2\text{O}_3$  content changes from 11.03 percent in the C to 17.58 percent in the D.

### Chemical Analysis

The chemical analysis of the Wabash soil, its separates and fractions, as obtained by A. O. A. C.<sup>15</sup> methods, are given in Table 5.

### Procedure for Determining Phosphorus Fixation

One gram of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  was dissolved in one liter of water. This was used as a stock solution for all applications up to and including the equivalent of 5,000 pounds of mono-calcium phosphate per 2,000,000 pounds of soil. For applications heavier than the equivalent of 5,000 pounds per 2,000,000 pounds of soil, a stock solution of double this concentration was used.

In all of the determinations a soil:solution ratio of 1:2½ was used, and in most cases 25 grams of the soil was agitated with 62.5 mls. of solution. To the 25 grams of the soil in a 500 ml. centrifuge bottle was added the number of mls. of the stock solution that was necessary for the desired application of mono-calcium phosphate and enough

---

<sup>15</sup> Methods of Analysis of the Association of Official Agriculture Chemist. 4th Ed.

Table 5. Chemical analysis.

[illegible]

CO<sub>2</sub> free water to bring the total amount of solution to 62.5 mls.<sup>14</sup> This mixture was agitated at 25° C. in a constant temperature room for 18 hours by rotating end over end at the rate of six revolutions per minute. At the end of 19 hours the samples were removed and centrifuged so as to obtain the extract. A portion of the extract was filtered through clay filters and the filtrate was analyzed for its phosphorus content by Denigé's coeruleomolybdate method as adapted by Atkins (1923). The color comparison of the standard and the unknown solutions were made in Nessler tubes. The difference in the concentration of phosphorus in the extract from the concentration of the phosphorus in the solution added to the soil was taken to be the amount of phosphorus fixed by the soil.

While this method of determining the amount of phosphorus fixed does not give as much fixation as the method of evaporating the solution from the soil after agitation and then extracting the water soluble phosphorus from the soil, it is an excellent method to represent relative results as the time of contact, which is very important, can be controlled.

---

<sup>14</sup> The technique employed was to add the water to the soil first.

### Preparation and Use of the Clay Filters

It has been pointed out by Parker (1925) and others that clay filters absorb phosphorus when using them in obtaining soil extracts. Knowing this to be true, considerable time was spent developing a method similar to that used by Perkins, King, and Benne (1932), whereby the clay filters could be used in preparing soil extracts. New filters were washed with  $N/10$  HCl until the filtrate developed no color when tested for phosphorus. This took from 20 to 40 hours. The filters were then tested by filtering solutions of known concentration of phosphorus through them. This was followed by washings of  $N/10$  and  $N/20$  HCl. The combined filtrates were then analyzed for phosphorus. The technique followed was to keep the phosphorus solution in the lower half of the filters and allow them to be drained of the phosphorus solution before washing them with dilute HCl. It was found that the filters could be washed clean from phosphorus after filtering a solution containing up to 1 p.p.m. of phosphorus by washing the filters with 50 mls. of  $N/10$  and 50 mls. of  $N/20$  HCl. The total amount of phosphorus could also be recovered in the combined filtrates. For solutions containing higher concentrations of phosphorus, smaller amounts of the solution were filtered and in turn the filters were washed

with larger amounts of dilute HCl. In some cases 5 mls. of the soil extract were filtered and followed by a washing of 395 mls. of dilute HCl. This dilution of the filtrate was quite satisfactory because, as stated by Parker (1925) and observed by others, the solution should not contain more than .3 p.p.m. of  $\text{PO}_4$  for the most satisfactory results when using Deniges' method for the determination of phosphorus. After each time the filters were used, they were washed with an additional 100 mls. of the dilute HCl and this filtrate was analysed to verify the procedure used. Before using the filters again they were washed with a brush and heated in a muffle to a dull red. By using this procedure of making the dilution through the filters with dilute HCl, consistent results were obtained and the filters were found to be washed free of phosphorus.

#### RESULTS OF PHOSPHORUS FIXATION

The first series of experiments were conducted with the entire Wabash soil in order to determine how the length of time of agitation influenced the amount of fixation. Table 6 gives the data collected. An application of 100 pounds of mono-calcium phosphate per 2,000,000 pounds of soil was over 90 percent fixed after 30 minutes of agitation, but continued to fix phosphorus slightly over a period of six

Table 6. Phosphate fixation as effected by time.

Time of agitation at 25° C.	Phos- phorus in sol- ution added :D.D.E.	Phos- phorus in ex- tract :D.D.E.	Phos- phorus in ex- tract % :D.D.E.	Phos- phorus fixed by soil %	Phosphorus added as mono-calcium phosphate to 25 gm. soil mg.	Phos- phorus fixed per 100 gm. of soil, mg.
-----------------------------------	---	---	--	---	--	---

100 pounds of mono-calcium phosphate per  
2,000,000 lbs. soil

30 min.	4.9	.348	7.1	92.9	.3063	1.140
1 hr.	4.9	.348	7.1	92.9	.3063	1.140
2 hrs.	4.9	.315	6.4	93.6	.3063	1.148
4 "	4.9	.315	6.4	93.6	.3063	1.148
6 "	4.9	.2418	4.96	95.05	.3063	1.164
12 "	4.9	.2160	4.4	95.6	.3063	1.168
1 day	4.9	.2147	4.39	95.62	.3063	1.169
2 days	4.9	.231	4.7	95.3	.3063	1.166
3 "	4.9	.21	4.3	95.7	.3063	1.172
4 "	4.9	.1732	3.54	96.46	.3063	1.180
5 "	4.9	.2205	4.5	95.5	.3063	1.166
6 "	4.9	.192	3.92	96.08	.3063	1.176

500 pounds of mono-calcium phosphate per  
2,000,000 lbs. soil

1 min.	24.5	2.895	11.75	92.25	1.551	5.4
1 hr.	24.5	1.26	5.15	94.85	1.551	5.76
2 hrs.	24.5	1.18	4.7	95.3	1.551	5.8
6 "	24.5	1.05	4.3	95.7	1.551	5.84
12 "	24.5	.6075	2.38	97.62	1.551	5.96
18 "	24.5	.479	1.95	98.05	1.551	6.0

5,000 pounds of mono-calcium phosphate per  
2,000,000 lbs. soil

1 day	245	52	21.2	78.8	15.51	49.08
2 days	245	50.4	20.6	79.4	15.51	48.6
3 "	245	50.4	20.6	79.4	15.51	48.6
4 "	245	47.2	19.2	80.8	15.51	49.28
6 "	245	42	17.1	82.9	15.51	50.6
6 "	245	39.4	16.1	83.9	15.51	51.28

days. Upon an application of 500 pounds, 88.25 percent of the phosphorus was fixed after the first minute. At the end of 18 hours, 98.05 percent of it was fixed. An application of 5,000 pounds per 2,000,000 pounds of soil showed that 78.8 percent of it had been fixed at the end of one day and that there was a slight increase in fixation continuing for six days. It was therefore observed to be necessary to agitate the samples for a definite length of time so as to get relative results. As the major portion of the phosphorus was fixed before the end of 18 hours of agitation the remaining experiments were agitated for only 18 hours.

The next series of experiments were conducted with the Wabash separates. The separates were agitated with applications of mono-calcium phosphate equivalent to from 200 to 10,000 pounds per 2,000,000 pounds of soil. The data and graphical representation of these experiments are given in Table 7 and Fig. 1, respectively. First, it was observed that with any one application, the amount of phosphorus fixed increased as the particle size decreased. This was true except for the single A separate, which was consistently higher in its fixing capacity than was separate B, and in several cases higher than C. Secondly, Fig. 1 shows that there is apparently a maximum in the ability of a separate to fix phosphorus; the three larger separates indicate this

Table 7. Data for Wabash separates.

Separate and pounds of Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O added per 2,000,000 of soil	:Phos- phorus in solu- tion added :P.P.M.	:Phos- phorus in ex- tract :P.P.M.	:Phos- phorus in ex- tract % :	:Phos- phorus fixed by soil % :	:Phosphorus added as Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O to 25 gm. of soil PP.	:Phos- phorus fixed per 100 gm. soil PP.	:Phosphorus fixed per square meter of surface PP.
A 200	9.8	.168	1.72	98.28	.6125	2.416	.632
B 200	9.8	.28	2.86	97.14	.6125	2.392	.326
C 200	9.8	.176	1.79	98.21	.6125	2.415	.17
A 300	14.7	3.36	22.9	77.1	.9186	2.84	.745
B 300	14.7	6	40.8	59.2	.9186	2.18	.326
C 300	14.7	3.15	21.5	78.5	.9186	2.88	.23
A 500	24.5	9.9	40.4	59.6	1.531	3.656	.959
B 500	24.5	13.86	56.5	43.5	1.531	2.472	.369
C 500	24.5	9.24	37.7	62.3	1.531	3.84	.27
D 500	24.5	.57	2.31	97.69	1.531	8.98	.157
E 500	24.5	.108	.44	99.56	1.531	6.083	.0799
F 500	24.5	.141	.58	99.42	1.531	6.02	.0396
D 1,000	49	2.58	5.26	94.74	3.0625	11.6	.305
A 2,000	98	67.2	68.8	31.2	6.125	7.64	1.99
B 2,000	98	92.4	94	6	6.125	1.47	.23
C 2,000	98	71.2	72.6	27.4	6.125	6.72	.472
D 2,000	98	10.5	10.73	89.27	6.125	21.84	.674
E 2,000	98	.515	.527	99.47	6.125	24.36	.319
F 2,000	98	.465	.474	99.53	6.125	24.4	.159
A 5,000	245	205	83.7	16.3	15.31	10.0	2.63
B 5,000	245	236	95.5	3.5	15.31	2.14	.32
C 5,000	245	211	86.3	13.7	15.31	8.4	.592
D 5,000	245	81.4	33.2	66.8	15.31	41.2	1.08
E 5,000	245	5.76	2.35	97.65	15.31	59.6	.73
F 5,000	245	2.83	1.16	98.84	15.31	60.4	.40
D 10,000	490	282	53.5	46.5	30.625	56.8	14.9
E 10,000	490	75.6	15.45	84.55	30.625	104	13.6
F 10,000	490	35.2	7.8	92.8	30.625	114	7.43

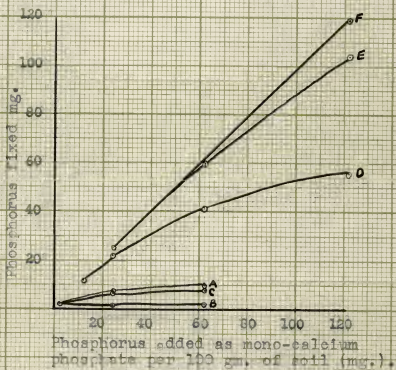


Fig. 1. Phosphorus fixed by the Wabash separates with increasing applications of mono-calcium phosphate.

very well. After they have fixed so much phosphorus, they appear to be saturated or nearly so, so that increased applications of phosphorus are not fixed by these separates. The separate D, which is in the silt range, appears to be definitely approaching a maximum limit of fixing power. The separate E, which is composed of the smallest of the silt particles and the larger particles of clay, shows a slight tendency to be approaching a maximum fixing power, while the separate F, which contains the colloidal material, was able to fix all of the phosphorus of the 10,000 pound application and shows no sign of approaching a maximum fixing capacity. Increased applications were not made to determine what application of mono-calcium phosphate would have been necessary to satisfy the fixing power of the clay material.

The fractions of the separates were agitated with an equivalent of 500 pounds of mono-calcium phosphate per 2,000,000 pounds of soil. The data collected are given in Table 8.

It was found that more phosphorus was fixed by the fractions than was fixed by the original separates with the same application. The only treatment the fractions had received different from that which the separates received was their centrifugation with the bromoform solution. To

Table 8. Data for the Wobash series.

Fraction and pounds of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ added per 2,000,000 lbs. added of soil	Phos- phorus in so- lution lbs. added	Phos- phorus ex- tract %	Phos- phorus ex- tract %	Phos- phorus added as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ fixed to 25 gm. of soil %	Phos- phorus fixed to 25 gm. of soil %
A+ 500	24.5	9.41	38.4	61.6	1.531
A- 500	24.5	1.64	6.69	93.31	1.531
B+ 500	24.5	5.46	22.3	77.7	1.531
B- 500	24.5	1.55	6.57	93.43	1.531
C+ 500	24.5	1.29	5.28	94.72	1.531
C- 500	24.5	1.08	4.28	95.72	1.531



see if the treatment with bromoform caused the increased fixation, portions of the separates were saturated with bromoform. The excess bromoform was leached out of the separates with ethenol, as was the excess bromoform of the fractions. When these bromoform treated separates were agitated with the phosphorus fertilizer, they too fixed more phosphorus than they originally did. It was also observed that the sum of the amounts fixed by the heavy and light fractions of a separate, times their respective percent of the separate, was approximately the same amount as that fixed by the separate when it was treated with bromoform. The pH of the extracts of the fractions was 4 to 5.5, whereas the pH of the extracts of the Wabash separates was between 5.3 and 6.5. Although the slight difference in reaction may have had some influence in the increased fixation it is believed that most of the increased fixation was accounted for by the presence of the bromoform. The exact cause of the increased fixation has not been determined, but it may have been caused by minute amounts of free bromine in the bromoform.

In the last series of experiments on phosphorus fixation the Ottawa sand was used. First, the four separates were agitated with an equivalent application of 500 pounds of mono-calcium phosphate per 2,000,000 pounds of the sand.

The data are given in Table 10. With the 500 pound application of phosphorus fertilizer the Ottawa sand separates fixed from 18.5 to 38.6 percent of the added phosphorus. The increased fixation followed decreased particle size. However, the similar sized separates of the Wabash separates fixed from 43.5 to 99.5 percent of the added phosphorus with the 500 pound application. This showed that even though the Ottawa sand did fix some phosphorus and that there was an increase in phosphorus fixation as the particles became smaller, neither the total amount fixed or the rate of increased fixation as the particles became smaller was as great as that of the Wabash separates. Secondly, a portion of the unseparated Ottawa sand was agitated for different periods of time with an application of 500 pounds of the fertilizer per 2,000,000 pounds of the sand. Upon analyzing the extracts it was found that as much phosphorus was fixed at the end of one minute as was fixed at the end of 18 hours of agitation. This was believed to be significant as it gives further evidence of anion adsorption when no iron and aluminum is present. Table 11 shows the data for this experiment.





## DISCUSSION OF RESULTS

It was evident with the Wabash soil that increased time of agitation increased the amount of phosphorus fixed. The prolonged agitation of the phosphate fertilizer with the Ottawa sand did not increase the amount of phosphorus fixed. Further inspection of the data showed that the Wabash soil contained 8.16 percent of iron oxide whereas the Ottawa sand was free of iron oxide. This would further verify the statements of Davis (1935), Eradfield, Scarseth, and Steele (1935) and others that infer the increased phosphorus fixation with time to be due to the gradual dissolving of the iron from the soil complex. The gradual dissolving of the iron would be brought about by the acid condition of the soil. The iron as it was brought into the soil solution would readily fix some of the soluble phosphate; thus, the phosphorus fixing power of the soil would increase with time.

Due to the fact that there were no heavy minerals obtained from the clay portion of the Wabash soil and to the difficulty encountered in the use of bromoform on the separates, both of which have been previously discussed, there was not much data collected from the fractionation of the separates. However, the amount of phosphorus fixed in most cases was in a direct ratio to the  $R_2O_3$  content of the fractions.

Interesting curves were obtained by first plotting the milligrams of phosphorus fixed on one square centimeter surface area of the separates against the diameter of the separates, as indicated by Fig. 2.

With the exception of the A separate, the other separates form nearly a straight line. A straight horizontal line would indicate that the amount of phosphorus fixed per square centimeter of each separate was constant. Secondly, Fig. 3 shows the curve that resulted when the percent of the phosphorus fixed by the separates was plotted against the surface area per gram of each separate. The rapid rise of this curve indicates that the phosphorus was fixed to a considerable degree on the surface of the particles. The data for these curves were calculated from the fixation that occurred with the application of 5,000 pounds of monocalcium phosphate per 2,000,000 pounds of soil. The data are given in Table 2. The third curve, as shown in Fig. 4, resulted when the percent of phosphorus fixed of the 5,000 pound application of the fertilizer was plotted against the percentage of  $R_2O_3$  in the separates. The percentage of  $R_2O_3$  was obtained from the chemical analysis, as indicated in Table 4. The rapid rise of this curve shows that the phosphorus fixed varies directly with the  $R_2O_3$  content. This of course agrees with most of the investigations of

Phosphorus  
fixed on one  
sq. cm. area  
of soil  
separates  
mg.

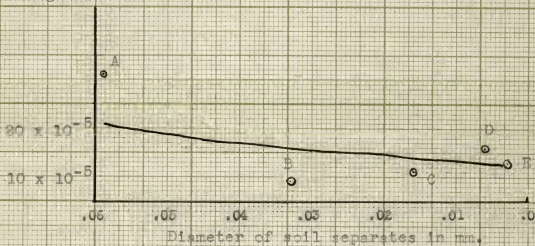


Fig. 2. Shows the amount of phosphorus fixed per square centimeter of each separate.

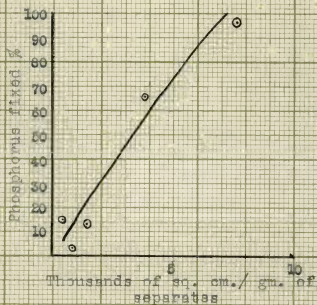


Fig. 3. Adsorption curve.

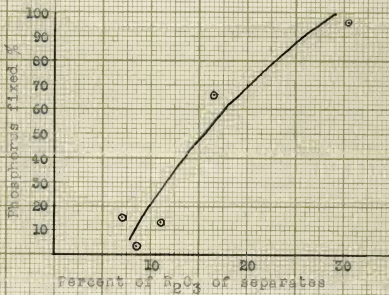


Fig. 4. Phosphorus fixation as caused by the iron and aluminum hydroxides.

phosphorus fixation.

Davis (1935) stated, "... characteristic 'adsorption' curves obtained are ambiguous, that they may imply any type of reaction." If only an adsorption curve is made and it is stated that the phosphorus fixed is therefore a surface phenomenon, he is probably correct, as Fig. 3 in comparison with Fig. 4 indicates. The two curves are quite similar, while Fig. 3 is an adsorption curve and Fig. 4 a curve of fixation as caused by the  $R_2O_3$  content. However, it was believed that the adsorption curve does have some value, for by superimposing the curves it would indicate that considerable of the  $R_2O_3$  active in fixing phosphorus was associated with the surface of the particles. The experimental data show that the total  $R_2O_3$  content of the separates increases as the surface area increases, so it would seem logical to assume that more  $R_2O_3$  was exposed to the surface in the smaller separates. In this manner, then, phosphorus fixation may be called a surface phenomenon. However, at the same time the mechanism of fixation is chiefly chemical precipitation.

It was previously stated that the Ottawa sand separates did not fix as much phosphorus as did the Wabash separates. It was also stated that the phosphorus that was fixed by the sand was fixed immediately. Scarseth and Tidmore (1934) and

Murphy (1939) have called particular attention to the large amount of phosphorus that is fixed immediately after the phosphate solution is added to the soil. In fact, that has been the major evidence for those who ascribe phosphorus fixation as surface adsorption. It has been pointed out in the review of the literature that phosphorus may be fixed by surface adsorption. The amount of phosphorus fixed by the Ottawa sand gives further evidence of this.

Considerable evidence has been given to show that phosphorus is fixed by both chemical precipitation, whether it be in the solution or on the surface of the particles, and by surface anion adsorption. The material cited, as well as the experimental data collected, show that the major portion of the phosphorus is fixed within a relatively short period, also that fixation increases as the time of agitation is lengthened. Both the cited literature and the observed data show that some of the phosphorus is fixed immediately as the phosphorus is added to the soil. It would appear, therefore, that both mechanisms operate in fixing phosphorus in the soil and that they operate at the same time. The rapid fixation at the time of the application is caused in part by the mechanism of surface anion adsorption and in part by the mechanism of chemical precipitation with the active iron and aluminum hydroxides free in the solution or on the surface

of the soil particles. The increased fixation with time is accounted for by the precipitation of the phosphorus with iron and aluminum as they are gradually dissolved from the soil complex.

### SUMMARY

A medium acid soil under cultivation and a pure  $\text{SiO}_2$  sand were used in the experimental procedure. The soil was separated into six separates of different sizes and these separates were in turn fractionated into heavy and light mineral groups. The sand was only separated into four separates and it was not fractionated. Various applications of mono-calcium phosphate were agitated with the soil and sand separates in a soil solution ratio of  $1:2\frac{1}{2}$ . Definite periods of agitation were used and the temperature was controlled by means of a constant temperature room. After the agitation the mixture was centrifuged and the extract filtered. A portion of the extract was analyzed for phosphorus. The difference in the amount of phosphorus in the extract and the amount of phosphorus in the solution added to the soil before agitation was taken to be the amount of phosphorus fixed by the sand or soil.

With the soil, which contained iron and aluminum, phosphorus fixation increased as the time of agitation

increased. With the sand, which contained no iron and aluminum, there was no increased fixation with time. The amount of phosphorus fixed by the soil and sand separates increased as the particle size decreased. The amount of phosphorus fixed by the soil separates was greater than the amount fixed by the sand separates of similar size. The difference between the amount of phosphorus fixed by the soil and sand separates, increased as the particle size decreased. In practically all cases of both the separates and the fractions of the soil, the amount of phosphorus fixed was in a direct relationship with the total  $R_2O_3$  content of the separates and fractions.

#### CONCLUSIONS

1. Phosphorus is chemically precipitated with iron and aluminum compounds.
2. Phosphorus is adsorbed on the surface of the particles.
3. Phosphorus fixation increases with time when there is iron and aluminum in the complex.
4. Phosphorus fixation may be regarded as a surface phenomenon, since a large portion of the chemical precipitation takes place on the surface of the particles and also the anion adsorption is on the surface of the particles.

5. The two mechanisms of phosphorus fixation, chemical precipitation and anion adsorption, operate together in fixing phosphorus in the soil. When phosphorus is added to the soil, the immediately fixed phosphorus is in part caused by the anion adsorption attaining equilibrium, and also by the phosphorus combining with the iron and aluminum compounds in the soil complex. The prolonged fixation with time was believed to be due to the gradual dissolving of iron and aluminum from the complex due to the slightly acid condition. The dissolved iron and aluminum would then readily combine with more of the phosphorus.

#### ACKNOWLEDGMENTS

The writer desires to express his indebtedness to Dr. H. H. King and Dr. A. T. Perkins for suggesting the problem and securing funds for financing it; to Dr. A. T. Perkins, his major instructor; and to Dr. W. H. Metzger of the Department of Agronomy for helpful suggestions.

#### REFERENCES

- Askinazi, D. L. and Yarusov, S. S.  
Liming as a factor of mobilizing phosphoric acid in the podsol soil. Trans. Sci. Inst. Fert. 57:59. 1928.  
Chem. Abs. 23:3535. 1928.
- Atkins, W. R. G.  
The rapid determination of available phosphate in soil by coeruleomolybdate reaction of Denigés. Jour. Agr. Sci. (England), 14:192-197. 1923.

- Beater, B. E.  
Measurement of phosphate fixation in soils. Soil Sci. 44:277-291. 1937.
- Benne, Erwin J.  
Factors affecting the solubility of inorganic phosphorus in aqueous solution and aqueous soil extracts. Unpublished thesis, Kans. St. Col. Agr. and Appl. Sci. 73 p. 1937.
- Benne, E. J., Perkins, A. T., and King, H. H.  
The effect of calcium ions and reaction upon the solubility of phosphorus. Soil Sci. 42:29-38. 1936.
- Bradfield, Richard; Scarseth, George, and Steele, J. G.  
Factors affecting the retention of phosphorus by clay. Internatl. Soc. Soil Sci., Proc. 1:74-75. 1935.
- Burgess, Paul S.  
Comparison of "active" aluminum and hydrogen ion concentration of widely separated acid soils. Soil Sci. 15:507-512. 1923.
- Comber, Norman M.  
Scientific study of the soil. New York. Longmore, Green and Co. 92 p. 1929.
- Crawley, J. T.  
Fixation of phosphoric acid in the soil. Amer. Chem. Soc. Jour. 24:1114-1119. 1902.
- Davis, L. E.  
Sorption of phosphates by non-calcareous Hawaiian soils. Soil Sci. 40:129-158. 1935.
- Dean, L. A.  
Electrodialysis as a means of studying the nature of the soil phosphates. Soil Sci. 37:253-266. 1933.
- Doughty, J. L.  
Phosphate fixation in soils, particularly as influenced by organic matter. Soil Sci. 40:191-202. 1935.
- Ellett, W. B. and Hill, H. H.  
Contribution to the study of phosphoric acid in soils and fertilizers. Va. Agr. Expt. Sta., Ann. Rpt. 1909-1910. 232 p. 1911.

Ford, M. C.

The nature of phosphate fixation in soil. Amer. Soc. Agron. Jour. 25:134-144. 1933.

Fraps, G. S.

Active phosphoric acid and its relation to the needs of the soil for phosphoric acid in pot experiments. Tex. Agr. Expt. Sta. Bul. 126. 72 p. 1910.

---

Effects of lime and carbonate of lime on acid phosphate. Tex. Agr. Expt. Sta. Bul. 223. 16 p. 1917.

---

The fixation of phosphoric acid by the soil. Texas Agr. Expt. Sta. Bul. 304. 22 p. 1922.

Gile, Philip L. and Smith, J. G.

Colloidal silica and the efficiency of phosphates. Jour. Agr. Res. 31:247-260. 1925.

Gordon, Neal E. and Starkey, E. B.

Influence of soil colloids on availability of salts. Soil Sci. 14:1-9. 1922.

Gortner, Ross Aiken, and Shaw, William M.

The organic matter of the soil: IV. Some data on humus-phosphoric acid. Soil Sci. 3:99-111. 1917.

Heck, A. Floyd

Phosphate fixation and penetration in soils. Soil Sci. 37:343-355. 1933.

---

A method for determining the capacity of the soil to fix phosphorus in difficulty available form. Soil Sci. 37:477-482. 1934a.

---

Effect of the degree of base saturation of a soil on its capacity to fix phosphorus in difficulty available form. Soil Sci. 38:463-470. 1934b.

Hendrichs, Sterling B. and Alexander, Lyle T.

Minerals present in soil colloids. I. Descriptions and methods for identification. Soil Sci. 48:257-267. 1939.

- Hibbard, P. L.  
Factors influencing phosphate fixation in soils. Soil Sci. 39:337-358. 1935.
- Hissink, D. J.  
The adsorption processes in soils. Internatl. Mitt. f. Bodenk. 12:81-172. 1922. Chem. Abs. 17:1100. 1922.
- Jeffries, Charles D.  
The mineralogical composition of the very fine sands of some Pennsylvania soils. Soil Sci. 43:357-365. 1937.
- Kappen, H. and Bollenbeck, K.  
Significance of the kind of soil acidity for the solution of sparingly soluble phosphates. Ztschr. f. Pflanzenernähr., Düngung u. Bodenk. 4A:1-29. 1925. Chem. Abs. 19:2719. 1925.
- Lichtenwalner, D. C., Flenner, A. L., and Gordon, Neil E.  
Adsorption and replacement of plant food in colloidal oxides of iron and aluminum. Soil Sci. 15:157-165. 1922.
- Mattson, Sante  
Anionic and cationic adsorption by the soil colloidal materials of varying  $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  ratio. Internatl. Cong. Soil Sci., Proc. Comm. 2:199-211. 1927.
- 
- The laws of soil colloidal behavior: VI. Amphoteric behavior. Soil Sci. 32:343-363. 1931.
- 
- The laws of colloidal behavior: IX. Amphoteric reactions and isoelectric weathering. Soil Sci. 34:209-240. 1932.
- Mattson, Sante, and Gustafsson, Yngve  
The laws of soil colloidal behavior: XVIII. Colloidal electrolytes. Soil Sci. 43:421-452. 1937.
- Mattson, Sante and Karlsson, Nils  
The electro-chemistry of soil formation: II. The phosphate complex. Ann. Agr. Col. Sw. 6:109-157. 1938.

- McGeorge, W. T. and Breazeal, J. F.  
Studies on iron, aluminum, and organic phosphates and  
phosphate fixation in calcareous soils. Ariz. Agr.  
Expt. Sta. Tech. Bul. 40. 111 p. 1932.
- Meyer, W. W.  
Colloidal nature and related properties of clays.  
Nat'l. Bur. Standards Jour. Res. 13:245-258. 1934.
- Miller, Lewis B.  
Retention of phosphates by hydrated alumina and its  
bearing on phosphates in the soil solution. Soil Sci.  
26:435-439. 1928.
- Murphy, H. F.  
Role of kaolinite in phosphate fixation. Hilgardia,  
12:343-382. 1939.
- Nemec, A.  
A contribution to the evaluation of requirements for  
the fertilizing soils with phosphorus. Vestnik Vatr.  
Jednoty Repare Cal. 11:277. 1930. Chem. Abs. 25:  
2508. 1930.
- Parker, F. W.  
The absorption of phosphorus by Pasture-Chamberlin  
filters. Soil Sci. 20:149-159. 1925.
- Perkins, Alfred T. and King, H. H.  
Base exchange in soils. Kans. Acad. Sci., Trans. 38:  
163-170. 1935.
- 
- Base exchange in soil separates and soil fractions  
(sand and silt). Soil Sci. 42:323-326. 1936.
- Perkins, A. T., King, H. H., and Benne, E. J.  
Effect of exchangeable base and soil treatments on  
phosphorus solubility. Soil Sci. 34:385-392. 1932.
- Peterson, P. P.  
Effect of heat and oxidation on the phosphorus of the  
soil. Wisc. Agr. Expt. Sta. Res. Bul. 19. 16 p. 1911.

Pugh, A. J. and duToit, M. S.

The composition and ionic exchange of ferric silicates and phosphates. Soil Sci. 41:417-432. 1936.

Ravikovitch, S.

Anion exchange: I. Adsorption of the phosphoric ions by soils. Soil Sci. 38:219-239. 1934a.

---

Anion exchange: II. Liberation of the phosphate ions adsorbed by soils. Soil Sci. 38:279-290. 1934b.

---

Influence of exchangeable cations on the availability of phosphate in soils. Soil Sci. 47:357-366. 1939.

Romine, Dale S. and Metzger, W. H.

Phosphorus fixation by horizons of various soil types in relation to dilute acid extractable iron and aluminum. Amer. Soc. Agron., Jour. 31:99-108. 1939.

Rostworowski, S. and Wiegner, G.

The absorption of phosphoric acid by "zeolites" (Permutite). J. Landw. 60:223-235. 1912. Chem. Abs. 6:3304-3305. 1912.

Rossmann, C. A.

Retention of phosphorus by soil colloids. Soil Sci. 24:465-474. 1927.

Russell, H. L. and Morrison, F. B.

Lime maintains availability of phosphorus. New Farm Facts. Wisc. Agr. Expt. Sta. Bul. 323. 98 p. 1920.

Scarseth, George D.

The mechanism of phosphate retention by the natural aluminosilicates colloids. Amer. Soc. Agron., Jour. 27:596-616. 1935.

Scarseth, G. D. and Tidmore, J. W.

The fixation of phosphorus by soil colloids. Amer. Soc. Agron., Jour. 26:138-151. 1934.

Spurway, C. H.

Some factors influencing the solubility of phosphorus in soil-acid phosphate mixtures. Soil Sci. 19:399-405. 1925.

Teakle, L. J. H.

Phosphates in soil solution as affected by reaction and cation concentrations. Soil Sci. 25:143-162. 1928.

Toth, S. J.

Anion adsorption by the soil colloids. Soil Sci. 44: 299-314. 1937.

---

The effect of free iron oxide removal on some properties of soil colloids. Soil Sci. 48:385-401. 1939.

Whitson, A. R. and Stoddard, C. W.

Availability of phosphates in relation to soil acidity. Wisc. Agr. Expt. Sta. Ann. Rpt. 23:171-180. 1906.

Wiley, R. C. and Gordon, Neil E.

Adsorption of plant food by colloidal silica. Soil Sci. 14:441-448. 1922.

Wityn, J.

The better use of  $P_2O_5$  in soils. Ztschr. f. Pflanzen-  
ernähr., Düngung u. Bodenk. 6A:27-51. 1926. Chem.  
Abs. 20:1682. 1926.