1932

The available phosphate content of soils and some factors affecting it

Samuel Shockley Obenshain
Iowa State College

Follow this and additional works at: https://lib.dr.iastate.edu/rtd
Part of the Agriculture Commons, and the Soil Science Commons

Recommended Citation
Obenshain, Samuel Shockley, "The available phosphate content of soils and some factors affecting it" (1932). Retrospective Theses and Dissertations. 14589.
https://lib.dr.iastate.edu/rtd/14589

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
NOTE TO USERS

This reproduction is the best copy available.

UMI®
THE AVAILABLE PHOSPHATE CONTENT OF SOILS
AND SOME FACTORS AFFECTING IT

BY

Samuel S. Obenshain

A Thesis submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY
Major subject Soil Fertility

Signature was redacted for privacy.

In charge of Major work.
Signature was redacted for privacy.

Head of Major Department.
Signature was redacted for privacy.

Dean of Graduate College.

Iowa State College
1932
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.
THE AVAILABLE PHOSPHATE CONTENT OF SOILS
AND SOME FACTORS AFFECTING IT

INTRODUCTION

The early agricultural chemists were the first to attempt to determine the needs of the soil by studying the soil itself. They believed that there should be a direct relation between the total amount of an element present in a soil and the amount of this element which would be available for plant growth on that soil. It was soon noted, however, that no such correlation existed between the total amount of phosphorus present in a soil and the crop response obtained with additions of phosphatic fertilizers. It became evident, therefore, that soils differ in their ability to provide available phosphorus for plant growth.

It has long been known that soils have the ability to remove phosphates from solution and hold them in a more or less insoluble form, and the term fixation has been applied to this phenomenon. An equilibrium apparently exists between the power of the soil to remove phosphates from solution and the rate at which the phosphates go into solution; and the point at which these two forces come to equilibrium determines, therefore, the
degree to which the phosphates in the soil are available for plant growth.

Many investigators have attempted to devise laboratory methods for the measurement of the amount of available phosphorus. Some of these methods have been more or less successful but none have been entirely satisfactory, probably partly due to a lack of knowledge of the factors responsible for the fixation of the phosphates by the soil. The author is of the opinion that any satisfactory test for the available phosphate content of the soil must take into account the various factors governing the fixation phenomenon. With this in mind, the following experiments were planned, not to determine the phosphorus available under certain soil conditions but rather to determine the effect of certain soil characteristics on the phosphate fixing power.
HISTORICAL

Fixation of Phosphorus by Soils.

Way (63) in 1850 first showed that soils have the ability to precipitate soluble phosphates. This discovery led to many investigations of the process, the earlier work dealing primarily with the amount of the fixation while many of the later studies centered about the mechanism of the process.

Huston and Goss (33) in 1890 working with Indiana soils reported that soils absorbed large amounts of phosphates. After treating several soils with solutions of different fertilizer salts, they concluded that surface soils to a depth of nine inches would take up 45 times as much phosphates as would be apt to be applied in a fertilizer. At about the same time Pagnoul (44) treated a number of soils with phosphates of potassium and found that there was a fixation of a large proportion of both ions. Crawley (12) studied phosphate fixation in two extremely basic Hawaiian soils, using containers nine inches square and nine inches deep. His results showed that when the superphosphate was applied immediately before the addition of water more than one-half of the
phosphoric acid in the fertilizer remained in the surface inch of soil, more than nine-tenths was held in the surface three inches, and practically all was fixed within six inches of the surface. When an interval of 15 hours elapsed between the application of the fertilizer and the addition of water, more than nine-tenths of the phosphoric acid remained in the first inch and practically all was fixed in the first three inches. In a study of the total capacity of the soil to fix phosphates 800 grams of soil and 50 grams of double superphosphate, containing 20.58 grams of water soluble phosphoric acid, were thoroughly mixed. The mixture was kept moist and samples were withdrawn from time to time for a determination of water soluble phosphoric acid. The mixture was made up on March 26, and the following percentages of the phosphorus were fixed: on March 27, 41.6; on March 29, 57.7; on April 3, 73.0; and on April 17, 85.65. Thus on the basis of an acre foot of soil weighing 3,500,000 pounds, 72,548 pounds of phosphoric acid would be fixed by the acre foot in 22 days.

Dusserre and Bieler (19) in a similar study determined the rate of absorption and the depth of penetration of the phosphoric acid added in a solution of superphos-
phosphate, in silicious clay, calcareous clay and peat. Glass cylinders were filled with successive layers of soil, separated by filter paper. The surface of the soil was covered with filter paper and the solution of superphosphate was poured on slowly, and distilled water was added until a given amount of solution had passed through the soil in the cylinder. The superphosphate was added at the rate of 3,410 killograms of phosphoric acid per hectare. After a period of one month the successive layers of soil were removed and analyzed. The results showed that in the peat soil the phosphoric acid penetrated to the greatest depth and also that the least amount of the phosphates had been retained by the soil. In the calcareous clay the phosphoric acid was retained near the surface and none passed through. The movement in the silicious clay was less than that in the peat soil but greater than that in the calcareous soil. The author concludes that, in general, 96.6 per cent of the phosphoric acid applied on the surface is rendered insoluble in the top 8 centimeters of soil.

Schreiner and Faillyer (54) allowed solutions of monocalcium phosphate and disodium phosphate, containing 200 p.p.m. of $\text{PO}_4^-$, to percolate slowly through four soils,
which differed widely in texture. Successive fractions of the percolates were collected and the phosphate content determined colorimetrically. The results showed that at first the phosphates were rapidly and completely absorbed but the absorption decreased with the later additions, becoming less and less marked until a saturated condition was reached. It was found that the absorption was sufficiently constant that it might be represented by a mathematical equation which expresses "that the quantity absorbed from a unit volume of the phosphate solution as it passes through the soil is proportional to the quantity which may yet be absorbed". The maximum quantity of phosphates which the different soils absorbed differed greatly, the absorption being higher in the heavier textured soils. Bogue (5) in a similar experiment verified the work of Schreiner and Fallyer (54).

The recent work of Stephenson and Chapman (60) and Midgley (40) on the movement of phosphates in soils also confirmed the earlier results. Stephenson and Chapman (60) found that when applications of a phosphatic fertilizer were made regularly for several years there was a definite penetration of phosphoric acid below the surface foot in the light and medium textured soils but
little or no movement occurred in heavy soils. Midgley
(40) applied superphosphate at the rate of 300 and 600
pounds per acre to the surface of the soil and after a
period of six months he found practically all of the phos-
phates remaining in the surface inch of soil.

Various workers have attempted to explain the
mechanism of the fixation process, attributing it to bio-
logical, physical, or chemical factors alone or to com-
binations of these factors. Others have studied the im-
portance of various soil constituents in their effect on
fixation without regard to the type of action involved.

As early as 1911 Dushechkin (17)(18) after study-
ing the biological fixation of phosphoric acid from solu-
tions in soils receiving starch and treated with thymol
and chloroform, concluded that in addition to the physico-
chemical absorption of phosphoric acid in soils there is
a biological absorption. Skalkij (56) in a similar study
attempted to differentiate between physico-chemical and
biological fixation. He used 50 c.c. of chloroform per
kilogram of soil to prevent biological action. The treat-
ment used was 1.3312 grams of acid phosphate per kilogram
of soil. In the surface soils studied, the physico-
chemical fixation accounted for 73.16 to 87.14 per cent
of the phosphorus added, while the biological fixation
accounted for 1.48 to 2.24 per cent. In the subsoil the
physico-chemical fixation accounted for 83.29 to 89.94
per cent of the phosphorus while the biological fixation
accounted for 0.22 to 1.70 per cent. In a similar experi-
ment Bytchihine (8)(9) verified the earlier work of
Skalkij (56).

Rudakov (51) inoculated a small amount of soil
into a medium consisting of conductivity water, mannitol,
and mono-ammonium phosphate and found a rapid decrease in
soluble phosphoric acid under anaerobic conditions. He
was able to isolate pure cultures of organisms, which
brought about this fixation which he attributed to a re-
duction process. He also found that different soils dif-
fered in their ability to reduce the phosphoric acid under
these conditions.

Those investigators who have favored the theory
of the physical absorption of phosphates as a partial or
complete explanation of the fixation of phosphates by soils,
have worked with soils, soil colloids or synthetic colloids.
Russell and Prescott (53) extracted phosphates from soils
with dilute acids and found that if the acid was allowed
to remain in contact with the soil, the soil removed from
the solution, some of the phosphates originally extracted.
They stated that "the absorption of the P₂O₅ ion from
solution in presence of acid is found to follow precisely
the ordinary lines of adsorption by colloids". This ob-
servation led to comments by many investigators. Some
concurred with the hypothesis while others opposed it,
favoring a chemical explanation. Many investigators have
found that a soil treated with acids will fix more phos-
phates than an untreated soil, while a few have secured
opposite results.

Demolen and Barbier (14)(15) found that a soil
delimed by hydrochloric acid fixed more phosphates than
one delimed by a neutral salt. They also showed that both
delimed and natural soils fixed more phosphates at a low
pH. Doughty (16) found that leaching a peat soil with
0.05 N hydrochloric acid to remove reactive aluminum,
iron, and calcium caused a loss of fixing power except be-
low a pH of 5. He stated that the formation of aluminum,
iron and calcium phosphates would account for the fixation
above a pH of 2.0, but that there was considerable fixa-
tion below that point which he considered must be physical.
Fraps (20) showed that treating soils with acids may re-
duce, yet not entirely eliminate their power to fix phos-
phoric acid. In later work he (22) found that soils of a
high fixing power were little affected by the removal of
calcium carbonate by acids. Weidemann (64) found that
leaching a high lime muck with hydrochloric acid decreased its power of fixation.

Roszmann (50) determined the amount of phosphates absorbed by electrodialyzed clay at various reactions. He found that the colloidal clay in the presence of calcium or sodium absorbed a maximum of phosphates between pH 3.0 and pH 4.0. The calcium clay when having its maximum effect absorbed one and one-half times as much phosphates as did the sodium clay. Since the maximum absorption occurred in the pH range of the greatest solubility of iron and aluminum the author concluded that these elements were not responsible for the absorption. Mattson (38) also studied soil colloidal material which had been electrodialyzed to remove the bases present. This colloidal material was treated with ammonium phosphates in which the ratios of acid and basic radicals were varied to give various pH values. He found that as the pH decreased the amount of phosphates fixed increased. By electrophoretic studies he determined the electrical charge on the colloidal material at the various pH values, and found that as the pH decreased, the electro-positive charge increased. He attributed the change in the phosphate fixing power of the soil, therefore, to the amphoteric nature of soil colloids.
Numerous attempts have been made to explain phosphate fixation in soils by means of experiments with synthetic colloids. Although the results cannot be interpreted too broadly, it is evident that this work has added materially to our present knowledge of the process.

Rostworowski and Wiegner (49) conducted experiments with artificial zeolites in an attempt to determine whether absorption of phosphoric acid by soils was not due in part to adsorption phenomena instead of entirely to chemical precipitation. They treated potassium permutite, which possessed normal base exchange properties, with a potassium phosphate, which had been made neutral to phenolphthalein by potassium hydroxide, and found no absorption of the phosphate ion. As the potassium permutite was similar to the colloidal material of the soil, the authors concluded, therefore, that the phosphate fixation in the soil was due to secondary reactions with previously exchanged cations which caused the formation of insoluble phosphates.

Berl and Schmittner (3) used a sodium permutite as a substitute for the colloidal aluminum silicates in soils and found that it absorbed phosphoric acid from a water solution of mono- and di-phosphates, compounds which occur in normal fertilizers. They found that this
phosphoric acid was taken up mainly as aluminum phosphate.

Gordon and his co-workers have carried on considerable work dealing with adsorption by synthetic colloids. Gordon and Starkey (27) treated hydrogels of silica, aluminum, and iron with solutions of various salts, analyzed the solutions before and after treatment, and calculated the amount of each ion adsorbed. When monocalcium phosphate was used slight or no adsorption occurred in the silica gels. However, alumina and iron gels showed a high adsorption capacity for both ions. When the concentration of the hydrogen ion was varied by the addition of sodium hydroxide or hydrochloric acid the adsorption of phosphates decreased as the pH decreased in the case of the silica gel, but increased with the alumina or iron gels.

Wiley and Gordon (65) treated both hydrogel and a hydrosol of silica with various soluble salts. Phosphates were adsorbed positively by the hydrogel and negatively by the hydrosol. Starkey and Gordon (59) used hydrogels of silica and iron in a study of the effect of the hydrogen-ion concentration on the adsorption by colloids. Their results confirm those previously noted. Lichtenwalner, Flenner, and Gordon (39) also used iron and alumina hydro-
gels. They found that the amount of adsorption increased with an increase in the concentration of the added salt. In the case of phosphates only about one-third of the amount adsorbed could be removed by leaching. Since only the water leached fraction followed the adsorption equilibrium law, the authors concluded that chemical forces probably held the non-leachable portion. Wiley and Gordon (66) showed that this non-leachable phosphates could be used by plants.

Since Liebig (52) made his famous mistake in preparing his phosphatic fertilizer it has been commonly believed that when a soluble phosphate is added to the soil it immediately reacts with the calcium in the soil to form an insoluble calcium phosphate. This belief has been greatly strengthened by much of the earlier work which was carried on with solutions of a soluble phosphate and of some calcium salt. Harris (30) has given a review of literature dealing with the mixing of different forms of lime with soluble phosphates. In all of the cases quoted it was shown that the lime caused a reversion of the soluble phosphate to the insoluble form.

Other workers soon learned, however, that the insoluble calcium phosphate compounds became soluble in
soils having low pH values. Therefore, some other element or elements must be responsible for the fixation at these pH ranges.

Fraps (22) studied the process of fixation in a large number of soils using 761 surface soils and 651 subsoils in the work. He calculated the correlation factor, R, between the phosphoric acid fixed and the per cent of iron and aluminum extracted and found that it was \(0.774 \pm 0.010\) for the top soils and \(0.701 \pm 0.013\) for the subsoils. The correlation factor between the phosphoric acid absorbed and the lime extracted was \(0.098 \pm 0.024\) and \(0.060 \pm 0.026\) respectively. The author concluded, therefore, that iron and aluminum were very important in the fixation process while lime was of no consequence.

Hall and Vogel (29) mixed acid phosphate alone and with calcium carbonate, with two acid soils and after 30 days determined the amount of phosphoric acid soluble in two per cent citric acid. No significant differences were noted where the lime was added. There was a large difference, however, between the two soils and it was noted that the soil having the highest fixing power had a much higher content of iron and aluminum. It was concluded that soils which contain the most iron and aluminum have the highest power of fixing phosphoric acid.
Comber (10) strongly opposed the idea set forth by Russell and Prescott (54) that phosphate fixation in soils treated with dilute acids could be explained as adsorption by colloids. He contended that when an acid radical is removed from solution by a soil, it is due to the formation of an insoluble precipitate. When a number of soils were treated with a solution of oxalic acid he found that in those soils which contained a small amount of calcium there was no removal of the oxalate radical, while in those containing a considerable amount of calcium some removal occurred. Soils from which the calcium had been extracted by treatment with 0.5 N hydrochloric acid were unable to absorb the oxalate. Since the absence of calcium in the soil prevented the soil from taking up the oxalate radical it was concluded that soils take up anions only by chemical precipitation. Comber's results, like those of Russell and Prescott (53), showed that a soil to which a dilute acid was added absorbed more phosphoric acid than one which received no acid. He stated that the increase in fixation was due to solvent action of the dilute acids on iron and aluminum and the insolubility of iron and aluminum phosphates in the dilute acids.

Treakle (61) added varying amounts of ammonium oxalate to three soils to precipitate the calcium, and
then he determined the phosphates present in the displaced soil solution. As the amount of ammonium oxalate added was increased, the content of calcium in the displaced solution decreased and the amount of phosphates increased; but if either calcium chloride or iron were added to the soil which had been treated with the oxalate, the phosphate content of the displaced soil solution was reduced to the same amount as was found in the soil solution from the untreated soil. This indicates that some of the phosphates in the soils used was held by the calcium. Treakle also treated a monosodium phosphate solution with the chlorides of calcium, iron, aluminum, and manganese and varied the reaction in the different tests by the addition of sodium hydroxide. The compounds formed with the different chlorides varied greatly in solubility, at the different reactions. The author concluded that the normal chemical process of precipitation is sufficient to explain the behavior of phosphates in soils when base exchange is considered, but he admitted that adsorption may play some part.

Wolkoff (69) found that when ferric chloride was added to three soils and phosphate was supplied either as double acid phosphate or Tennessee rock phosphate, the
phosphoric acid recovered by 0.2 N nitric acid was decreased, while when aluminum chloride was used no such depressing effect occurred. When aluminum chloride, ferric chloride or calcium carbonate was added alone to quartz flour, no depressing effect was noted, but when added in combination, the amount of phosphates recovered was somewhat decreased. The author stated that this might have been due to formation of a double salt.

Gemmerling (26) treated a disintegrated chernozem, a red soil, and a podsolized clay soil with potassium chloride in an attempt to replace the calcium in calcium phosphate, if any were present in the soil. No phosphate was recovered. However, since rock phosphate treated with sodium chloride gave results which indicated that such a replacement was possible, the author assumed that the phosphates were not combined with calcium in the soils under investigation. Ten successive extractions were made of these same soils using a N/4 solution of monosodium phosphate and after each extraction the filtrate was analyzed for monosodium phosphate, calcium and magnesium.

The chernozem soil absorbed 0.62 per cent phosphoric acid, the red soil 1.88 per cent, and the podsol 0.76 per cent. The chernozem absorbed most of its phosphoric acid in the first few extractions, while the podsol
absorbed very little at the first extraction, the amount absorbed gradually increasing, and then decreasing. The calcium and magnesium determinations showed that, in each soil, the amount of calcium and magnesium displaced by the monosodium phosphate was less than the amount displaced by ammonium chloride. The author assumed that the amount of calcium and magnesium remaining in the soil was combined with phosphate, and also that the phosphoric acid not combined with calcium and magnesium was combined with aluminum and iron. On the basis of this assumption he concluded that in the chernozem soil 0.576 per cent of the phosphoric acid was combined with calcium and magnesium and 0.044 per cent with sesquioxides. In the red soil only 0.007 per cent was combined with calcium and magnesium and in the podsol only 0.196 per cent. The general conclusion was drawn that phosphorus occurred in the chernozem as tricalcium phosphate but that in the red soil and in the podsol it occurred in combination with iron and aluminum.

Austin (1) titrated monocalcium phosphate against calcium oxide, magnesium oxide, calcium carbonate, freshly prepared aluminum hydroxide and ferric hydroxide and determined the phosphate content and the pH of the resulting
solutions. In each case a large part of the phosphate added was soluble in solutions having a pH less than 6.0.

Miller (42) in his study of the effect of hydrated alumina on the retention of phosphates treated a solution of .02 molar aluminum chloride, containing an equivalent quantity of monopotassium phosphate, with varying quantities of sodium hydroxide and brought the total volume up to 500 c.c. The pH was determined colorimetrically, and the precipitate was washed and analyzed. From the pH at which a precipitate was first formed up to a pH of 4.5 the ratio of Al to PO₄ was found to be 1 to 1, while at higher pH values the phosphate content of the precipitate decreased.

Gaarder (23)(24) studied the solubilities of iron, aluminum, calcium and magnesium phosphates in dilute solutions at varying reactions. Each of these compounds had a narrow reaction range for minimum solubility when an equivalent quantity of the base and phosphoric acid was present, but an excess of the base gave a wider reaction range for minimum solubility and a great decrease in its solubility. The author believed that within the pH range of normal soils, iron and aluminum phosphates were primarily in control of phosphate solubility. He con-
cluded that while lime additions may bring the pH up to
the point where sesquioxide phosphates will be hydrolyzed,
if there is a large excess of iron and aluminum, the
lime will be of little value. He believed, however, that
phosphates may be liberated by the deactivation of iron,
aluminum, or calcium by silica or acid humus.

Nomico (43) determined the effect of increasing
the amounts of water soluble phosphoric acid on its fixa-
tion in several soil types. With applications of water
soluble phosphoric acid varying from 0.39 to 3.12 mgs.
per 25 grams of soil, from 69.2 to 99.4 per cent of the
phosphoric acid was fixed in 24 hours. In soils which con-
tained large amounts of iron soluble in one per cent citric
acid, there was an increase in the relative percentage of
phosphoric acid fixed with an increase in the total amount
applied, while, on the other hand, the relative fixing
power of the soils low in iron soluble in one per cent
citric acid, decreased with an increase in the phosphoric
acid applied.

A number of workers contend that phosphate fixa-
tion is carried on both by an absorption by colloids and
by chemical precipitation. As early as 1915 Pratolongo
(46) found that if a soil free of limestone was treated
with a monometallic phosphate, the phosphate was fixed by
the formation of compounds with the electropositive colloids of the soil - the hydroxides of iron, aluminum, and manganese. When limestone was present calcium phosphate was formed. On account of the different velocities at which these processes take place, however, if the time of contact between soil and solution was short enough, and the soil contained a great excess of phosphate, it appeared that the fixation as calcium phosphate was of limited importance or negligible compared to that fixed by the colloids.

Sen (55) reported that in calcareous soils phosphoric acid was fixed by the calcium carbonate and was less available than that in non-calcareous soils, while the phosphoric acid in non-calcareous soils was held by adsorption.

Harrison and Das (30) made an extensive study of the reaction between calcium carbonate and monocalcium phosphate, as a preliminary to their fixation studies with soil. They found that when this reaction occurred at ordinary temperatures there was a rapid formation of insoluble calcium phosphates. To determine the factors governing fixation in soils a calcareous and a non-calcareous soil were used in the study. From the data secured the
authors concluded that soluble phosphates which do not react with calcium carbonate are fixed by adsorption in both calcareous and non-calcareous soils. The importance of calcium carbonate in the fixation was confirmed as they found that the addition of calcium carbonate to a non-calcareous soil led to the same type of fixation as was found in a calcareous soil.

Demolon and Barbier (15) studied fixation by a clay soil, by the same soil which had been delimed with hydrochloric acid, and by extracted colloids, and concluded that fixation in a mineral soil is the result of two types of phenomena; precipitation by calcium in an alkaline soil or in a soil well provided with calcium in the soil complex, and by adsorption by clay colloids, the latter being the most important in acid soils.

The importance of organic matter in the fixation of phosphates in soils has been studied by a number of investigators. Berthelot and Andre (4) in 1892 treated humic acid with sodium and ammonium phosphates and determined the amount of both ions absorbed. Only a small amount of phosphate was fixed with either phosphate but the proportion of anions to cations absorbed was greater where the ammonium salt was used.

Petit (45) determined the amount of phosphate removed from a solution of monocalcium phosphate by a garden
soil containing 54.6 per cent of organic matter and by a forest soil equally high in organic matter. The garden soil removed much more phosphate from solution than was removed by the forest soil. Humus which had been extracted from the garden soil removed practically no phosphate from the solution, and the residue left after igniting the soil fixed a larger proportion of phosphate than was fixed by the original soil. The author then concluded that organic matter was not important in fixation, but that fixation was due to the calcium, iron or aluminum of the soil.

Rossmann (50) suggested that since organic matter is dissolved in sodium clay and phosphate fixation decreases, organic matter may be of some importance in retaining phosphates. Weidemann (64) studied the fixation of phosphates by four muck soils and found no fixation in the case of the acid mucks while some fixation occurred in the case of the high-lime mucks. He found a regular increase in fixation with additions of lime varying from one to 25 tons per acre, but the increase was not proportional to the amount of lime added. He found also that high lime mucks decreased in fixing power when treated with hydrochloric acid.
Balanesco (2) studied the amount of phosphates fixed by humus prepared from peat, hydroquinone, and sugar and found that no fixation occurred and that variations in the reaction of the humus did not alter the results. With calcium and iron humates there was some fixation which he attributed to the calcium and iron present.

The effect of replaceable bases on phosphate fixation has been considered briefly by a number of investigators. Pratolongo (46) stated that when a bimetallic alkali phosphate comes in contact with the soil there is a secondary reaction consisting of an exchange of bases between the soil and the solution and a separation out of dicalcium and dimagnesium phosphates.

Spurway (57), in a study of the effect of a single base of the solubility of phosphates replaced the natural bases of the soil with calcium, magnesium, and potassium and determined the solubility of the phosphates in the treated soils. He found that potassium increased the solubility over that in the untreated soil in every case, magnesium did the same in most cases and calcium increased the solubility in acid soils, but decreased it in neutral and basic soils. Doughty (16) found that, in the peat soils which he studied, calcium in the replaceable base complex had no effect on fixation even when the complex was saturated.
Davuidov (13) saturated a chernozem soil with calcium, sodium, and hydrogen by the use of the chlorides. After the soil was leached free of chlorine, calcium, sodium and hydrogen phosphates were added to the soils in amounts varying from 0.01 to 0.1 per cent phosphoric acid. Oats were planted in Neubauer pots and the phosphates were determined by the method proposed by Spurway (58). In each case in the calcium saturated soil the phosphates were released the most readily.

The effect of ignition of the soil on its power to fix phosphates has not been extensively studied. Fraps (22) ignited 50 grams of soil in a platinum crucible until all of the organic matter was destroyed, treated it with potassium phosphate, and compared the fixation with that obtained in the same soil not ignited. In most cases the ignition increased fixation. The author stated that this may have been due to the conversion of calcium carbonate to calcium oxide or to the change in the nature of the iron and aluminum compounds. To test this point samples of the soil were treated with acid before ignition and others after ignition. The acid alone reduced the amount of phosphoric acid absorbed but the phosphoric acid absorbed was greater in the soils ignited and treated with
acid than in those treated with acid and not ignited. This was true whether the acid was added before or after ignition. The author therefore concluded that the increase in fixation by ignition was due to a change in the iron and aluminum compounds. Petit (45) found that the residue left after igniting a garden soil, which contained 54.6 per cent organic matter, removed a larger proportion of phosphoric acid from solution than was removed by the soil which was not ignited.

**Effect of Ignition on Soils.**

Since the effect of igniting the soil on its power to fix phosphates is one of the factors considered in the experimental work reported here, it seems desirable to include a brief review of the literature which deals with the effects of ignition on certain properties of the soil. In 1850, Way (63) found that a clay which had been thoroughly ignited lost its power of absorption. Fraps (21) has shown that the ignition of soils renders a considerable quantity of iron and aluminum oxides soluble in acids.

Bouyoucos (6) studied the effect of heating on the physical properties of natural soils, fullers earth, and Fe₂O₃, Al₂O₃, and silica gels. Each was heated to 110,
230, 485, and 800°C. and the effect on heat of wetting, amount of unfree water present and plasticity noted. At 800°C, the heat of wetting and unfree water content was negligible and the soils had completely lost their plasticity.

Kapp (34) ignited soil particles which varied from .0005 mm in diameter to molecular in size at a temperature up to 850°C. After ignition it was found that the per cent of particles .02 mm or larger in size was over 89 per cent.

Coutts (11) after studying the effect of exposing soils to high temperatures stated that, "the loss in weight of soils can be ascribed in the main to a loss of free water up to 100°C.; to destruction of organic colloids between 100° and 250°; and to destruction of inorganic colloids at higher temperatures". Since his values are fairly constant above 450° it appears that most of the inorganic colloids must have been destroyed at 450°C. or less.

**Effect of Hydrogen Peroxide on Soils.**

The following literature is cited to show the effect of hydrogen peroxide on certain properties of soils.
After studying the value of hydrogen peroxide in the
determination of the organic matter of the soil Robinson
(48) stated that practically all the organic matter is
decomposed in some soils whereas in others considerable
amounts are not affected. He also stated that the hydrogen
peroxide method of determining organic matter is not appli-
cable to soils high in calcium carbonate, manganese
dioxide, and strontium sesquioxide.

McLean (39) stated that in an average mineral soil
free of carbonates about 85 per cent of the total carbon
was oxidized by hydrogen peroxide. Hasking (31) gives
data to show that a portion of the organic matter of the
soil is oxidized by hydrogen peroxide irrespective of the
reaction, while the oxidation of the remainder is a
function of the pH. The amount of organic matter oxidized
in the soils studied varied from as much as 90 per cent
in acid soils to 51 per cent for the very alkaline soils.
However, in soils having a pH of 8 or less, 80 per cent
or more of the organic matter was oxidized.

Oedroiz (25) stated that in a chernozem there are
some stable forms of organic matter which are not completely
oxidized by hydrogen peroxide. His results also showed
that hydrogen peroxide treatment did not change the base
exchange capacity of the mineral fraction of the soil and he concluded that for this reason this treatment could be used to differentiate between the base exchange capacity of the mineral and organic fraction of the soil.
EXPERIMENTAL

Purpose of Investigation.

The results reported by various workers show clearly that soils have the power of removing soluble phosphates from solution and that soils differ widely in their ability to bring about this removal. However, the literature dealing with the mechanism of phosphate fixation is very confusing. Those who have studied fixation of phosphates by biological factors agree that there is such a fixation but that it accounts for only a small part of the total fixing power of the soil. The workers who have investigated fixation by other factors, however, fail to agree on the subject. Those who claim to have demonstrated that the fixation of phosphate in soil is a physical phenomenon are about equal in number to those who contend with equal zeal that they have proven that the process is chemical. It is, therefore, evident that our present knowledge in regard to the fixation of phosphates by the soil is neither satisfactory nor adequate.

It is desirable to know more about the manner in which phosphates are fixed in soil and factors affecting the ability of soil to hold phosphates before we can ex-
pect to study intelligently the practical aspects of phosphate fertilization. The purpose of this investigation was to study the effects of certain factors on the ability of soils to fix phosphates.

Soils Used in Phosphate Fixation Studies.

The following soils were selected for this study:

1. Tama silt loam,
2. Tama silt loam which had received an application of Ca(OH)$_2$ equivalent to three tons of calcium carbonate per acre,
3. Carrington loam,
4. Webster clay loam,
5. Cass silt loam,
6. Clarion loam,
7. Grundy silt loam.

They will be designated in the investigations by number rather than by name.

A comparison of some of the characteristics of these soils is given in table 1. The pH was determined electrometrically by the quinhydrone electrode method and the colloidal content by the Bouyoucos (7) hydrometer method. Total phosphorus was determined by the official method and the phosphorus soluble in 0.002 N sulfuric acid
### TABLE 1

Some properties of the soils used.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>pH</th>
<th>Per cent colloid</th>
<th>Total phosphorus in mgm. P in 100 gms. soil</th>
<th>Phosphorus sol. in .002 N H$_2$SO$_4$</th>
<th>Per cent carbonates in soil</th>
<th>Per cent p.p.m. P in soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.62</td>
<td>36.28</td>
<td>87.88</td>
<td>38.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6.54</td>
<td>36.28</td>
<td>87.88</td>
<td>49.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>6.25</td>
<td>23.81</td>
<td>53.10</td>
<td>8.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>8.27</td>
<td>36.60</td>
<td>84.37</td>
<td>3.2</td>
<td>36.65</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>8.03</td>
<td>17.13</td>
<td>74.80</td>
<td>19.4</td>
<td>4.61</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>7.93</td>
<td>30.07</td>
<td>75.27</td>
<td>49.4</td>
<td>2.18</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>5.04</td>
<td>38.74</td>
<td>64.63</td>
<td>14.54</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
according to the procedure proposed by Truong (62). The carbonates were determined by adding an excess of acid to a small amount of soil, boiling the mixture one minute and then titrating the excess acid with sodium hydroxide using methyl red as an indicator.

The results given in table 1, show a wide variation in certain characteristics of these soils. The pH varied from 5.04 to 8.27 and although there was a considerable variation in the colloidal content, four of the seven soils are very similar showing a wide variation in reaction with about the same colloidal content. In the soils having a basic reaction there was a wide variation in the carbonates present. The results also show considerable variation in total phosphorus and phosphorus soluble in 0.002 N sulfuric acid and it is evident that there was no relation between total phosphorus content of the soil and that extracted by the 0.002 N sulfuric acid. It is probable that this relation would have been different if the carbonates present in the soil had been neutralized with acid so that the extracts from the different soils would have had approximately the same pH values. The pH was determined on the 0.002 N sulfuric acid extract of these soils and was found to vary between 3.06 and 3.12 for the acid soils,
while for soils 4, 5 and 6, the values were 7.41, 4.82 and 3.54, respectively.

**Methods of Procedure.**

**Preliminary Studies.**

Since there is a lack of uniformity in the methods used in the study of phosphate fixation it seemed advisable that some preliminary work be carried out before an arbitrary method of procedure was adopted. A number of workers have shown that the length of time the phosphate solution is exposed to the soil will markedly influence the amount of phosphate fixed, and also the relative amount of fixation for different soils. In order to determine whether or not the amount of phosphate fixed in a short period of time is indicative of the power of that soil to fix phosphates, a preliminary experiment was set up in which samples of soil were allowed to remain in contact with the solution of soluble phosphate for different lengths of time. Five hundred c.c. portions of a $\text{K}_2\text{HPO}_4$ solution containing 127 p.p.m. of phosphorus and 100 gram samples of soil were placed in quart milk bottles, agitated 30 minutes in an end-over-end shaker and allowed to stand for 30 minutes,
12, 24 and 48 hours before filtering. Eight samples of each soil were treated so that duplicate determinations might be made for each time interval. Two c.c. portions of the filtrate were diluted to 1000 c.c. and the phosphorus content determined colorimetrically by the method proposed by Truog (62).

The results of this experiment are given in table 2 and figure 1. These data show that the amount of phosphate fixed increased with an increase in the time of contact and that the amount of this increase was approximately the same for each soil. This indicated that a shorter time of contact would be as satisfactory as a longer period when determining the relative phosphate fixing power of the different soils. The decided increase in fixation during the interval between 30 minutes and 12 hours indicates that the fixation may increase rapidly during the earlier part of this period. If this is true considerable inaccuracy might result if one were to attempt to make a large number of filtrations at one time, due to the interval of time between the first and last filtration. In order to determine the rate of increase in fixation during the first 12 hours, sixteen 50-gram samples of soil 3 were each added to 250 c.c. portions of a K$_2$HPO$_4$ solution containing 91 p.p.m. of phosphorus. After shaking for 30 minutes duplicate samples were filtered at intervals of 0, 1, 2, 4,
### TABLE 2

Effect of time on fixation of phosphate by soils.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2 hour</td>
</tr>
<tr>
<td>1</td>
<td>17.2</td>
</tr>
<tr>
<td>2</td>
<td>22.5</td>
</tr>
<tr>
<td>3</td>
<td>19.9</td>
</tr>
</tbody>
</table>
Figure 1. Effect of time on fixation of phosphate by soils.
6, 8, 10 and 12 hours. Five c.c. of the filtrate were made up to 1000 c.c. and the phosphorus content of the solution determined as before. The results are given in table 3. While these data show that a steady increase in fixation took place through the 12 hour period, this increase was so slow that any small difference in time between the filtrations of different determinations would not give differences in fixation large enough to be measured by the methods used.

Methods Used in This Study.

The soils were ground sufficiently fine so that practically all of the material passed through a 60 mesh sieve. The untreated soils were used in an air dry condition, while soils which had been moistened by treatments were dried in an oven at 50°C. A solution of \( \text{K}_2\text{HPO}_4 \) containing 100 p.p.m. of phosphorus was used.

The general method of procedure used for determining the phosphate fixing power of the soil consisted in shaking 50 grams of soil with 250 c.c. of the phosphate solution in a quart milk bottle in an end-over-end shaker for 30 minutes. After standing for 30 minutes these samples were filtered through Bushner funnels. Five c.c. of the filtrate were then diluted to 1000 c.c. and the phosphate
TABLE 3

Effect of short intervals of time on fixation of phosphate by soil 3.

<table>
<thead>
<tr>
<th>Hours before filtering</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.8</td>
</tr>
<tr>
<td>1</td>
<td>15.1</td>
</tr>
<tr>
<td>2</td>
<td>16.7</td>
</tr>
<tr>
<td>4</td>
<td>16.3</td>
</tr>
<tr>
<td>6</td>
<td>16.5</td>
</tr>
<tr>
<td>8</td>
<td>17.3</td>
</tr>
<tr>
<td>10</td>
<td>17.3</td>
</tr>
<tr>
<td>12</td>
<td>17.5</td>
</tr>
</tbody>
</table>
content determined colorimetrically.

The hydrogen ion determinations were made electrometrically by the quinhydrone or glass electrode method using 10 grams of soil and 25 c.c. of distilled water. The quinhydrone electrode was used for all values below a pH of 8 while the glass electrode was used for those values above 8. In cases where the general procedure could not be followed, the specific procedure will be given. All determinations were made in duplicate and where close agreements were not secured the procedure was repeated.

Effect of Ignition on Fixation.

A number of workers have found that soils which had been heated to temperatures ranging from 450 to 850°C. lost their colloidal properties. If phosphates are fixed in soil by colloidal adsorption then a soil should lose this power of fixation after being heated at high temperatures. In order to determine the effect of ignition on the phosphate fixing power of soils, samples were heated for one hour in a muffle furnace at approximately 750°C. and determinations made of their pH values and ability to remove phosphates from solution. Using the general procedure previously outlined, it was found that, in the case of
soils 4 and 5, all of the phosphate was removed from the 250 c.c. of solution. It was necessary, therefore, to use different proportions of soil to phosphate solution in order to determine the fixing power. For soil 4 the proportion used was 0.5 grams of soil to 500 c.c. of solution and for soil 5, 25 grams of soil to 250 c.c. of solution. The phosphate fixing power of the untreated soils was also determined and these results are given in table 4.

These data show that ignition caused the acid soils to lose, almost completely, their power to fix phosphates. However, with the soils containing carbonates the results were different. Soil 6 which contained only a small amount of carbonates lost only part of its power to fix phosphates while soils 4 and 5 which contained large amounts of carbonates showed a decided increase. It is also evident that there was a much smaller change in pH in the acid soils due to ignition than in the soils which contained carbonates. It is likely that the large change in the pH values in the soils containing carbonates was due to a conversion of the basic carbonates to the oxide form.

It has been stated that if colloidal adsorption is responsible for the fixation of phosphates by soils, a soil should lose this property of fixation when ignited. However, the fact that ignition will cause a soil to lose its power
<table>
<thead>
<tr>
<th>Soil No.</th>
<th>pH Untreated</th>
<th>pH Ignited</th>
<th>Mgm. of P fixed per 100 gms. soil Untreated</th>
<th>Mgm. of P fixed per 100 gms. soil Ignited</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.62</td>
<td>5.33</td>
<td>14.2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6.64</td>
<td>5.82</td>
<td>18.8</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>6.25</td>
<td>5.92</td>
<td>14.9</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>8.27</td>
<td>12.80</td>
<td>28.3</td>
<td>1154.0</td>
</tr>
<tr>
<td>5</td>
<td>8.03</td>
<td>13.00</td>
<td>23.0</td>
<td>65.8</td>
</tr>
<tr>
<td>6</td>
<td>7.93</td>
<td>10.50</td>
<td>15.5</td>
<td>4.6</td>
</tr>
<tr>
<td>7</td>
<td>5.04</td>
<td>5.28</td>
<td>26.0</td>
<td>0</td>
</tr>
</tbody>
</table>
to fix phosphates does not prove that the phosphate was fixed by colloidal adsorption. It does indicate, however, that the phosphate was fixed by some agent which was destroyed or altered by high temperatures. Since it was found that the soils high in carbonates showed an increase in their phosphate fixing power after ignition, it is improbable that ignition decreased the power of the calcium salts present to remove phosphates from solution. In order to determine whether or not such a decrease occurred Ca(OH)$_2$ was added to duplicate 50 gram samples of soil 3 at the rate of 20 tons per acre (2,000,000 pounds of soil), the additions being made before ignition in one case and after ignition in the other. The amounts of phosphate which these soils were able to fix indicated that the high temperatures did not materially influence the ability of the calcium compounds to remove phosphates from solutions.

It is evident, therefore, that some factor or factors other than the calcium salts present was responsible for the fixation of the larger part of the phosphates in the acid soils. Since organic matter is destroyed by ignition it is possible that it might be a factor contributing to the fixation of phosphates in these acid soils.

If it were possible to remove the organic matter from the soil without disturbing the mineral portion some evidence
might be secured in regard to the importance of the organic matter in the fixation of phosphates.

A number of investigators have shown that hydrogen peroxide will remove from 85 to 90 per cent of the organic matter from an acid soil and 50 per cent or more from an alkaline soil. Gedroiz (25) has also shown that hydrogen peroxide does not disturb the base exchange complex of the mineral fraction of the soil. On the basis of these investigations hydrogen peroxide was used to remove the organic matter from the soils in the following studies. The procedure used was that suggested by Millar (41). In order to prevent any possible removal of any of the mineral salts none of the $H_2O_2$ solution was allowed to drain from the soil with the exception of soils 1 and 7. However, these soils were placed on a filter and leached free of the peroxide solution by small additions of distilled water. After the soils had been dried their phosphate fixing power was determined and compared with that of the untreated soil. These results are given in table 5.

Soils 1 and 7 showed the greatest proportionate loss in the amount of phosphate fixed and since these soils were the only ones which had the material dissolved
TABLE 5

Effect of removing soil organic matter by hydrogen peroxide on the phosphate fixing power of soil.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>1</td>
<td>14.3</td>
</tr>
<tr>
<td>3</td>
<td>12.7</td>
</tr>
<tr>
<td>4</td>
<td>30.5</td>
</tr>
<tr>
<td>5</td>
<td>22.2</td>
</tr>
<tr>
<td>6</td>
<td>18.8</td>
</tr>
<tr>
<td>7</td>
<td>23.0</td>
</tr>
</tbody>
</table>
by the hydrogen peroxide leached from them, it is probable that this decrease in fixation was partially due to a loss of salts. As the other soils which had been treated with hydrogen peroxide showed only a slight decrease or an increase in the amount of phosphate fixed, it would seem that the organic matter was not of major importance in the fixation process. Likewise it appears likely that the hydrogen peroxide was responsible for other changes in the soil which were more pronounced in their effect on the phosphate fixing power than the removal of the organic matter.

Fraps (22) concluded from his work dealing with the effect of ignition on the power of the soil to fix phosphates that the increase in fixation after ignition was due to an activation of iron and aluminum. If ignition increased the activity of iron and aluminum in fixing phosphates, then it would be reasonable to assume that iron and aluminum were of no importance in the fixation of phosphates by the acid soils studied since their power of fixing phosphates was lost or greatly reduced when the soils were ignited. Since so many workers contend that iron and aluminum are very important in the fixation of phosphates in acid soils, it would hardly be justifiable to conclude from one experiment that iron and aluminum were
of no importance in these soils studied. In order to determine whether or not ignition did increase the activity of iron and aluminum in fixing phosphates, 50 gram samples of soil 1 were treated with 300 mgm. of either ferric chloride or aluminum chloride and ignited at approximately 775°C. for 1 hour. The results secured were compared with those obtained on samples which received a like application of aluminum chloride and ferric chloride but which were not ignited. The results given in table 6 show clearly that ignition rendered the iron and aluminum inactive towards the phosphate added. Since the iron and aluminum chlorides added to the soil which was not ignited increased materially the amount of phosphate removed from solution it is probable that the iron and aluminum salts were converted to the insoluble oxide form by ignition.

If the increase in fixation by soil 4 (table 4) after ignition was due to the large amount of carbonates present, an increase in acidity should decrease the amount of phosphate removed from solution. To determine the effect of reaction on the amount of phosphate fixed by soil 4 after ignition, 1 gram samples of the soil were placed in quart milk bottles and 100 c.c. of the phosphate solution added. Amounts of 0.1 N HCl varying from 30 to 100 c.c. were then added to these samples and the total volume of the solution brought up to 200 c.c. by the addition of
TABLE 6

Effect of ignition of soil previously treated with ferric chloride, and with aluminum chloride on the amount of phosphate fixed.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ignited</td>
</tr>
<tr>
<td>No</td>
<td>0.00</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>0.00</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.00</td>
</tr>
</tbody>
</table>
distilled water. After shaking and filtering, the phosphate content and the pH of the filtrates were determined. The results are given in table 7 and figure 2.

These data show that there is a very decided decrease in phosphate fixation between pH 8.44 and pH 7.37 whereas practically no change in the amount of fixation occurred between a pH of 7.37 and 4.44. However, below pH 4.44 there was a decided decrease in the amount of phosphate removed from solution. These results show a decided decrease in fixation with a decrease in pH as might be expected on the basis of previous work, yet the close agreement in the amount of fixation over the wide reaction range between pH 7.37 and pH 4.44 can not be explained with the data at hand.

**Effect of Replaceable Bases on Fixation.**

Many investigators contend that soils remove phosphates from solution only by chemical precipitation. If this were true it would appear that soils from which the soluble salts and exchangeable bases had been removed would lose their power of fixation.

There are two methods which are commonly used for the replacement of exchangeable bases and ionizable salts in the soil, electrodialysis and leaching with dilute acids.
### TABLE 7

The effect of reaction on the phosphate fixed by soil 4 after ignition.

<table>
<thead>
<tr>
<th>C.c. of 0.1 N HCl added</th>
<th>pH of filtrate</th>
<th>Mgs. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.77</td>
<td>991.1</td>
</tr>
<tr>
<td>30</td>
<td>9.05</td>
<td>995.5</td>
</tr>
<tr>
<td>40</td>
<td>8.94</td>
<td>1000.0</td>
</tr>
<tr>
<td>50</td>
<td>8.44</td>
<td>993.2</td>
</tr>
<tr>
<td>60</td>
<td>7.37</td>
<td>818.2</td>
</tr>
<tr>
<td>70</td>
<td>6.95</td>
<td>795.3</td>
</tr>
<tr>
<td>80</td>
<td>6.43</td>
<td>795.8</td>
</tr>
<tr>
<td>90</td>
<td>4.96</td>
<td>795.9</td>
</tr>
<tr>
<td>100</td>
<td>3.56</td>
<td>500.0</td>
</tr>
</tbody>
</table>
Figure 2. The effect of reaction on the phosphate fixed by soil 4 after ignition.
Since Kelley and Brown (36) have shown that leaching with dilute acids releases iron and aluminum from the soil and this does not occur with treatment with neutral salt solutions it seemed best to replace the bases of the soils to be used in this study by electrodialysis. This procedure was carried out in Mattson cells according to the method outlined by Humfeld and Alben (32), and replacement was considered complete when 0.3 M.E. or less of bases was removed in a period of 12 hours.

In order to study the effect of electrodialysis on the phosphate fixing power of the soil a number of soils were dialyzed free of bases and their pH and phosphate fixing power determined. Soil 4 was not included in this study since 407 hours of electrodialysis did not noticeably reduce the amount of bases removed with each change of the dialysate. The results secured from this study are given in table 8. These data show that in every case there is an increase in the amount of phosphate fixed by the treated soils. Before drawing conclusions from this work, however, it seemed advisable to know what effect removing a part of the exchangeable bases would have on the amount of phosphates removed from solution. Therefore, soils 1 and 3
<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Hours dialyzed</th>
<th>M.E. bases removed</th>
<th>Original, dialyzed</th>
<th>100 gm. soil</th>
<th>Mgm. P fixed per 100 gm. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58</td>
<td>5.62</td>
<td>14.3</td>
<td>39.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>6.28</td>
<td>14.9</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>6.25</td>
<td>8.03</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>125</td>
<td>6.22</td>
<td>3.04</td>
<td>35.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>93</td>
<td>4.93</td>
<td>7.93</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>5.88</td>
<td>5.04</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>12.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
were dialyzed for varying periods of time and their pH and phosphate fixing power determined. The results secured are given in tables 9 and 10, and are represented graphically in figures 3 and 4.

These data show that up to a certain point, an increase in the length of time the soils were dialyzed, was associated with an increase in the amount of phosphate fixed. It is also evident that the increase in fixation was more pronounced for the first few hours of dialysis. The data further indicate that the decrease in pH values gave a better indication of the degree of displacement than did the M.E. of bases removed. The lack of correlation between the number of hours the soils were dialyzed and the M.E. of bases removed was probably due to some defect in the cells used.

Figure 3 shows the relation of pH to the amount of phosphate fixed by soils 1 and 3. It is evident that the increase in fixation by soil 1 between a pH of 5.62 and 4.88 was very marked while below a pH of 4.88 the increase is gradual. Soil 3 showed an increase in fixation with a decrease in pH to approximately a pH of 3.7 and then a slight decrease beyond this point. The increase in fixation was more pronounced at the higher pH values, but the difference in fixation at the different reaction ranges was not as great as in the case of soil 1. The relation between reac-
### TABLE 9

Effect of the replacement of varying amounts of bases in soil 3 on pH and phosphate fixation.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Hours dialyzed</th>
<th>M.E. bases removed</th>
<th>pH soil</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>6.25</td>
<td>14.9</td>
</tr>
<tr>
<td>I</td>
<td>1</td>
<td>2.12</td>
<td>5.48</td>
<td>26.2</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>6.83</td>
<td>4.97</td>
<td>31.4</td>
</tr>
<tr>
<td>D</td>
<td>9</td>
<td>10.11</td>
<td>4.50</td>
<td>32.9</td>
</tr>
<tr>
<td>C</td>
<td>21</td>
<td>9.00</td>
<td>3.94</td>
<td>34.6</td>
</tr>
<tr>
<td>B</td>
<td>45</td>
<td>12.96</td>
<td>3.71</td>
<td>36.0</td>
</tr>
<tr>
<td>F</td>
<td>57</td>
<td>12.86</td>
<td>3.68</td>
<td>32.8</td>
</tr>
<tr>
<td>A</td>
<td>70</td>
<td>10.50</td>
<td>3.50</td>
<td>33.3</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Hours dialyzed</td>
<td>M.E. bases removed</td>
<td>pH soil</td>
<td>Mgm. of P fixed per 100 gms. soil</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>--------------------</td>
<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>I</td>
<td>0</td>
<td>0</td>
<td>5.62</td>
<td>14.2</td>
</tr>
<tr>
<td>J</td>
<td>1</td>
<td>3.47</td>
<td>5.37</td>
<td>26.9</td>
</tr>
<tr>
<td>H</td>
<td>3</td>
<td>7.27</td>
<td>4.88</td>
<td>36.6</td>
</tr>
<tr>
<td>G</td>
<td>58</td>
<td>16.662</td>
<td>3.37</td>
<td>39.6</td>
</tr>
</tbody>
</table>
Figure 3. Relation between pH and phosphate fixation in soils from which varying amounts of bases have been replaced.
Figure 4. Relation between M.E. of bases removed and phosphate fixation in soils from which varying amounts of bases have been replaced.
tion and phosphate fixed at low pH values in the case of
soil 3 would indicate that a similar relation existed in
soil 1.

Figure 4, which represents the relation between
the amount of phosphate fixed and the M.E. of bases removed
from the soil shows the same general relation as that re­
presented in figure 3. This indicates that at least up to
a certain point, an increase in fixation occurred when in­
creased amounts of bases were removed. It is likely that this
increase was due to the decrease in pH which was accompanied
by a removal of bases.

Although the removal of bases caused an increase
in fixation, the data above does not show whether or not
the bases present in the soil played any part in fixation.
It would seem that, if the reaction of the dialyzed soil
could be brought up to approximately that of the original
soil by the addition of a cation which would form a soluble
salt with phosphate, some evidence could be gained con­
cerning the role of the replaceable bases in the fixation
process. To check this assumption, undialyzed and dialyzed
samples of soil 3 were saturated with sodium and ammonium
ions and their pH values and phosphate fixing power com­
pared with those of untreated soils. The following pro­
cedure suggested by Kelley and Brown (36) was used to
saturate the soils with these bases: Twenty-five grams of
soil and 250 c.c. of a normal chloride solution were shaken in an end-over-end shaker for 30 minutes and were then allowed to digest over night at 70°C. The soil was then transferred to Buchner funnels, leached with more of the chloride solution until 1000 c.c. of the filtrate had been secured, and then washed free of chlorides with distilled water. After the soil had been dried the pH values and phosphate fixing power were determined. The results are given in table 11.

These data show that replacing the exchangeable bases of the undialyzed soil by ammonium, without bringing about any noticeable change in reaction greatly decreased the fixation of phosphates. This would indicate that the bases replaced by ammonium were of considerable importance in the fixation process. This same soil which contained sodium in its exchange complex showed a greater decrease in fixation than did the one containing ammonium. This would be expected on the basis of the experiment above since the soil containing the sodium had a higher pH value.

The dialyzed soils which had been saturated with ammonium and sodium showed a decided decrease in fixation in comparison with the dialyzed soil. A direct comparison of the dialyzed and undialyzed soils which had been saturated with ammonium and sodium would be unfair because
TABLE 11

The effect of treating untreated and electrodialyzed soils with NaCl and NH₄Cl on phosphate fixation.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undialyzed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>6.25</td>
<td>15.2</td>
</tr>
<tr>
<td>&quot; + NaCl</td>
<td>7.25</td>
<td>7.0</td>
</tr>
<tr>
<td>&quot; + NH₄Cl</td>
<td>6.37</td>
<td>8.3</td>
</tr>
<tr>
<td>Dialyzed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>3.68</td>
<td>29.8</td>
</tr>
<tr>
<td>&quot; + NaCl</td>
<td>5.30</td>
<td>10.8</td>
</tr>
<tr>
<td>&quot; + NH₄Cl</td>
<td>5.70</td>
<td>10.8</td>
</tr>
</tbody>
</table>
of the great difference in pH value. However, the above experiment would indicate that this difference in pH value would account for a large part of the difference in fixation. If this assumption is correct the results from both the dialyzed and undialyzed soil would indicate that the replaceable bases in this soil were important in the fixation process.

It seemed that a more accurate comparison of the value of the displaced bases and the material remaining in the soil might be obtained if the dialyzed soil were adjusted to varying degrees of saturation by the addition of a base which would form soluble phosphate compounds. Since the degree of saturation of the soil complex can be determined if ammonium is the base present it was decided to add varying amounts of NH₄Cl to samples of soil which had been dialyzed and determine the amount of ammon present in the soil, the pH values and the phosphate fixing power.

The soils which were saturated with ammonium, were treated according to the procedure used above. Those receiving smaller amounts of NH₄Cl had the salt added before shaking and were then treated in the same manner as the soils which were saturated except that they were not leached with additional NH₄Cl solution. The amount of
ammonium present in the soil was determined by the aeration method as suggested by Kelley (35).

The results of these determinations are given in table 12 and the relation between pH values and phosphate fixed is shown in figure 5. By interpolation of the values in figure 5, it is evident that a dialyzed soil containing an amount of ammonium sufficient to give the same pH value as that of the undialyzed soil would fix approximately the same amount of phosphates. Thus in this soil it appears that the bases removed from the soil were of no appreciable importance in the fixation process. It is also evident that there is a decided increase in fixation with an increase in pH up to approximately 3.75 and a decrease above that point.

Effect of Replacing Bases by HCl on Fixation.

Previous work on the effect of HCl on the fixation of phosphates by soils varied not only in the nature of the experiments but also in the results secured. It seemed desirable, therefore, to determine the effect on the fixation process of removing the bases from the soil by means of dilute HCl.
**TABLE 12**

Effect of replaceable ammonia on phosphate fixation by electrodialyzed soil.

<table>
<thead>
<tr>
<th>Soil</th>
<th>M.E. of NH$_4$ added per 100 gm. soil</th>
<th>M.E. of replaceable NH$_4$ per 100 gms. soil</th>
<th>pH</th>
<th>Mgm. of P fixed per 100 gms. soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>#7 dialyzed</td>
<td>0</td>
<td>0.00</td>
<td>3.04</td>
<td>30.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>8</td>
<td>2.88</td>
<td>4.07</td>
<td>35.7</td>
</tr>
<tr>
<td>&quot;</td>
<td>20</td>
<td>3.85</td>
<td>4.39</td>
<td>34.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>40</td>
<td>5.29</td>
<td>4.46</td>
<td>32.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>1000</td>
<td>14.15</td>
<td>5.48</td>
<td>16.7</td>
</tr>
<tr>
<td>#7 undialyzed</td>
<td>0</td>
<td>0.00</td>
<td>5.04</td>
<td>25.0</td>
</tr>
</tbody>
</table>
Figure 5. Relation between pH and phosphate fixation in samples of a dialyzed soil which have been treated with varying amounts of NH₄Cl.
The procedure suggested by Kelley and Brown (36) was followed. The only measure of the degree of displacement was the pH value of the soil which was determined after the soil had been washed free of chlorides. For soil 5 it was necessary to use 1.5 liters of the 0.05 N HCl in order to get complete displacement of the bases in 25 grams of soil, while one liter was sufficient for the other soils used. Soil 4 was not included in this study since leaching with six liters of the dilute acid decreased the pH only slightly. After drying, the pH and phosphate fixing power of the soils were determined. These data, which are given in Table 13, show a decided increase in fixation in each case.
TABLE 13

Effect of the removal of bases from soil by extraction with .05 N HCl on pH and phosphate fixation.

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>pH Original</th>
<th>pH Treated</th>
<th>Mgm. of P fixed per 100 gms. soil Original</th>
<th>Mgm. of P fixed per 100 gms. soil Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.62</td>
<td>3.05</td>
<td>14.20</td>
<td>30.8</td>
</tr>
<tr>
<td>3</td>
<td>6.25</td>
<td>3.10</td>
<td>14.90</td>
<td>26.6</td>
</tr>
<tr>
<td>5</td>
<td>8.03</td>
<td>3.03</td>
<td>23.00</td>
<td>26.7</td>
</tr>
<tr>
<td>6</td>
<td>7.93</td>
<td>2.76</td>
<td>15.52</td>
<td>30.8</td>
</tr>
<tr>
<td>7</td>
<td>5.04</td>
<td>3.09</td>
<td>23.00</td>
<td>29.20</td>
</tr>
</tbody>
</table>
DISCUSSION

A comparison of the phosphates fixed by the untreated soils (table 4) shows that the greatest fixation occurred in the soil containing the largest amount of carbonates, while the next largest amount was fixed by the soil with the lowest pH value. Soils having a basic reaction showed a greater fixation when greater amounts of carbonates were present.

Ignition caused an increase in fixation only in the case of soils containing considerable amounts of carbonates while the soils having the lower pH values wholly or partially lost their power of fixation. High temperatures did not affect the ability of calcium salts to remove phosphates from solutions, yet rendered aluminum chloride and ferric chloride inactive towards phosphates. This does not bear out the work of Fraps (22) who concluded that the increase in fixation by ignited soils is due to an activation of iron and aluminum.

Although the results secured on the effect of removing organic matter by hydrogen peroxide were far from uniform, they agreed in general with the findings of Petit (45), Weidemann (64), and Balanesco (2), who reported that the organic matter of the soil was of very little importance in the fixation of phosphates.
The increases noted in fixation caused by the replacement of bases by electrodialysis (table 8) agree with the results secured by Rossmann (50) and Mattson (38) who worked with dialyzed soil colloids.

A comparison of the data in tables 9, 10, and 12, and figures 3 and 5 shows some very interesting relationships. The type of curve representing the relation between reaction and fixation is, in general, the same whether the change in reaction is secured by replacing varying amounts of the bases present in the soil by electrodialysis or by adding varying amounts of ammonium to a dialyzed soil. In each case the amount of phosphate fixed increased with a decrease in pH until approximately 3.75 was reached, and then decreased with further decreases in pH. It is also evident that at the higher pH values studied, the change in the amount of fixation with each unit change in reaction was more striking. However, the degree of change in fixation with each unit change in reaction varied with the different soils. This relation may have some practical significance as is pointed out later.

Soils 1 and 7 had approximately the same colloidal content. If the fixation process were similar in the two soils, then at the same reaction their power of fixation should be approximately the same. It is interesting to note that if the curve for the fixation of soil 7 (figure 5)
was extended to a pH of 5.62, the reaction of soil 1, the theoretical fixation by soil 7 would be approximately the same as the fixation determined for soil 1. If this process was reversed and the theoretical fixation of soil 1 was determined (figure 3) at a pH of 5.04, the reaction of soil 7, it is evident that this theoretical fixation would be approximately the same as that actually determined for soil 7. Thus it seems that most of the difference in fixation between soils 1 and 7 can be accounted for on the basis of reaction.

Therefore if availability is dependent upon the power of the soil to fix phosphates, the available phosphorus in soil 1 should be greater than in soil 7. The data in table 1 show that the ratio of phosphorus soluble in 0.002 N sulfuric acid to total phosphorus is 1:23.1 in soil 1 while for soil 7 it is 1:44.5. This higher content of phosphorus soluble in the 0.002 N sulfuric acid is no doubt due to a large extent to the reaction of the soil. Therefore, it seems that increasing the pH of soil 7 by the addition of lime should decrease its power to fix phosphates and increase the availability of the phosphorus present.

A comparison of soils 1 and 2 should give additional evidence. Soil 2 is the same as soil 1 except that it had received an application of lime sufficient to change the reaction of the original soil from pH 5.62 to pH 6.54.
Table 1 shows that soil 2, which has the same total phosphorus content, contained approximately 30 per cent more phosphorus soluble in .002 N sulfuric acid than did soil 1. However, a comparison of their fixation power failed to verify the above explanation since soil 2 showed a slight increase in fixation over that of soil 1 (table 4).

It is known that an addition of lime to soils in some cases not only fails to increase availability of the phosphorus but may even cause a decrease. This fact may be easily explained in a soil with an alkaline reaction, since it has been pointed out that in such soils there is an increase in fixation with an increase in the amount of carbonates present. However, a comparison of the data dealing with the importance of replaceable bases in the fixation process would tend to indicate that under slightly acid conditions the bases present may play a major part in fixation (tables 11 and 12). It has been shown that in soil 7, having a pH of 5.04, replaceable bases played no noticeable part in the fixation process, while in soil 3, having a pH of 6.25, the replaceable bases are responsible for approximately 50 per cent of the fixation. It seems logical to assume that at higher
pH values the replaceable bases would become of more importance until their effect was overshadowed by that of the carbonates present. Thus it would seem that under slightly acid conditions where replaceable bases are of major importance, lime would fail to increase the availability of the phosphates present in the soil.

It is interesting to note that some workers who have studied the effect of replaceable bases on fixation contend that they are of importance while others hold the opposite view. The results reported here would indicate that the difference in the soils used by the various investigators may account for this variation in conclusions.

Leaching with .05 N HCl (table 12) caused an increase in fixation with each soil used. It is interesting to note that soils 1, 6 and 7, each of which contained about the same amount of colloidal material, showed about the same power of fixation, while soils with a lower colloidal content showed a smaller power of fixation. Soil 5 showed the smallest proportionate increase in fixation while soil 7 was second in this respect, the former showing a high power of fixation due to its high carbonate content and the latter a high fixing power due to a low pH value. If soil 4 had been completely leached of its bases it would probably have shown practically no gain in
fixation since soils 1 and 7, which contained about the same colloidal content, when leached free of bases gave about the same fixation as the untreated soil 4. It is probable from the results secured that if a soil had a lower pH than that of soil 7 or a larger amount of carbonates than that present in soil 5 leaching with dilute HCl would increase fixation very little if at all. This would agree with the work of Fraps (21) who showed that a soil with a very high power of fixation was affected very little by the removal of carbonates with HCl. It can not be explained why leaching with HCl would cause a decided decrease in fixation by a mineral soil unless the soil was only partially washed free of bases. A soil containing considerable carbonates would probably show a decrease in fixation after leaching with HCl if the leaching was not complete.

A comparison of the power of fixation of the soils leached by dilute HCl (table 12) and those from which the bases had been removed by electrodialysis shows that in each case the latter had a higher power of fixation. It is also evident that, with the exception of soils 5 and 7, the soils leached with HCl had a lower pH value. This comparison would substantiate the results reported before which show that below a pH of approximately 3.75 there was
a decrease in fixation with a decrease in pH. Soil 7 which had approximately the same pH value after both leaching and dialysis showed approximately the same power of fixation in each case. These results would indicate that replacement of bases by leaching with dilute HCl would probably be as satisfactory as replacement by electrodialysis for the study of the effect of reaction on the power of the soils to fix phosphates.
SUMMARY AND CONCLUSIONS

1. Seven Iowa soils similar in texture but varying widely in reaction, were used in a study of the factors affecting fixation of phosphates.

2. Igniting the soils at a temperature of approximately 750°C. for one hour increased fixation by soils having a high content of carbonates, but decreased or entirely prevented fixation in acid soils and in alkaline soils, containing only a small amount of carbonates.

3. Ignition did not materially affect the power of calcium hydroxide to remove phosphates from solution, yet it rendered aluminum chloride and ferric chloride inactive towards phosphates in aqueous solutions.

4. Removal of bases from the soil by electrodialysis caused an increase in the amount of phosphates fixed.

5. The effect of the reaction of the soil on its power to fix phosphate, was studied, both in soils which had varying amounts of the exchangeable bases removed by electrodialysis and in dialyzed soils adjusted to varying degrees of saturation by the addition of ammonium ions. The three soils used in this study had reactions varying from pH 5.04 to pH 6.25. In each case the soils showed
an increase in fixation with a decrease in pH value to approximately 3.75 and below this value there was a decrease in fixation.

6. The importance of replaceable bases on the fixation process was determined by replacing the bases present in the soil by a cation which would form soluble phosphate compounds. In a soil having a pH of 5.04 replaceable bases were of no apparent importance while the opposite was true in a soil having a pH of 6.25.

7. Soils which had been leached free of bases with .05 N Hydrochloric acid, showed an increase in phosphates fixed. This increase was less evident in soils having the highest power of fixation.

8. Soils having an alkaline reaction showed a greater fixation when greater amounts of carbonates were present.

9. The results secured indicate that the factors influencing fixation of phosphates by soils should be taken into account in any study on available phosphorus.
ACKNOWLEDGEMENTS

The author wishes to express here his appreciation for the advice given by Dr. P. E. Brown and Dr. F. B. Smith in planning and carrying on this experiment, and for their assistance in the preparation of this manuscript. Thanks are also due Dr. M. H. Brown for many helpful suggestions.
LITERATURE CITED


19. Dusserre, C. and Bieler, T. 1904. Investigations on
the absorbent power of cultivated soils.
(translated title). Ann. Agr. Suisse,
5:110-119. Original not seen; Abstracted
in Exp. Sta. Rec. 16:547.

20. Fraps, G. S. 1909. Active phosphoric acid and its
relation to the needs of the soil for
phosphoric acid in pot experiments.

21. ——— 1911. Effect of ignition on solubility
of soil phosphates.

22. ——— 1922. The fixation of phosphoric acid
by the soil.

23. Gaarder, T. 1930. Fixation of phosphoric acid in
soils. (translated title).
14:140. Original not seen; Abstracted

24. ——— 1931. The binding of phosphoric acid in
the soil (translated title).
Original not seen; Abstracted in Chem.
Abs. 26:1054.

25. Gedroiz, K. K. 1931. The influence of hydrogen per-
oxide in soils. (translated title).
Udobrenie i Urozhai. 3:314-327, 310-922.
Original not seen; Abstracted in Chem.
Abs. 26:2264.

26. Gammerling, V. V. 1926. The absorption of phosphoric
acid by soils. (translated title).
Trudy Nauch. Inst. Udobr. 34:46-60.
Original not seen; Abstracted in Exp.

27. Gordon, N. E. and Starkey, E. S. 1922. Influence of
soil colloids on availability of salts.


34. Kapp, L. C. 1930. The approximate size of soil particles at which the heat of wetting is manifested. 
Soil Sci. 29:401-412.


Soil Sci. 15:157-165.

Soil Sci. 32:343-365.


44. Pagnoul, A. 1894. Terres Arables des Pas-de-Calais, Arras, 1894. Original not seen; Abstracted in Exp. Sta. Rec. 6:118-123.


54. Schreiner, O. and Failyer, G. H. 1906. The absorption of phosphates and potassium by soils.


56. Skalkij, S. 1915. Conversion of soluble phosphoric acid into insoluble phosphoric acid in the soil under the influence of physical, chemical, and biological factors.


