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The fixation of phosphorus by iron and its replacement by organic and inorganic ions.

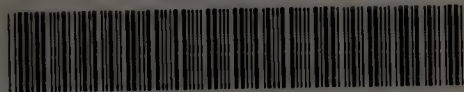Richard Merrill Swenson
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The Fixation of Phosphorus by Iron and its Replacement

By Organic and Inorganic Ions

Swenson - 1948

THE FIXATION OF PHOSPHORUS BY IRON AND ITS REPLACEMENT

BY ORGANIC AND INORGANIC IONS

by

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INTRODUCTION

There are many soils which lack the ability to supply sufficient phosphorus for proper plant growth. To these soils it becomes necessary to add additional phosphorus in the form of a phosphate fertilizer. A little over a hundred years ago, Sir John Lawes first produced a soluble phosphate fertilizer by treating ground bones with sulphuric acid. Since that time, the industry has steadily grown. Today, in the United States, eight million tons of rock phosphate are mined yearly for the production of superphosphate fertilizers and for direct application to the soil. The cost to the American farmer annually is about four hundred million dollars and this still does not meet the demand of all the soils requiring phosphorus.

Most soils contain a large amount of total phosphorus, but usually a very small amount of this is available to the plant. In certain areas as high as 80 per cent of the total phosphorus added to the soil as a fertilizer becomes fixed in unavailable form. This fixation of phosphate by the soil is of such magnitude to be of economic importance. If a means could be developed whereby this phosphorus could be made available to the plant, it would result in a great monetary saving to the farmer and would prolong the productivity of many soils. Also, if phosphorus fixation could be prevented, smaller amounts of phosphate fertilizers would be required to obtain maximum plant yields. Through the savings in transportation, labor, and fertilizer costs the farmer would be able to make a phosphorus ammendment to many soils that are now not

fertilized because of the expense.

Several theories have been advanced as to the cause of phosphorus fixation and methods have been devised and used for the purpose of either preventing phosphorus fixation or making fixed phosphorus available to the plant. One of the methods used involves the placement of the fertilizer. Some investigators advocate the application in bands or strips while others advise a deep placement of the fertilizer near the root zone. The method employed would depend upon the type of crop and soil conditions. Other workers have suggested pelleting of the fertilizer on the theory that the larger sized particles would expose less surface to the fixing agencies of the soil. Midgley (36)[1] and others have shown that the application of manure and phosphate together results in better crop yields. It has been reported in many cases that the addition of lime to acid soils results in an increase in available phosphorus. Still another method is the addition of sodium silicate to the soil. None of these methods, however, have proved to be the solution to the problem and there still exists a need for the development of a method of preventing phosphate fixation.

The greatest amount of phosphorus fixation occurs in those soils that have either a high iron or aluminum content. In 1943 seven of the South Eastern states used more than 40 per cent of the total amount of phosphate fertilizer used in the United States. It has been well established that iron and aluminum are important

[1]Figures in parenthesis refer to "Bibliography", p. 64.

factors in causing the unavailability of phosphorus in acid soils.

The purpose of this investigation is to determine the mechanism of the fixation of phosphorus by iron and also to determine the ability of fluoride and certain amino, hydroxy, and aromatic acids to prevent the formation of the iron-phosphate complex. It is believed that if the mechanism by which phosphate is fixed by iron could be determined, it would be of value in formulating agronomic practices to prevent it. If it could be shown that the organic acids prevent phosphorus fixation, it would give further evidence of the importance of organic matter in soil management, as well as offer a practical means of reducing phosphorus fixation in acid soils.

REVIEW OF LITERATURE

Phosphorus fixation has been the object of intensive study for many years. The literature concerning the subject is very extensive; therefore, no attempt shall be made to give a detailed survey of all phases of phosphate fixation. This review will include a report of the representative papers dealing with the role of iron in the fixation process.

SOILS WITH HIGH PHOSPHORUS FIXING CAPACITY

It is generally accepted that podzolic and lateritic type soils have high phosphorus fixing capacities and require large amounts of phosphate fertilizers for good crop growth. According to Pierre (39), 40 per cent of the total amount of phosphate fertilizers used in the United States in 1943 was used by seven South Eastern states. Neller and Comar (37) working with soils taken from virgin areas in Florida report that the fixation capacity of these soils, especially the loams and clays, is very high on the basis of the amounts of phosphate usually applied in fertilizer practice. They found that the Coxville clay retained over 80 per cent of the phosphorus added in large amounts, even though its fixation capacity had been partially satisfied before the application. They concluded that their experiments indicate that the loam and clay soils of the type studied will continue to fix large amounts of phosphate even after many reapplications. It is stated by Weiser (59), that the magnitude of fixation by New England podzol soils is such that when calculated to superphosphate it assumes

the proportions of five to six tons per acre. When the possibility
of so much fixation exists, plant recoveries of only 10 to 20 per
cent of a 600-pound application are to be expected.

Davis (13) reports that most upland Hawaiian soils are
lateritic with a high content of hydrated iron oxides, and that
their phosphorus fixation capacity is very pronounced. He states
that in some cases there is little or no crop response to moderate
applications of phosphatic fertilizers, but a response to rather
large applications. Heck (25) found the laterite soils he worked
with to have a high phosphorus fixing capacity. He substantiates
this in a later paper (26), and further states that when soluble
phosphorus is applied to these Hawaiian laterites, the majority of
them fix over 80 per cent of the applied phosphorus in a slowly
available form.

The data of Dean (14) show that the rate of removal of
phosphorus by electrodialysis from lateritic soils is extremely
slow even though these soils were normal in total phosphorus.
Romine and Metzger (45) reported that heavily leached soils ab-
sorbed from two to five times as much phosphorus as did relatively
unleached soils. The work of Scarseth and Tidmore (50) indicates
that the native phosphorus of the red soils had a lower availa-
bility than that of the gray soils, per unit of colloid, and that
the greater the degree of weathering in a subtropical climate, the
less the solubility of the native phosphorus. Hall and Vogel (23)
found that acid soils of South Africa had low phosphorus availa-
bility. It has been shown by Martin and Doyne (31) that the

laterite and lateritic soils of Sierra Leone readily remove soluble phosphorus from solution.

SOIL HORIZONS AND PHOSPHORUS FIXATION

It is interesting to note that soil horizons differ in their ability to fix phosphorus, the B horizon being the region of greatest fixation in podzolic soils. Midgley and Dunklee (36) used the B horizon of a podzol soil for their studies of phosphorus fixation, because "its phosphorus fixing capacity is known to be high". From his chemical determinations of phosphorus fixation in podzol soils, Weiser (59) found that the B horizon fixed much more phosphorus than did the A horizon. Using a laboratory plant method, he found that rye seedlings recovered 100 per cent of added phosphate from the A_1 horizon, 52.4 per cent from the A_2 horizon, while from the B_1 and B_2 horizons they recovered less phosphate than was added in the seeds. The work of Romine and Metzger (45), with heavily leached and relatively unleached soils, shows that in all cases the B horizons fixed more phosphorus than the A horizons. Toth and Bear (58, 4) found, in the case of soils showing advanced podzolization, that their phosphorus adsorbing capacity was greater in the B horizon than in the A or C horizons.

PODZOLIC AND LATERITIC SOILS HIGH IN IRON

The processes of podzolization and laterization result in a greater percentage of iron in the soil. Polynov (41 p.98) states that hydrated ferric oxide is the result of normal weathering, and that its high state of oxidation and hydration indicate that

it is an end product of the weathering processes. The data of
Russell (47 p.283) show that the percentage of iron increases as
the laterization process proceeds towards the formation of a
laterite soil. The laterization process, according to Byers et al.
(7 p.973), results in the conversion of the rock minerals to silicic
acid, aluminum hydroxide, and iron hydroxide or their more or less
complete dehydration products. Since, in general, silica is more
rapidly removed by solution than iron oxide and alumina, a fully
developed laterite may consist of only aluminum and iron hydroxides,
although the process is not normally complete in any soil. Pugh
and Du Toit (43) make statements indicating that laterite soils are
high in iron and aluminum hydroxides, and from the results of their
experiment, they advance a theory as to how the hydrous oxides of
both iron and aluminum would be formed and exist in a free state
in these soils. One of the processes, Byers et al. (7 p.972) state,
in the formation of podzols is the removal of clays and iron
compounds from an upper to a lower layer, resulting in an accumula-
tion of iron in the B horizon. Bear and Toth (4) report that where
soils are podzolized, iron and aluminum tend to concentrate in the
very acid B horizon, with the result that this horizon has an
extremely high fixing capacity for phosphates. Ford (20) states
that in addition to the laterites, certain soils of the temperate
zones, especially if subjected to reducing conditions, may contain
appreciable amounts of the hydrated iron oxides.

IRON AND ALUMINUM COMPOUNDS RESPONSIBLE FOR PHOSPHORUS FIXATION

That iron and aluminum play an important role in the availa-

bility of phosphorus in the soil has been proved by numerous in-
vestigators. Powter (5) reports, that within the pH range of most
acid soils, iron and aluminum are responsible for the fixation of
phosphorus. Studying the effect of adding iron and aluminum
chlorides on the retention of phosphorus by certain Southern soils,
Davis (11) reports, that the addition of ferric chloride markedly
increased the retention of phosphorus in all series, and that the
amount retained was plainly related to the amount of iron added.
Mehling (53), working with activated kaolin, found that its active
phosphorus sorbing constituent could be removed by extraction with
0.1 N HCl, 0.1 N Tartaric acid or 10 per cent HCl. He believed
this active constituent to be a hydrous alumina such as γ-AlOOH,
and he concluded that it was the free hydrous alumina present in
kaolin that was responsible for phosphate sorption.

Hall and Vogel (23), working with acid soils of South Africa,
found that the soils highest in iron and aluminum had the greatest
phosphorus fixing capacity. They also showed that the solubility of
the iron in each soil was practically the same, and they concluded
that the different rates of reversion, therefore, were not due to a
greater proportion of soluble iron. The data of Ronins and Metzger
(45) show a relationship between the reduction in phosphorus fixing
capacity of soils resulting from dilute acid extraction and the
amount of sesquioxides removed by the extraction. Chandler (9),
working with the clay fraction of certain Southern soils, found
that the extraction of the free iron and aluminum oxides caused a
reduction in their phosphorus fixing capacity. He gives consider-

able evidence to show that, within the range of most acid soils, the fixation was due to the formation of insoluble iron and aluminum compounds. He concluded that his work verifies the belief of many investigators that iron and aluminum oxides are very important in controlling phosphate solubility.

Using the colloidal clay fraction of a natural alumino-silicate (bentonite), Scarseth (49) found that the retention of the phosphate ion by the colloid was greatly increased when the alumino-silicate was enriched with iron. Metzger (38) found that the removal of free oxides of iron and aluminum from ten different soils, at pH varying from 5.0 to 6.0, decreased their phosphorus fixing capacity from 20 per cent to 94 per cent, only three of the ten showing less than 50 per cent decrease and five showed decreases of more than 70 per cent. He gives evidence to prove that the dilute acid extraction of the soil, for the removal of the iron and aluminum oxides, does not disrupt the crystal structures of the particles; therefore, that cannot be given as a reason for the decrease in the phosphorus fixing capacity. Doing work with various types of soils, Doughty (17) found that the removal of iron and aluminum by leaching with hydrochloric acid greatly reduced their fixing power, the peats completely losing their fixing power, the loam and clay being reduced by 50 per cent. He further shows that the iron and aluminum obtained in the leachate were the active materials in the fixation. When they were separated from the extract and tested, they caused the fixation of as much phosphate as the original material.

Coleman (9), working with coarse and fine clay fractions, found that the amount of phosphorus fixed is not influenced so much by the type of clay mineral as by the amount and activity of the free iron and aluminum oxides contained. The coarse clays, which contained about half as much iron and aluminum oxides as the fine clays, fixed about half as much phosphate. He concluded that the activity of the free oxides determined the amount of phosphate fixed by the clay. Ghani and Islam (22) concluded from their work with acid soils of India, that the amount of phosphorus fixed in the different treatments was highly correlated with the phosphorus recovered as iron and aluminum phosphates. More than 90 per cent of the fixed phosphorus was recovered as iron and aluminum phosphates, showing that chemical precipitation of soluble phosphorus into phosphates of iron and aluminum accounts very largely for the fixation that takes place in acid soils. The removal of the iron oxides, by either chemical means or by biological reduction, reduced the phosphorus fixing capacity of colloidal clay, reports Allison and Scarseth (1).

Toth (57) states that the removal of the free iron oxide from the soil colloid reduces the magnitude of phosphate adsorption. The results of Hibbard (27) indicate that most of the phosphate in the soils was held in combination with iron. He also found that the soil having the greatest proportion of hydrated iron oxide had the highest fixing power of any of the soils studied. Scarseth and Tidmore (50) found iron to be active in phosphate fixation. Heck (26) reports that iron is responsible for the greater part of

phosphorus fixation in laterite soils.

The results of both chemical analysis and plant growth, reports Weiser (50), clearly show that the zone of iron and aluminum accumulation in the profile is where pronounced fixation occurs. He further states that from the evidence presented in literature, and the data obtained on fixation in podzol profiles, it seems reasonable to assume that in the main, phosphate fixation in these soils is brought about by iron and aluminum. Doar and Toth (4) found soils high in ferric oxide and alumina to have high phosphorus fixing capacities. Brown (6) states that iron, aluminum and calcium are the main elements responsible for phosphate fixation.

Metzger (34), working with some of the soils of the prairie zone, ranging in pH from 5.0 to 7.0, found that close relationship existed between both total Fe_2O_3 and Al_2O_3 and the phosphorus fixing capacity of the soil. The amount of easily soluble Fe_2O_3 present showed no significant correlation with phosphorus fixing capacity, nor with the reduction of the fixing capacity brought about by dilute acid extraction of the soil. However, when the reduction of phosphorus-fixing capacity due to dilute acid extraction was expressed as percentage of the original fixing capacity, it showed a highly significant correlation with easily soluble iron. The percentage of the total Fe_2O_3, which was in easily soluble form, was highly correlated with percentage reduction of phosphorus-fixing capacity resulting from acid extractions. He concludes that since fixing capacity was found to be closely correlated with total Fe_2O_3 and Al_2O_3, it appears that dilute acid

extractable and nonextractable forms of both iron and aluminum
function in phosphorus fixation processes in the soil. He suggests
that this explains, in great measure, why the removal of free iron
and aluminum in previous work failed to destroy more completely
the fixing capacity of the soil.

It has been shown by Doughty (16) that leaching peat with iron
and aluminum chlorides caused a decided increase in its fixing
capacity. He concludes that in the material studied the formation
of iron, aluminum, and calcium phosphates will account for the
fixation of phosphorus under field conditions.

RELATIVE AVAILABILITY OF FIXED PHOSPHATES

Weiser (59) states that the availabilities of fixed phosphates
may vary considerably, depending upon the soil constituent respon-
sible for the reaction. Phosphorus held by one compound may yield
readily to the feeding roots while that held by a different sub-
stance may be almost entirely unavailable. Ford (20) reports that
of the phosphates fixed by soil, the calcium and magnesium phosphates
are the most available, the ferric and aluminum compounds formed
with the relative soluble iron and aluminum compounds of the soil
are of intermediate solubility. The iron phosphate compound is
more slowly available than the aluminum phosphate compound, accord-
ing to Heck (25, 26). Pugh (42) agrees with Heck, stating that the
phosphates of ferric iron and aluminum are of the same type, but
ferric phosphate is more stable in the very acid ranges than is
aluminum phosphate. Metzger (34) concludes, from the data he
obtained, that the easily soluble aluminum of the soil is much less

active than the easily soluble iron in fixing phosphorus. Austin (3) has also shown that aluminum hydroxide is much less active than iron hydroxide in rendering phosphate insoluble.

Beater (5) explains that soils of high alkalinity increase the calcium in the mass action equilibrium with soluble phosphates, whereas, in acid soils calcium is thrown out in preference for iron and aluminum. In general he concludes that fixation in acid soils is of a far more permanent nature than that in alkaline soils, and that in very acid soils iron phosphate is more stable than aluminum phosphates. The order of stability of the three compounds varies directly with the pH value. He further found that at pH 6.0 the solubility of calcium, aluminum, and iron phosphates was the same, and consequently each has an equal chance for the applied phosphate, therefore, the compound formed would depend upon the relative amounts of the bases present in active form.

pH AND PHOSPHORUS FIXATION

The soil reaction has an influence upon phosphorus fixation. Pugh and Du Toit (43) state that a solution of normal sodium hydrogen phosphate completely precipitated the iron from a ferric chloride solution at pH 4.3. They also found the isoelectric point of ferric hydroxide, when prepared from its chloride, to be at pH 7.1. Working with minerals ground to pass a 100-mesh sieve, Perkins and King (38) found the pH for maximum phosphate fixation was about 3.5. Doughty (16), working with pure solutions, found that iron phosphate was least soluble at pH 3.8 to 4.0. These results agree with those of Rossmann (46) who, using electro-

dialysed colloidal clay, found that the maximum phosphate absorption
occurred at pH 3.0 to 4.0. He states, however, that this is the
region where iron and aluminum are most soluble; therefore, they
could not be responsible for the absorption. Teakle (56) reports
that iron phosphate is least soluble under acid conditions
corresponding to pH 3.0. This would agree with Davis (11), who
observed that on the addition of ferric chloride the minimum
solubility of phosphate occurs at a pH of 3.0. He further states
that under the conditions of the experiment the formation of iron
and aluminum phosphates is not the major form of fixation at soil
reactions above pH 4.5. Coleman (9) gives the pH of maximum phos-
phate fixation as ranging from 3.3 to 3.6.

Russell (47 p.342) writes that iron compounds in the soil
remain insoluble over a range of pH 5.5 to 9.0, the minimum
solubility occurring at about 6.3. The measurements of Halvorson
and Starkey (24) indicate that at reactions more alkaline than 5.0,
very small amounts of ferrous iron will be in solution under at-
mospheric conditions and even smaller amounts of ferric iron are
soluble.

The results of Arnold (2) demonstrate that much larger amounts
of phosphorus were held in an absorbed form when the pH of the soils
was low. He was comparing soils of pH 5.5 and 7.3. Metzger (33)
states that while other forms of fixation account for a portion of
the phosphorus-fixing capacity of soils, fixation by iron and
aluminum oxides apparently accounts for a large part of the fix-
ing capacity, even in the pH range 5.0 to 6.0. He further reports

that the results of the experiment indicate that the order of
magnitude of the reductions in fixation, due to dilute acid extrac-
tion, is not likely to be greatly different when fixation takes
place in the pH range 5.0 to 6.0 than when this range is consider-
ably lower. According to Davis (12), the amount of water-soluble
and carbonic acid-soluble phosphate in the H_3PO_4 treated series,
decreased at pH values below 5.0 and 6.5 respectively. It has
been shown by Schollenberger (51), that phosphate fixation in
certain Ohio soils occurred at pH 4.0 to 5.0. This was also the
range at which arsenate displaced the least amount of phosphate.
He also concludes from his results that the observed effect of liming
in increasing the solubility of phosphorus in the soil is largely
from the increase in the pH value of the soil. Romine and Metzger
(45) show that in all horizons low availability was associated with
low pH values, these values ranging from 4.8 to 5.6. The values
where the phosphorus was more available ranged from 5.6 to 7.8.

Pugh (42) states that the phosphates have a lower isoelectric
point than the corresponding hydroxides. With increasing pH the
amount of phosphate in the precipitates diminishes, the hydroxyl ion
displacing the phosphate. Both acid and alkaline hydrolysis occur,
and there is an optimum pH at which these compounds can be pre-
cipitated. This is about the isoelectric pH, but flocculation ex-
tends to both sides. The quantity of phosphate adsorbed in the
precipitate need not be a maximum at the isoelectric pH, for both
Cl^- and PO_4^{---} enter into the structure of the ionic micelle and
which predominates at the isoelectric point is not known.

The effect of pH, according to Dexter (5), is not the dominant factor in fixation, since large excesses of active iron and aluminum are believed to overshadow its influence on the products of chemical action. He further states that from pH 6.5 upward, calcium predominates in combining with soluble phosphates. Below this figure it is largely eliminated from the fixation equilibrium.

IRON COMPOUNDS THAT FIX PHOSPHORUS

It has been shown by Ford (20) that hematite (Fe_2O_3) does not fix phosphorus, but that the hydrous oxides of iron do in forms not soluble in sulphuric acid of pH 3.0. On complete dehydration goethite lost its fixing capacity, and it gave an X-ray pattern identical with that of hematite. Attempts to rehydrate the de-hydrated goethite were unsuccessful. He then showed that heating soils at 185 C. for 12 to 30 days greatly decreases fixation, and he concluded that this decrease may be attributed to the dehydration of goethite. He believes that goethite, when once formed, persists in soils because of insufficient heat in soils to dehydrate it.

The work of Ford (20) has been confirmed by Weiser (59) who found that goethite and limonite fixed phosphorus while hematite did not, and by Doughty (17) who showed that the heating of goethite at 800 C. for two hours, entirely destroyed its capacity to fix phosphorus. Dean (14) also agrees with Ford in that limonite and goethite react in a similiar manner in their fixation of phosphates. Perkins and King (38), however, report that no phosphate was fixed by 100-mesh magnetite, but considerable quantities were fixed by limonite and hematite ground to the same

size. They concluded that both the physical condition of the mineral and the chemical composition are important factors in phosphate fixation.

Hibbard (27) reports that the colloids of iron and aluminum may fix phosphate over the pH range from 3.0 to 8.0. Heck (25) states that it is not necessary for the iron compounds to be in solution in order to react with the soluble phosphate to form phosphates of low solubility, since the natural hydrated oxides react directly. In a later paper Heck (26) shows that the yellow in laterite soils is related to high phosphorus fixation, and states that this is in accord with the theory that fixation by iron is brought about by the hydrated oxides, such as ferric oxide monohydrate, or perhaps the dihydrate, should this substance exist in nature. Yellow soils have a greater fixing power than red soils containing the same amounts of iron oxides, states Bear and Toth (4), because of the greater degree of hydration of their oxides.

COMPOUND FORMED WITH IRON

The compound resulting from the fixation of phosphorus by iron has not been clearly determined. Scarseth (49) states that his data do not clearly indicate whether the phosphate is sorbed as a mono-, di-, or trivalent anion. He does report that the investigations of Steele (54) indicate that the phosphate is sorbed by clays as the tri-valent ion. The marked effect of pH upon the arsenate displacement, is considered by Schollenberger (51), to be evidence that a ferric phosphate, or similar complex, may be present in the soil. Deater (5) believes that phosphorus is fixed

as iron or aluminum phosphate or as the basic phosphates of these ions.

Dean (14) concluded that when a soluble phosphate is added to some soils, basic iron phosphates, similar to dufrenite, are formed. Dufrenite is given as $Fe_2(OH)_3PO_4$. He further concluded, from his efforts to determine the nature of the phosphate formed, that the type of insoluble phosphate formed was similar in all the soils studied. According to Ford (20), the phosphate formed with goethite has a solubility in sulphuric acid at pH 3.0 comparable to that of dufrenite.

Pugh and Du Toit (43) found it impossible, under the conditions of their experiment, to prepare a ferric phosphate with a PO_4/Fe_2O_3 ratio higher than 0.71, for the compounds decomposed until this ratio was formed. Sieling (53) concluded, from his work with kaolin, that a basic phosphate was formed from γ-AlOOH by replacing the hydroxyl with a chemically equivalent $H_2PO_4^-$, and that this led to a compound having a $P_2O_5/Al_2O_3^2$ ratio of unity. Sieling's results are in agreement with those of Mattson and Pugh (32). They give the following reaction as taking place between aluminum hydroxide[a] and phosphoric acid:

$$Al(OH)_3 + H_3PO_4 \longrightarrow \begin{array}{c} HO \\ \diagdown \\ HO \diagup \end{array} Al-PO_4 \begin{array}{c} H \\ \diagup \\ \diagdown H \end{array} + H_2O$$
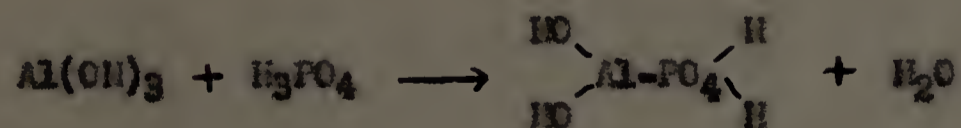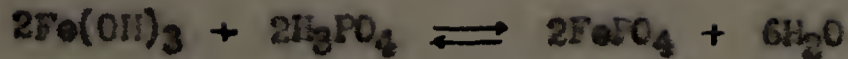
Heck (25) states that if the iron oxide is fully hydrated

[a]It is believed that iron would react in the same manner due to its chemical similarity with aluminum.

the normal phosphate may be formed:

$$2Fe(OH)_3 + 2H_3PO_4 \rightleftharpoons 2FePO_4 + 6H_2O$$

However, the tri-hydrated iron oxide is unstable and has the tendency to change to the monohydrate (goethite $Fe_2O_3.H_2O$). The reaction then is one of simple addition, making it unnecessary for the iron to go into solution:
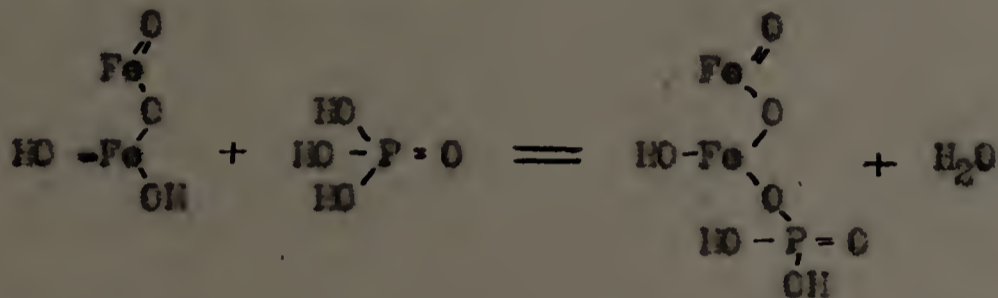
Ferric oxide   Ferric oxide monophosphate
monohydrate (goethite)   (dufrenite)

Heck (26) has recently reported that in the laterites with which he worked, most of the applied phosphorus is fixed in the soils as the basic iron phosphates. The discovery of an iron compound which is responsible for the fixation of phosphorus in Southern soils has been reported by Meyer (35). It exists in concretions and fixes phosphates either as a basic ferrous or basic ferric phosphate depending upon drainage conditions.

MECHANISM OF PHOSPHATE FIXATION

There have been several theories advanced to explain the mechanism of phosphate fixation. These theories may be grouped according to Davis (13) as follows: 1. Cations of soluble salts present in the soil, or cations replaced from the soil by those present in the solution, form precipitates with the phosphate ions. 2. By double decomposition, relatively insoluble soil minerals

react to form insoluble phosphates. 3. Phosphates are adsorbed at the extensive soil-solution interface. 4. Phosphates are absorbed by the soil minerals to form complex systems in one or more of the solid soil phases.

Bear and Toth (4) state that microbiological consumption, chemical precipitation, and physicochemical adsorption are responsible for phosphate fixation in soils. The amount of phosphate consumed by soil micro-organisms is relatively small, most of the fixation being the result of precipitation and adsorption. Iron and aluminum serve as precipitating agents at pH values below 5.5, calcium plays a dominant role at pH 6.5, and magnesium enters the picture at 7.5. But precipitation by these ions is inadequate to explain the high phosphate fixation which normally occurs and which, for Penn silt loams, may amount to 125 tons of 20 per cent super-phosphate equivalent per two million pounds of soil. In soils of such high fixing capacity, most of the phosphate is colloid-bound or saloid-bound, the colloid-bound phosphate being replace-able by hydroxyl, humate and silicate ions, and the saloid-bound phosphate by sulfate, chloride, citrate, and tartrate ions. Colloid-bound must be considered as an integral part of the soil complex while saloid-bound is present as $H_2PO_4^-$ in the ion atmosphere sourrounding the soil particles, rather than as a definite part of the soil complex. No sharp line of distinction, however, can be drawn between the two.

Studies with prairie soils led Metzger (33, 34) to conclude that for acid soils under field conditions absorption, or chemical

precipitation, may account very largely for phosphorus fixation and that adsorption, a surface phenomenon, is probably of small practical significance. While Doughty (16) concludes from his data, that it is evident that both precipitation and physical adsorption are functioning in the removal of phosphate from solution. Davis (13) working with Hawaiian soils freed from exchangeable calcium, magnesium, etc., tentatively concludes that the fixation of phosphorus is due to absorption of the phosphate by the soil minerals and the formation of equilibrium complexes. He explains that phosphates may penetrate the liquid-solid phase interface and form new compounds with the hydrated minerals, such as Werner coordination compounds. He gives two conditions that may occur at the interface: (a) hydroxyl groups oriented outward in a negative surface are replaced by phosphate ions and (b) metal ions oriented outward react with phosphate ions.

The mechanism of phosphate fixation by the alumino-silicate colloid is pictured by Scarseth (49) as being a surface phenomenon, the phosphate ion being held in such a way as to be able to enter into anion exchange. He gives explanation for fixation over a range of pH values, at the lower pH values when iron is present, the phosphate is precipitated as insoluble iron phosphate, at the intermediate range it is the aluminum valences in the surfaces of the colloid that retains the phosphate in the low-iron colloids. At the higher pH values the phosphates are replaced by the hydroxyl ions and then precipitated as insoluble calcium phosphates.

In a recent paper Sieling (53) gives the mechanism of phosphate sorption as one of anionic exchange. He concluded that the replacement of anions depended upon the relative activity (i.e. effective concentration) of the ions involved; therefore, at very low pH values $H_2PO_4^-$ would be expected to replace the less active hydroxyls. Pugh and Du Toit (43) believe that phosphate fixed by iron may be ionically exchanged for the hydroxyl ion. The anion-exchange reactions of soils is described by Dean and Rubins (15) as the substitution of one anion by another, which is present in solution in greater concentration, or possesses a stronger tendency to hold its position on the soil. They support the theory that soils have a definite anion-exchange capacity, and they believe that anion exchange is the mechanism causing much of the phosphorus retention of acid soils. They believe this phosphate to be held in this exchange system in such a way as to be replaceable by other ions. The following reaction is given as a means of explaining phosphate fixation in some soils:

$$XOH + H_2PO_4^- \rightleftarrows XH_2PO_4 + OH^-$$

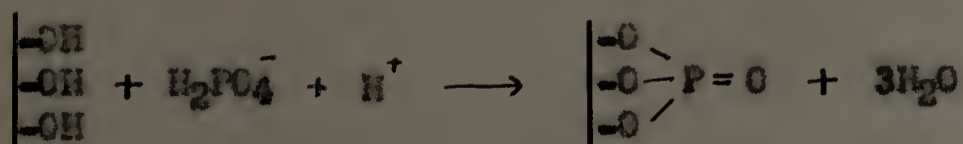soil surface   solution   soil surface   solution
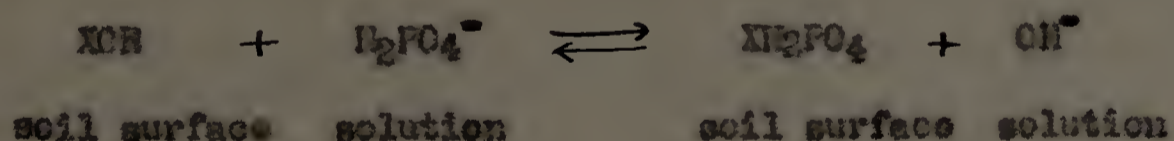
There being an exchange between certain of the hydroxyl ions of the clay minerals or hydrous oxides and the phosphate ions in solution.

Ravikovitch (44) believes that anionic exchange takes place in the soil and that it is the process responsible for phosphate adsorption. He states that the adsorption of phosphate by the

soil complex proceeds on the principle of an equivalent anion ex-
change. The amount of adsorption depends upon the anion exchange
capacity of the soil complex and on the valence of the phosphoric acid
ions which take part in the adsorption. In the first form of
adsorption for the H-soils, there occurs an equivalent exchange
between the exchangeable hydroxyls of the complex and the tri-
valent PO_4 ions. In the second form of adsorption, an equivalent
exchange between the exchangeable hydroxyls of the complex and the
divalent HPO_4 ions is proposed. For the third and fourth forms
there occurs an equivalent exchange between the exchangeable
hydroxyls of the complex and, probably, a combination of phosphoric
acid ions of the various valences.

Phosphate fixation is described by Stout (55) as a simple
ionic exchange of phosphate ions for hydroxide ions on the surface
of the clay minerals. He bases his assumption on a measurement of
the water formed, on X-ray studies of the phosphated kaolinite, and
on the fact that in suspensions of ground kaolinite in acid phosphate
solutions, the reaction is shifted to a more alkaline pH which would
indicate a displacement of OH ions for phosphate ions. He gives the
following equation for the reaction:

$$
\begin{vmatrix} \text{—OH} \\ \text{—OH} \\ \text{—OH} \end{vmatrix} + H_2PO_4^- + H^+ \longrightarrow \begin{vmatrix} \text{—O} \\ \text{—O} \\ \text{—O} \end{vmatrix} \! \! P = O \; + \; 3H_2O
$$

He further suggests that kaolinitic minerals in soils might form
crystalline phospho-alumino-silicates by exchange of lattice
hydroxyl ions for phosphate ions. He reported that he was able to

change the crystal structure of kaolinite by phosphating it, as
indicated by X-ray studies, but reports that he restored the
original structure by leaching the kaolinite with an alkaline
solution (pH 9.0) and washing with dilute HCl (pH 3.0).

Kurtz, DeTurk, and Bray (30), studying phosphate fixation in
Illinois soils, found it difficult to explain their data on the
basis of the formation of a phosphate compound, stating that there
is no apparent stoichiometry involved. They hold that the phosphorus
is adsorbed by the soil and held in a replaceable form, also that
the amount so held depends upon phosphate concentration. They
postulate that this adsorption might take place either at points
where hydroxyl, silicate, or organic anions could be exchanged, or
at points where aluminum or iron ions are exposed on the surface.
If hydroxyl ions are present where iron and aluminum occur at the
lattice edge, adsorption at this point would be essentially an
exchange of hydroxyl and phosphate ions.

According to Pugh (42), phosphate can enter into anionic-
exchange. When the pH is increased the hydroxyl group replaces the
phosphate and on the theory of coordination, in the absence of
double bonds, only one hydroxyl group would be required to replace
a large group like H_2PO_4 or $HSiO_2$.

THE ABILITY OF ORGANIC MATTER TO PREVENT PHOSPHORUS FIXATION

Several investigators have reported results indicating that
organic matter increases the amount of available phosphorus in
the soil, while others have been of the opinion that organic
matter itself fixed phosphorus. Heck (26), working with laterite

soils, found that dark soils, high in organic matter, had more available phosphorus than did the red or yellow soils. He concluded that this would tend to indicate that organic matter plays a very important part in maintaining a high availability of native soil phosphorus. Using specially prepared humus, Weiser (59) found that it reduced by 40 per cent the amount of phosphorus fixed by bog ore and freshly precipitated iron and aluminum hydroxides. Doughty's (17) work with natural and synthetic humus, showed that they did not have any phosphate fixing power. His evidence shows that organic matter, as such, has only a minor role, if any, in the fixation of phosphorus.

Jensen (28) prepared artifical humus free from phosphoric acid by hydrolyzing green manures with strong acid, washing them free from acid and extracting with ammonia. He found that these organic solvents, when free from ammonia, increased the solubility of phosphoric acid in the soil. The extracting solutions were neutral to phenolphthalein and methyl orange. He states that three per cent green manures and stable manure mixed with soil and allowed to undergo partial decomposition, increased the solubility of calcium and phosphoric acid in the soil from 30 to 100 per cent. He concludes that the solubility of calcium, magnesium, iron, and phosphoric acid is measurably increased by the addition of green manure, stable manure, or their extracts.

The effectiveness of organic matter in preventing phosphate fixation in the soil, according to Sieling (53), is related to occupancy of the coordinated valences of the alumina by organic

anions that are not replaced by the active phosphate ions. While
Metzger (34) concludes that the greater availability of phosphate
in surface layers of soils as compared to that in subsoils may be
accounted for to a considerable extent by the reducing action of
organic matter in the surface soil upon the iron combined with
phosphate.

Scarseth (49) believes that the carbon dioxide produced by
decaying organic matter reduces the amount of active iron in the
soil. Iron carbonate would be formed, thus reducing the amount of
free iron in solution that would otherwise precipitate the
phosphate. He also states that the benefits derived from organic
matter may be attributed in part to the humates replacing phos-
phates, since the humates are anions that may be sorbed similarly
to the phosphate ions.

Midgley and Dunklee (36) report that their greenhouse and
field experiments show, that the plant responses to the use of
manure and phosphorus were almost universally better when the two
materials were applied together than when they were applied
separately. They attribute the benefits to the reduction in the
solubility of superphosphate caused by the manure, thus reducing
excessive soil contact, and to the pelleting effect of the wet
manure on the superphosphate. They also believe that the large
number of organisms in the manure may change some of the phosphate
into organic compounds which are less soluble but still slowly
available to the plants.

THE ABILITY OF ANIONS TO REPLACE FIXED PHOSPHORUS

If the mechanism of phosphorus fixation is one of anionic
exchange, the phosphate ion would be held in such a way as to be
replaceable by other anions that have a greater affinity for the
phosphorus fixing agency. Dean and Rubins (15) state that the
phosphorus retained by soils, as an exchangeable anion, is
virtually completely removed by fluoride, hydroxide, and citrate
solutions, but anion exchange is probably not involved when ad-
sorbed phosphates are extracted from soils by citrate solutions.
They further explain that it seems likely that the solvent action
of citrate solutions involves the formation of complex ions. Their
work shows the following order in the ability of various ions to
remove adsorbed phosphate: citrate and hydroxide removed all,
fluoride removed all from five soils but not all from soils having
a high anion-exchange capacity, arsenate and tartrate removed only
a part of the total adsorbed phosphate, acetate removed the least.
Schollenberger (51) found no significant displacement of phosphate
by the acetate ion.

Working with neutral salt solutions, Kurtz, DeTurk, and Bray
(30) give the following order as to the ability of various anions
to replace adsorbed phosphate: fluoride > oxalate > citrate >
bicarbonate > borate > acetate > thiocyanate > sulfate > chloride.
The borate, acetate, thiocyanate, sulfate, and chloride removed
amounts similar to or smaller than the amounts removed by water.
They state that fluoride, oxalate, and citrate form complexes of
considerable stability with iron and aluminum. They concluded

that the replacing abilities are related to the tendency of different ions, in comparison with phosphate, to form stable complexes with ions in the clay mineral lattice. However, Metzger's (33) extraction of phosphorus from soils at pH 5.0 to 6.0 with ammonium oxalate, shows oxalate to be very weak in its ability to replace fixed phosphorus.

Weiser (59), using greenhouse and chemical studies to determine the effect of silica and silicates on phosphorus fixation, found that they apparently increased phosphate availability. He concluded that this was a result of deactivation of the sesquioxides by the silica. Chandler (8) states that Gaarder (21) found sodium silicate effective in increasing phosphate solubility, presumably by the precipitation or deactivation of the sesquioxides. Soluble silica, added as Na_2SiO_3, always increased the solubility of phosphate, states Hibbard (27). He concluded that it had a replacing power by which phosphate was set free from the complex.

According to Pugh and Du Toit (43), the hydroxyl ion displaces the SiO_3^{--} and PO_4^{---} in equivalent proportions, and therefore, ferric silicates and ferric phosphates can be regarded as substituted hydroxides. It has been shown by Scarseth (49) that the silicate ion has the ability to replace the phosphate ion. The magnitude of the amount of phosphate ions replaced was not too great, but replacement actually occurred, and the curve obtained was a characteristic double log curve. He also gives evidence to indicate that as the pH is raised the hydroxyl ions replace the phosphate ions, thus throwing more phosphate ions in solution. Cook (10)

shows that increasing additions of lime to fine acid soils consistently lowered the power of these soils to fix added soluble phosphate in a difficultly soluble form. Everson (19), working with acid soils of Massachusetts, found an increase in soluble phosphorus resulting from the addition of calcium hydroxide to the soil. He reports that the release of phosphorus occurred at the pH range 6.5 to 7.0.

Studying the effect of dilute acids on phosphorus compounds in the soil, Russell and Prescott (48) found that hydrochloric and nitric acids were less potent in replacing fixed phosphate than were equivalent concentrations of the weaker citric and oxalic acids. They further report that the different acids have markedly different effects on the adsorption of phosphates from solutions of sodium phosphate. Adsorption goes on readily in the presence of hydrochloric and nitric acids, but it is notably smaller in the presence of citric acid. They conclude that the greater net action of citric acid, in comparison with hydrochloric acid or nitric acid, is not due so much to a greater solvent power, but to a greater power of reducing adsorption.

Doughty (17) oxidized black peat with hydrogen peroxide and found that its fixing capacity was considerably reduced. However, the substances in the water extracts and washings showed some fixing power, but not enough to account for the loss in the corresponding residues.

EXPERIMENTAL

MECHANISM OF PHOSPHATE FIXATION

It is usually stated in soils textbooks that in the fixation of phosphorus by iron the compound $FePO_4$ is formed. This compound has a P/Fe ratio of unity. It is possible, however, for another compound to be formed having this same ratio through the reaction of $H_2PO_4^-$ with iron, forming the compound $Fe(OH)_2H_2PO_4$. It was believed from the beginning of the investigation that this is the mechanism of the fixation of phosphorus by iron. Davis (13) shows that on the dissociation of H_3PO_4 there are virtually no PO_4^{---} below pH 9 and that the $H_2PO_4^-$ is present over the pH range 7 to 2. This is the reaction over which iron is active in phosphorus fixation. Potentiometric titrations and the reaction of iron with varying concentrations of phosphate were employed as experimental methods to establish the formation of the above named compound.

When the term "ferric hydroxide" is used in this report it shall refer to the compound $Fe(OH)_3(H_2O)_3$. Since the coordination number of iron is six, the hydrated ion can be considered as being $\left[Fe(H_2O)_6\right]^{+++}$. When the hydroxyl ion is added to such a solution it has the ability to attract the hydrogen ion from the coordinatively bound water molecules. In solution, therefore, there is the possibility of the following substances: $\left[Fe(OH)(H_2O)_5\right]^{++}$, $\left[Fe(OH)_2(H_2O)_4\right]^{+}$, and $\left[Fe(OH)_3(H_2O)_3\right]^{o}$, the latter being ferric hydroxide.

Potentiometric titrations

It is believed that much can be learned regarding iron phosphate

fixation in the soil by studying the reaction that takes place between solutions of iron and phosphorus under controlled conditions. Also, reactions can be studied that would be impossible if complex soil systems were used. For this reason solutions rather than soils were employed through out most of the investigation.

Preparation of solutions

Ferric chloride solution was prepared by diluting 21.60 grams of ferric chloride (Bakers $FeCl_3.6H_2O$) to 4 liters with distilled water. The resulting solution was standardized by the 8-hydroxyquinoline method as given by Kolthoff and Sandell (29 p.80 & 372).

Sodium hydroxide solution was standardized with potassium acid phthalate using phenolphthalein as an indicator.

The phosphate solutions were prepared from potassium dihydrogen phosphate (Sorensons KH_2PO_4).

Method used

The following method was used for the potentiometric titration of ferric chloride with sodium hydroxide: 150 ml. of 0.02 M $FeCl_3$ were pipetted into an open porcelain casserole, 90 ml. of distilled H_2O were added, the solution was titrated with 0.209 N NaOH with constant stirring, the stirring rod being driven with an air motor. Readings were taken with a Beckman pH meter, using the glass electrode, at exactly two minute intervals after each addition of NaOH. In this report the term "fast titration" is given this procedure in order to distinguish it from a slow method

that will be described later. The results are given in table 1, and shown in graph form in figure 1. Theoretically there were 9.0 M.e.[3] of iron to be titrated. The results show that the equivalence point was reached on the addition of 42 ml. (8.78 M.e.) of NaOH which indicates that the titration was only 97.5 per cent complete. The rapidity of the titration and the fact that a portion of the iron was in colloidal suspension probably explain why the theoretical quantity of NaOH was not required. The isoelectric point of the ferric hydroxide compound formed occurs at approximately pH 7.0.

It has been shown that under the conditions of the experiment 8.78 M.e. of NaOH are required to completely precipitate 150 ml. of the ferric chloride solution. If another ion were introduced that formed an insoluble precipitate with iron, then less NaOH would be required for precipitation. The difference would be equivalent to the precipitating power of the added ion. For example, if 3 M.e. of KH_2PO_4 were added and the $H_2PO_4^-$ occupied one of the coordinating positions on the iron, then only 5.78 M.e. of NaOH, or enough to fill the two remaining positions, would be required to reach the equivalence point. If, however, when the phosphate was added the compound $FePO_4$ were formed, then no NaOH would be required to induce precipitation. Likewise, if the HPO_4^{--} reacts with iron, two positions would be occupied and only 2.78 M.e. of NaOH would be

[3]Milliequivalent. In this report this term refers to the millimolar weight of H_3PO_4 and NaOH and 1/3 millimolar weight of $FeCl_3$ and is equivalent to 30.98 milligrams of P, 17.008 milligrams of OH and 18.62 milligrams of Fe.

required to reach the equivalence point. This approach was used to determine the stoichiometric nature of the compound formed.

The same procedure was used as described previously for the titration of the ferric chloride solution except that 30 ml. of 0.1 M KH_2PO_4 (3 M.e.) were added and only 60 ml. of H_2O, making the total volume the same in both cases. The results are given in table 1 and figure 1. It will be noted that only 29 ml. (6.06 M.e.) of NaOH were required to reach the equivalence point.

TABLE 1

Potentiometric titration of $FeCl_3$ with NaOH in the presence of varying concentrations of KH_2PO_4 using "fast titration" procedure

| Molarity of KH_2PO_4	M.e.of H_2PO_4	M.e.of Fe	M.e. of NaOH theoretically required	M.e. of OH actually required	Deviation from theoretical, in M.e.
0	0	9.0	9.0	8.78	- .22
.0025	.75	8.78	8.03	8.05	.02
.005	1.5	8.78	7.28	7.32	.04
.01	3.0	8.78	5.78	6.06	.28
.03	9.0	8.78	5.78	6.00	.22
.09	27.0	8.78	5.78	6.00	.22

*Based on $H_2PO_4^-$ replacing 1 chemically equivalent OH group.
#The $FeCl_3$ solution contained no excess acid, therefore, slight hydrolysis was evident as indicated by opalescence and the somewhat lesser quantity of OH required for complete precipitation.

Another titration was run using 1.5 M.e. of phosphorus; it was found that 35 ml. of NaOH were required for precipitation. This is 7.32 M.e. of NaOH and 1.5 M.e. of phosphate required to

FIGURE 1

POTENTIOMETRIC TITRATION OF $FeCl_3$ WITH NaOH
IN THE PRESENCE OF VARYING CONCENTRATIONS OF
KH_2PO_4, USING "FAST TITRATION" PROCEDURE
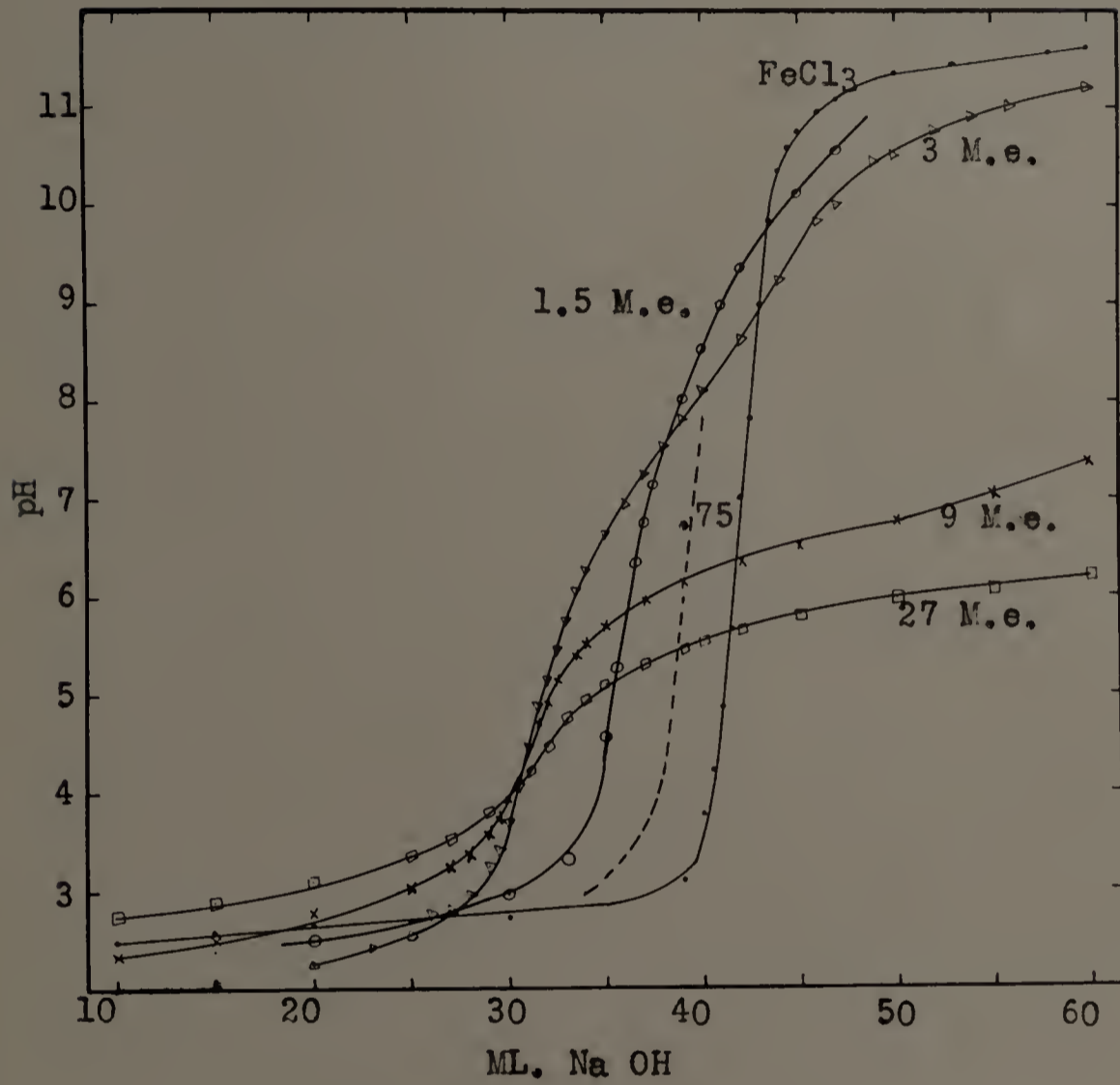
precipitate the 8.78 M.e. of iron, which is in good agreement with the theoretical value. The same procedure was followed using .75 M.e. of phosphorus. See table 1 and figure 1 for results.

The above data give good indication that it is the $H_2PO_4^-$ that reacts with the iron and eliminates the possibility of it being either the di- or tri-valent ion that enters into the reaction. The next step was to determine whether $H_2PO_4^-$ can occupy more than one coordinating position on the iron, thus taking the place of two equivalent OH groups, which would result in a compound having a P/Fe ratio of two. Titrations were run using 9 M.e. and 27 M.e. of phosphorus which would supply enough $H_2PO_4^-$ to occupy all three positions in the former, and an excess in the latter, in which event no NaOH would be required for precipitation. The results show that the equivalence point occurred in the same region as obtained when titrating in the presence of 3 M.e. of phosphorus. (See figure 1 and table 1.) This indicates that only one OH$^-$ is replaced by the chemically equivalent $H_2PO_4^-$ and that the P/Fe ratio of the compound formed is unity.

Slow Titrations

Under the conditions of the "fast titration" it was believed that the reaction did not go to completion. It was decided, therefore, to use another experimental procedure whereby the reaction could be accelerated through the use of heat.

Preparation of solutions

A stock solution of ferric chloride was prepared by adding 110 ml. of concentrated hydrochloric acid to approximately 200 grams of ferric chloride. The solution was standardized as before. From this solution was prepared 0.02 M ferric chloride solutions which were used as the source of iron for the remainder of the investigation.

A 0.20 N sodium hydroxide (carbonate free) solution was prepared and standardized as before.

Potassium di-hydrogen phosphate was used as the source of phosphorus.

Method used

50 ml. of ferric chloride solution (0.02 M) were pipetted into 250 ml. beakers, enough distilled water was added so that the final volume would be adjusted to 100 ml. after the addition of the varying amounts of sodium hydroxide. The solutions were brought to a boil, NaOH was then added from a burette with constant stirring. The solutions were placed on a hot plate and kept at a slow boil for 30 minutes, after which they were allowed to cool until they reached room temperature before determining the pH with a Beckman pH meter. The term "slow titration", when used in this report, shall refer to this procedure. It will be noted from table 2 and figure 2 that the titration of FeCl$_3$ with NaOH reached the equivalence point at the theoretical value.

The same procedure was used for the titration of iron in the presence of varying concentrations of KH$_2$PO$_4$. The results are

FIG. 2 POTENTIOMETRIC TITRATION OF $FeCl_3$ WITH NaOH IN THE PRESENCE OF VARYING CONCENTRATIONS OF KH_2PO_4, USING "SLOW TITRATION" PROCEDURE
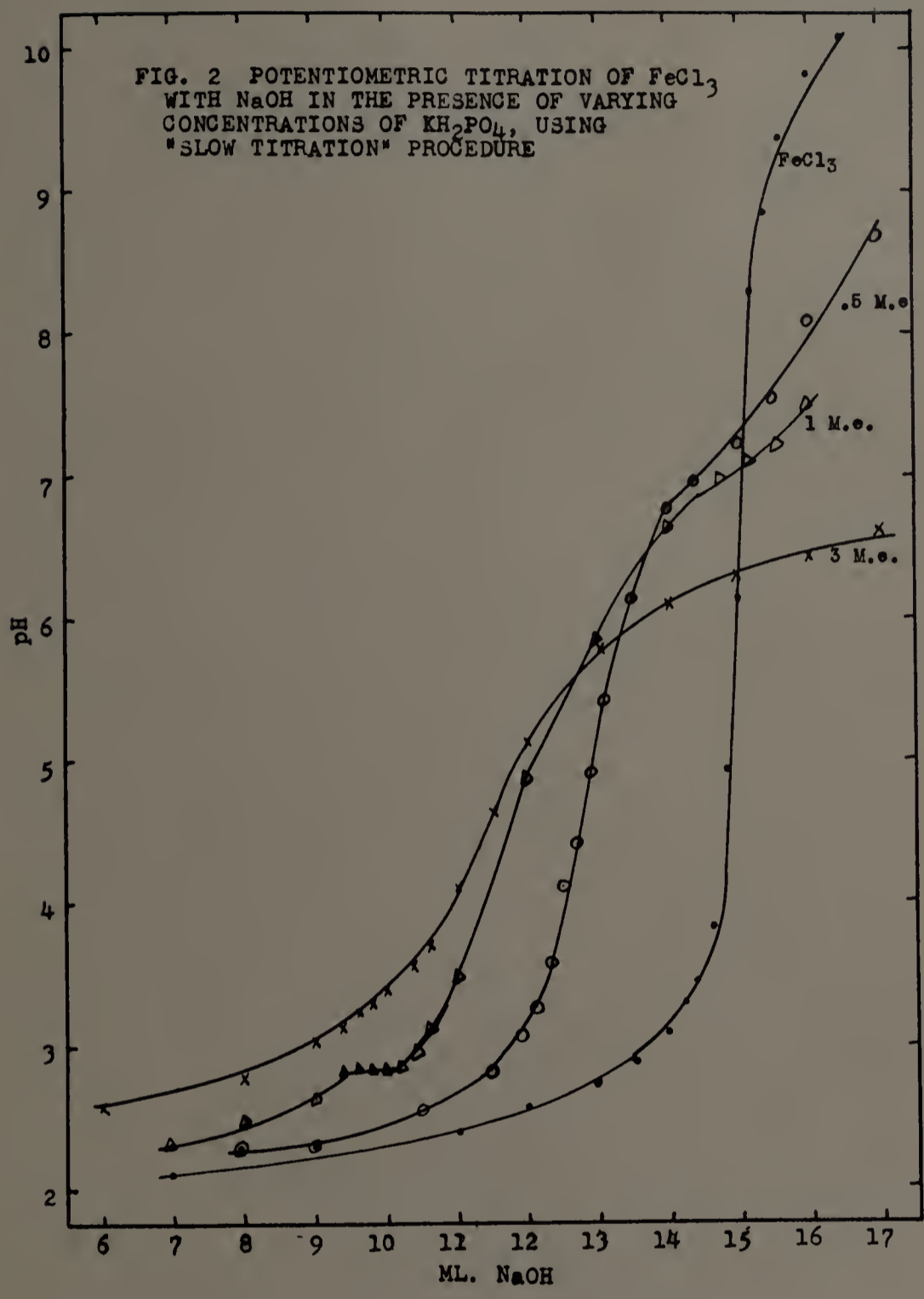
given in table 2 and figure 2. In the titration containing .5 M.e. of phosphate the pH curve is an admixture of the $FeCl_3$ curve and the curve when 1 M.e. of phosphorus was present (see Fig. 2). The amount of iron-phosphate complex formed in comparison to the amount of ferric hydroxide is small; therefore, the hydroxide exerts the greatest influence on the pH curve and masks the effect of the phosphate. This tends to obscure the equivalence point in the titration curve. However, the determination of the amount of H_2PO_4 in the precipitate shows that the equivalence point is reached on the addition of 12.8 ml. of NaOH.

TABLE 2

Potentiometric titration of $FeCl_3$ with NaOH in the presence of varying concentrations of KH_2PO_4 using "slow titration" procedure

Molarity of KH_2PO_4	M.e. of H_2PO_4	M.e. of Fe	M.e. of NaOH theoretically required[†]	M.e. of OH actually required[‡]	Deviation from theoretical, in M.e.
0	0	3.0	3.0	3.0	0
.005	.5	3.0	2.5	2.56	.06
.01	1.0	3.0	2.0	2.12	.12
.03	3.0	3.0	2.0	2.0	0

[†]Based on $H_2PO_4^-$ replacing 1 chemically equivalent OH group.
[‡]The amount of NaOH required to neutralize the HCl contained in the $FeCl_3$ solution has been deducted in each case.

The results show that it is the $H_2PO_4^-$ that reacts with iron and that $Fe(OH)_2H_2PO_4$ must be the compound formed since the equivalence point was reached at pH values where only $H_2PO_4^-$ were present, and in all cases only the theoretical amount of OH re-

quired to form this compound was needed to reach the equivalence point in the reaction. Determination of the amounts of H_2PO_4, which were combined in the iron-phosphate complex in a similarly conducted experiment, were shown to be .44 M.e. phosphorus in the case where .5 M.e. phosphorus was added, and .88 M.e. phosphorus where 1 M.e. was added. Thus the .06 M.e. excess OH required for reaching the equivalence point when .5 M.e. phosphorus was added, and the .12 M.e. of excess OH required for reaching the equivalence point when 1 M.e. phosphorus was added, are exactly the theoretical quantities required to reach the equivalence point. Only one coordinating position of the hexahydrated iron ion was occupied by the $H_2PO_4^-$ even when sufficient quantity of $H_2PO_4^-$ were added to theoretically occupy three of these coordinating positions, and in this case exactly the theoretical amount of OH was needed to complete the reaction and to occupy the two coordinating positions remaining after the first position was completely occupied by $H_2PO_4^-$.

Determination of P/Fe ratio

To substantiate the data obtained from the potentiometric titrations regarding the stoichiometric composition of the iron-phosphate complex and to show that the fixation is a chemical reaction, studies were made to determine the amounts of H_2PO_4 combined in the iron-phosphate complex under varying conditions.

Method used

The experimental procedure was the same as that employed for

the "slow titrations" except that enough sodium chloride solution
was added to each beaker to make a final salt concentration of 1
per cent. The purpose of the salt solution was to prevent ad-
sorption of $H_2PO_4^-$ by the iron-phosphate complex. The total volume
of solution in each beaker was adjusted with distilled water so as
to make the molar concentration of KH_2PO_4 the same in all cases.
After the solutions had been boiled, cooled, and the pH determined,
they were heated again to near boiling and filtered while hot. The
precipitates were washed five times with a hot 1 per cent sodium
chloride solution to remove all phosphate that was not chemically
combined with the iron. The phosphorus that remained after this
treatment was termed "fixed phosphorus" or "chemically combined
phosphorus". These terms shall refer to this definition throughout
this report. In some cases the phosphorus determinations, according
the the method given by Sherman (52), were made on the precipitates
to determine the amount of fixed phosphorus. In other cases the
determination was made on the filtrate, and the amount of fixed
phosphorus was calculated by difference. This was permissible,
since test samples were run using both methods and it was found
that the two procedures gave the same results.

The results are shown in figure 3 and table 3. It will be
noticed that the reaction did not go to completion[4] until 2 M.e.
of phosphorus had been added for each 3 M.e. of iron. Below that

[4]It is understood that technically no reaction ever reaches 100
per cent completion. However, the experimental methods used
were not sensitive enough to detect such small amounts and,
therefore, would indicate that the reaction reached virtual
completion.

FIGURE 3

INFLUENCE OF PHOSPHATE CONCENTRATION ON THE AMOUNT OF
PHOSPHORUS FIXED BY IRON
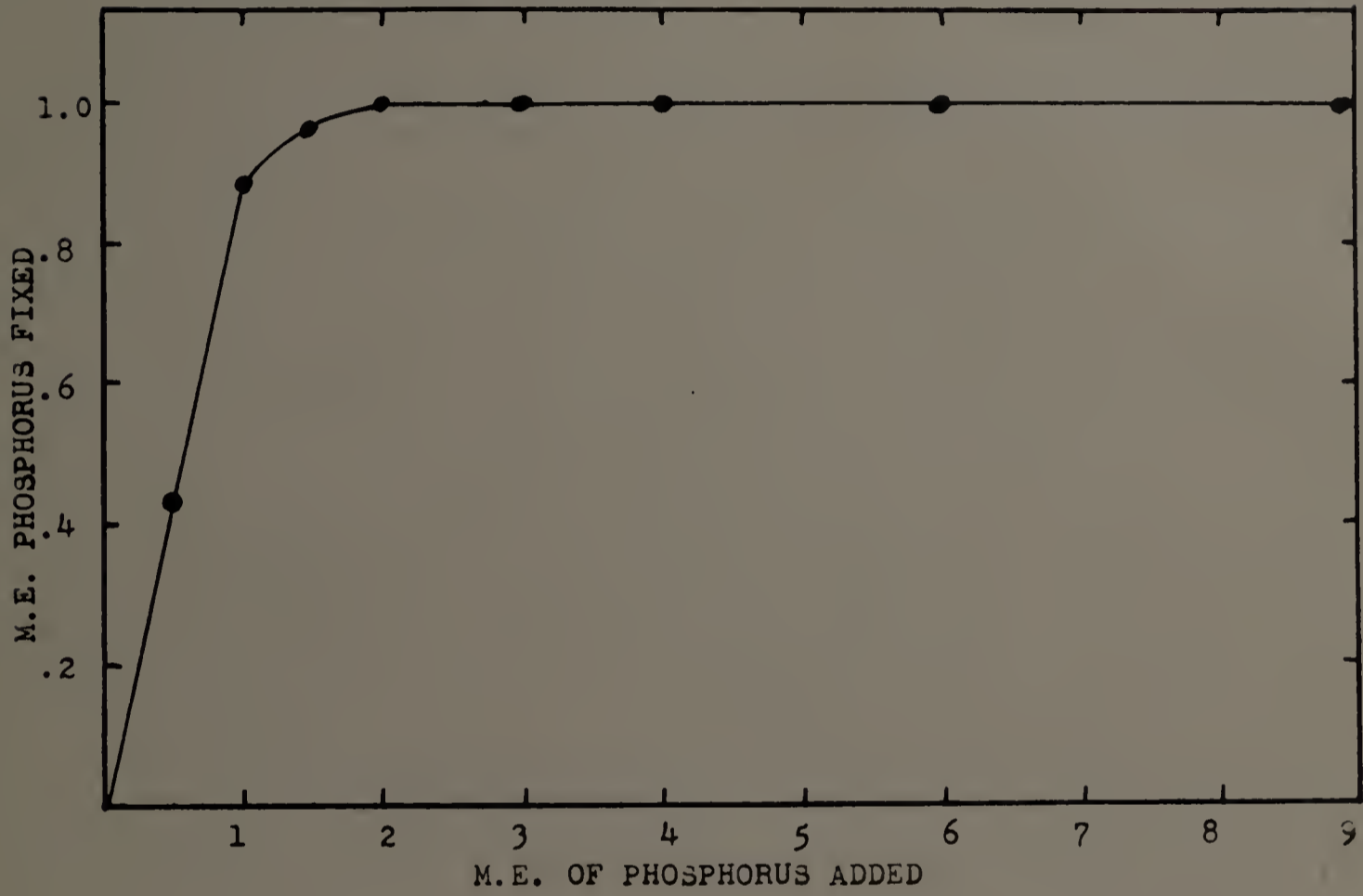
amount the concentration of $H_2PO_4^-$ was not high enough to cause the reaction to go to completion. The results clearly indicate that the P/Fe ratio of the compound formed is unity and that it does not exceed that value even though 9 M.e. of phosphorus are added for each 3 M.e. of iron. They also indicate a chemical reaction rather than a simple adsorption process. The maximum phosphorus fixation occurred over the pH range 2.5 to 3.0.

TABLE 3

Determination of the amounts of H_2PO_4 combined in the iron-phosphate complex under varying concentrations of phosphorus.

M.e. of phosphorus added	M.e. of iron	M.e. of phosphorus chemically combined in the complex
.5	3.0	.448
1.0	3.0	.880
1.5	3.0	.956
2.0	3.0	.995
3.0	3.0	.997
4.0	3.0	.997
6.0	3.0	1.007
9.0	3.0	.981

REPLACEMENT OF FIXED PHOSPHORUS BY VARIOUS ANIONS

Dean and Rubbins (15), Scarseth (49), and Sieling (53) have stated that the mechanism of phosphate fixation is one of anionic exchange, and that the phosphate is held in the complex in such a way as to be replaceable by other anions that will coordinate more strongly with iron. It has been shown in this experiment that iron phosphate fixation is the result of a chemical reaction between $Fe^{\bullet\bullet\bullet}$ and $H_2PO_4^-$ and that the $H_2PO_4^-$ replaces a chemically equivalent OH^-, which is evidence that the $H_2PO_4^-$ is eligible for anion exchange. Several investigators (59,28,49,36) have reported that organic matter increases phosphate availability. It is the author's belief that the increased availability of phosphorus in the presence of organic matter, which was noted by the various investigators, was due to organic acids formed as decomposition products of the organic matter. The organic anions would coordinate with iron to form a complex more stable than the iron-phosphate complex and thus release phosphate to the soil solution, or they would fill the coordinating valences of the iron and thus prevent the formation of the iron-phosphate complex. An experimental procedure was adopted to determine the ability of certain anions to replace fixed phosphate and to determine a lyotropic series of anion exchange for the various anions studied.

Method used

50 ml. (3 M.e.) of 0.02 N $FeCl_3$ were pipetted into 250 ml. beakers, 20 ml. (1 M.e.) of 0.05 N KH_2PO_4 were added and 10 ml. of 10 per cent sodium chloride solution. The calculated amount of

the organic acid or organic salt solution, the pH of which had
been adjusted to 3.4 with NaOH or HCl, was then added. Enough
distilled water was added to adjust the final volume to 100 ml. in
each case. The solutions were heated to boiling before adding
15.8 ml. of 0.20 N NaOH to each beaker. The 15.8 ml. of NaOH
being the theoretical amount required to reach the equivalence
point under the conditions of the experiment, this amount having
been determined in the preceding section of this investigation.
The solutions were then placed on a hot plate and kept at a slow
boil for 30 minutes. They were allowed to cool to room temperature
before determining the pH with a Beckman pH meter using a glass
electrode. The solutions were heated to almost boiling and filtered
while hot. The precipitates were washed five times with a hot
1 per cent sodium chloride wash solution. The phosphorus in the
combined filtrate and washings was determined according to the method
of Sherman (52). It has been established that .88 M.e. of phosphorus
is fixed under these experimental conditions in the absence of the
organic anion, therefore, any phosphorus in the filtrate in excess
of .12 M.e. would be the amount of phosphorus the added anion
prevented from being fixed.

This procedure was followed for the following anions which
are listed in the order of their replacing ability: citrate,
isoascorbic acid, gallic acid, pyrocatechin, tartrate, mucic acid,
fluoride, gluconic acid, silicate and glycine. Glutamic acid,
malic acid, and p hydroxy benzoic acid exhibited little or no
replacing ability. The results are shown in figure 4.

FIGURE 4

THE ABILITY OF VARIOUS ANIONS TO REPLACE FIXED PHOSPHORUS
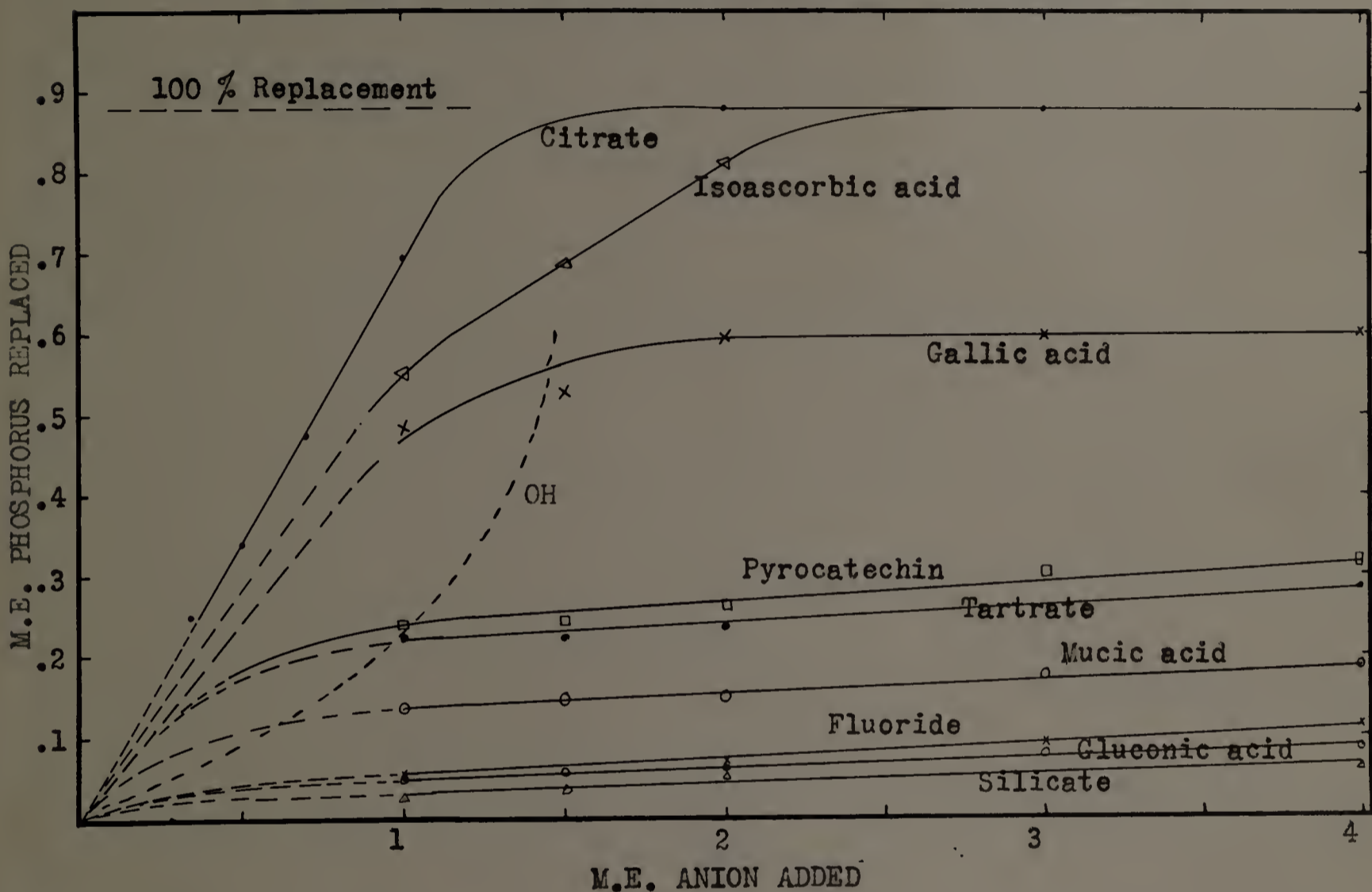
The results show that several of the anions studied have the ability to prevent the fixation of phosphorus by iron and that the amount of phosphorus replaced varied with the nature and concentration of the anion. Their relative replacing abilities are related to their ability to coordinate with iron and thus on the nature of the complex formed. If the added anion has greater affinity for iron than the $H_2PO_4^-$, the $H_2PO_4^-$ will be replaced in the complex by the other anion and consequently will not be fixed by iron. It is concluded that organic acids have the ability to prevent iron phosphate fixation and it is believed that organic acids other than the ones studied possess the same chemical ability. The results also show that the maintenance of the organic matter content of acid soils is an important factor in phosphorus availability.

Ability of humus and lignin to prevent phosphorus fixation

Scarseth (49) states that humates can enter into ionic exchange and it may be possible that they have the ability to replace the phosphate ion. Studies were made to determine the ability of humus and lignin to prevent phosphorus fixation. The samples of acid humus that were used for this study had been obtained from electrodialysis of peat. The procedure used was the same as that employed for the replacements with the pure solutions except that the varying amounts of peat were dissolved in the 15.8 ml. of NaOH, the peat and NaOH then being added together. This same procedure was used to determine the replacing power of lignin. The results are given in figure 5. They show that humus and lignin have the ability to prevent phosphate fixation even though the magnitude

FIGURE 5

THE ABILITY OF HUMUS AND LIGNIN TO PREVENT PHOSPHORUS FIXATION
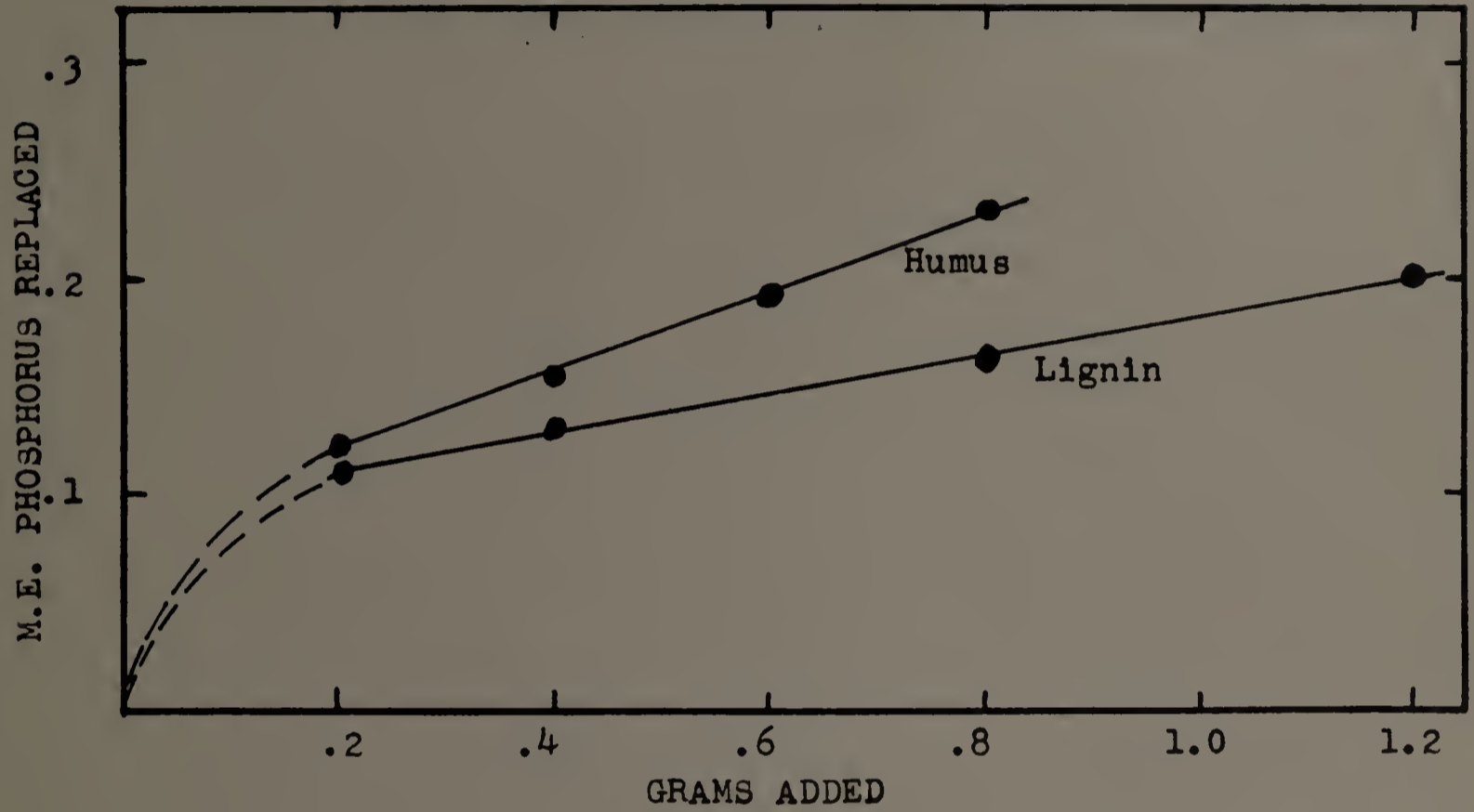
of replacement obtained with the size samples used was not as
great as that obtained with some of the other anions. Since the
molecular composition and equivalence, with respect to complex
formation, is not known for humus and lignin, it is impossible to
determine their order in the lyotropic series.

HYDRATED FERRIC OXIDES AND PHOSPHORUS FIXATION

Preceding results in this investigation have shown that iron
is active in phosphorus fixation and that various anions have the
ability to prevent the formation of the iron-phosphate complex.
It was decided to apply this information to hydrated iron compounds
that are found in the soil, for the purpose of relating the problem
more to soil conditions. Ford (20), Weiser (59), and others (25,
26,14) have shown that the hydrous oxides of iron fix phosphorus.
It has also been shown by Perkins and King (38) that grinding the
iron compound to reduce the size of the individual particles
increases its phosphorus fixing capacity.

Method used

A sample of limonite in powder form was obtained from the
Ward's Natural Science Establishment, Rochester, New York. The
sample was taken near Cartesville, Georgia (name given as Limonite,
var. Yellow Ocher $2Fe_2O_3.3H_2O$). The limonite was activated by
grinding in a ball mill for 24 days, after which it was phosphated
according to the following method: 150 grams of the ball-milled
limonite were placed in a two liter round bottom flask. Approx-
imately 1 liter of a saturated solution of KH_2PO_4, pH adjusted to

3.4, was added and the contents boiled with constant stirring for approximately 5 hours. The solution was filtered with suction (pH of filtrate was 4.4). The phosphated limonite was replaced in the flask and 1 liter of a 1 per cent sodium chloride solution was added, the contents were boiled and stirred for 15 minutes and filtered again. This washing with sodium chloride was repeated three times. The washed phosphated limonite was placed in a casserole and dried at 42 C. for two days. The dried material was ground in a mortar and pestle before storing in an air tight reagent bottle.

The amount of phosphorus fixed by the activated limonite was determined by boiling a 1 gram sample of the phosphated limonite with 50 ml. of 0.20 N NaOH for 30 minutes. The solutions were filtered and the precipitate washed 5 times with hot 0.20 N NaOH. The phosphorus determinations were made on the combined filtrate and washings. It was found that under these experimental conditions a 1 gram sample of phosphated limonite contained 1.28 M.e. of phosphorus.

A sample of goethite ($Fe_2O_3.H_2O$), in rock form, was obtained at the same time as the limonite from the Ward's Natural Science Establishment. The goethite was activated by first grinding in a Braun Pulverizer and then passing the ground material through a Braun "Chipmunk Crusher" several times. The powdered goethite was ball-milled for 15 days and then phosphated and washed in the same manner as was the limonite described above. It was found that the phosphated goethite contained 1.09 M.e. of phosphorus per gram

sample.

ABILITY OF VARIOUS ANIONS TO REPLACE FIXED PHOSPHATE FROM PHOSPHATED GOETHITE AND LIMONITE

It has been shown that the hydrated ferric oxides, goethite
and limonite, have the ability to fix phosphorus. An experimental
procedure was employed to determine the ability of certain anions
to replace fixed phosphorus from the phosphated goethite and
limonite.

Method used

.81 gram samples of phosphated goethite, containing .88 M.e.
of phosphorus, were placed in 250 ml. beakers. The desired amounts
of the organic acid solution (pH adjusted to 3.4) were added,
followed by 10 ml. of 10 per cent sodium chloride solution and
enough distilled water to make the final volume 100 ml. in all
cases. The solutions were kept at a slow boil on a hot plate for
30 minutes, after which they were allowed to cool to room temper-
ature before determining the pH. The solutions were heated again
and filtered while hot. The precipitates were washed 5 times with
a hot 1 per cent sodium chloride solution. Phosphorus determinations
were made on the combined filtrate and washings using the method
according to Sherman (52).

In order to determine the amount of "free phosphorus" contained
in .81 gram of the phosphated goethite, blank samples were run as
above in the absence of the added anion. It was found that each
.81 gram sample contained .14 M.e. of "free phosphorus". The
"free phosphorus" is a result of the solubility product of the
iron-phosphate complex, and it is also due to the incomplete

removal of all the adsorbed phosphate by the three washings employed for that purpose. The amount of fixed phosphorus replaced by the various anions would be the amount of phosphorus in the filtrate in excess of .14 M.e..

The results are shown in figure 6. It will be noted that the order of replacement is the same as obtained in the studies with the pure solutions; however, the magnitude of replacement is less in each case. This is to be expected, as Weiser (59) states that the availabilities of fixed phosphates may vary considerably, and Ford (20) found that goethite fixed phosphorus in a more insoluble form than did the relative soluble iron compounds of the soil.

In the studies with limonite .69 gram samples of phosphated limonite, containing .88 M.e. of phosphorus, were used. The amount of "free phosphorus" contained in .69 gram of phosphated limonite was found to be .14 M.e.. The results given in figure 7 show that the replacement is in the same order and magnitude as that obtained with goethite, which is evidence that the mechanism of fixation is the same with both hydrated oxides.

INFLUENCE OF TIME OF REACTION ON AMOUNT OF PHOSPHORUS REPLACED

Since the phosphate is so strongly held by the hydrous oxides, it was decided to determine if an increase in the time of boiling would result in the replacement of more phosphorus from the phosphated goethite by the anions. The solutions were prepared as previously in the goethite studies except that the solutions were placed in 300 ml. Erlenmeyer flasks instead of the 250 ml. beakers. These flasks were fitted with rubber

FIGURE 6

THE ABILITY OF CITRATE, FLUORIDE, AND GALLIC ACID
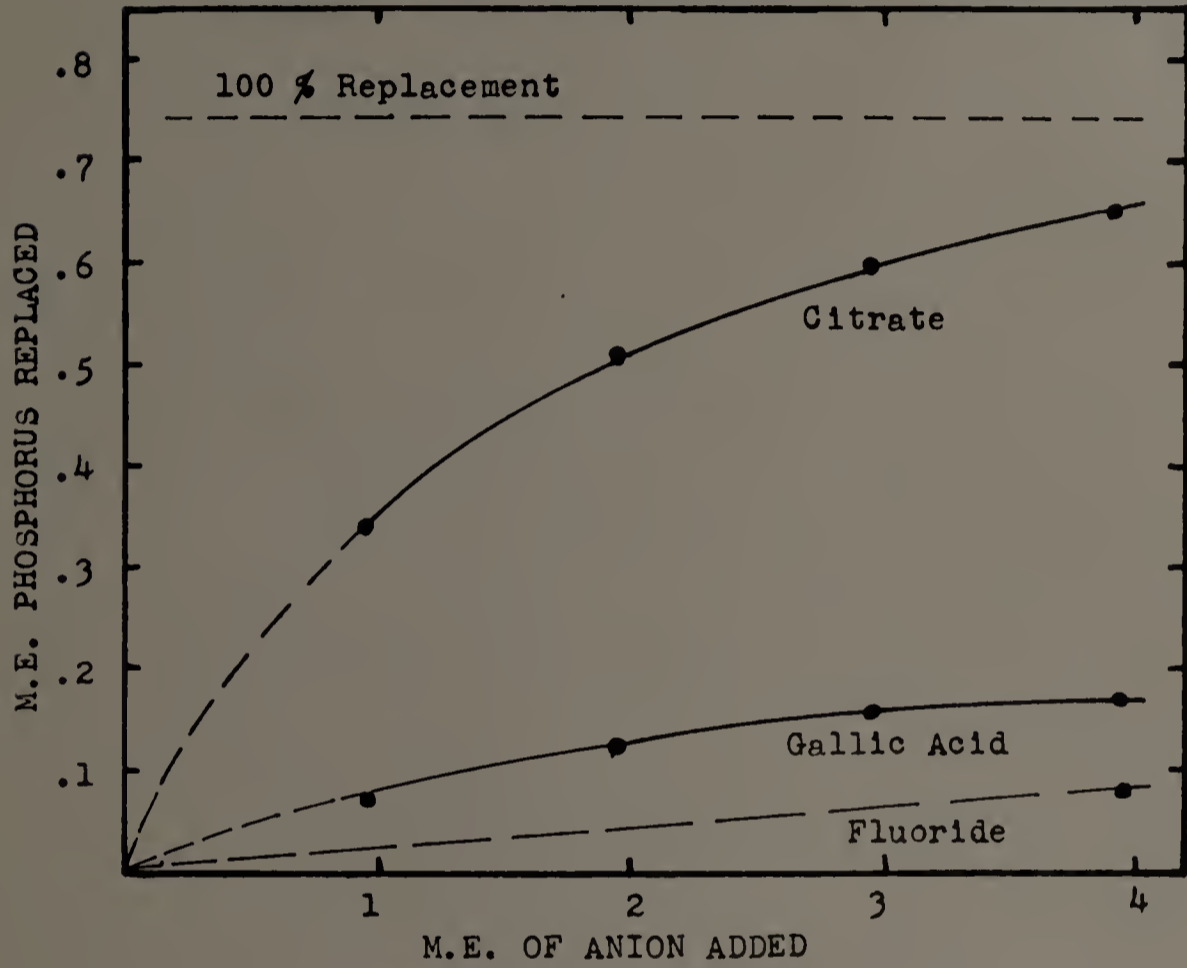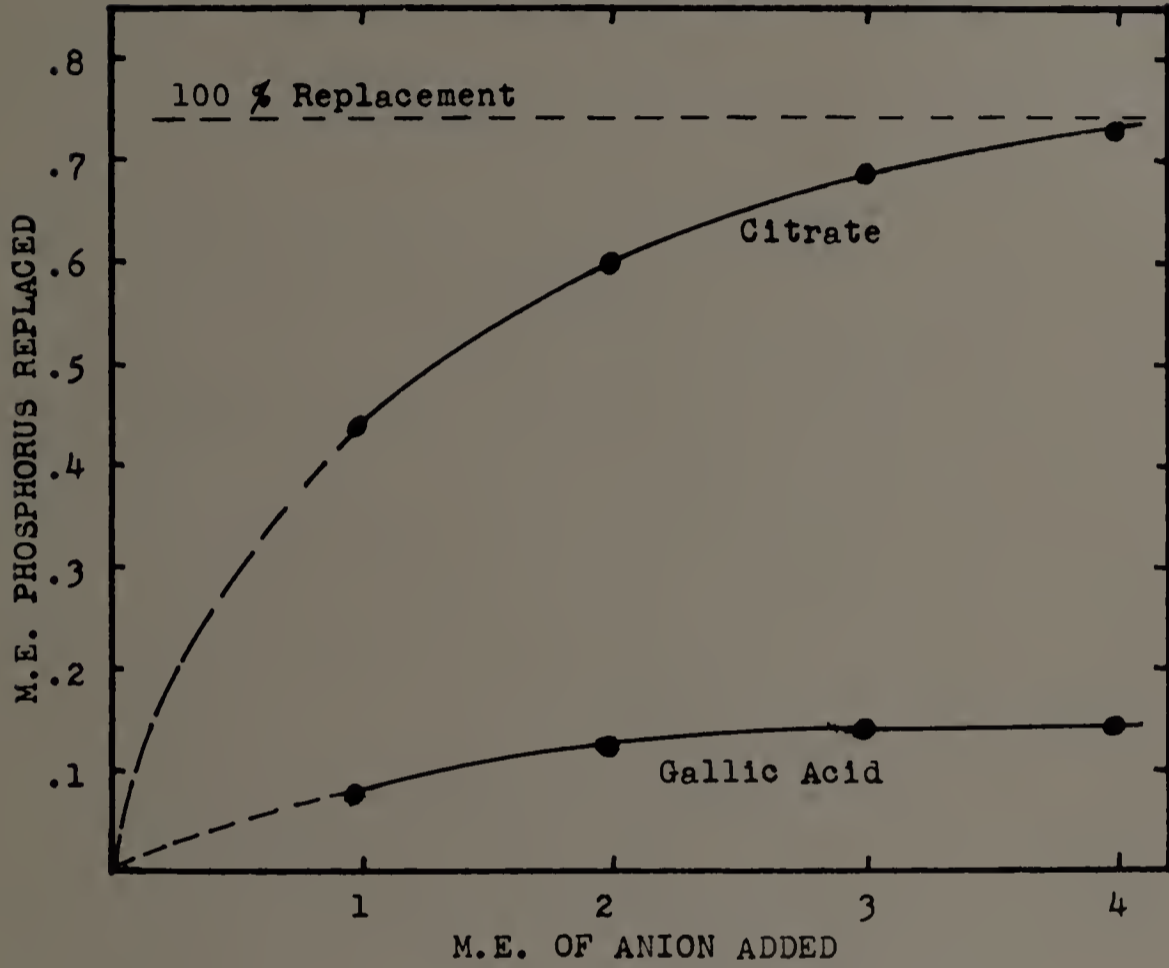TO REPLACE FIXED PHOSPHORUS FROM PHOSPHATE GOETHITE

FIGURE 7

THE ABILITY OF CITRATE AND GALLIC ACID TO REPLACE
FIXED PHOSPHORUS FROM PHOSPHATED LIMONITE

stoppers and attached to water cooled condensers for the purpose
of keeping the total volume constant throughout the boiling periods.
The amount of phosphorus replaced by tartrate was found to in-
crease with the length of time of boiling as shown in figure 8.
This indicates that in the replacement of phosphorus from the
hydrous oxides by the anions the reactions did not go to completion.
Since the organic acids are in contact with the iron-phosphate
complex for long periods of time in the soil, it would result in a
slow continual release of phosphorus to the soil solution.

Since solutions were used for the reactions to determine the
lyotropic series for anion replacement (see p. 43), the conditions
were more favorable for rapid reaction than in the above where the
hydrous oxides were used. According to Ford (20), phosphate is
fixed in a more insoluble form by hydrous oxides than by iron from
solution. Therefore, it is believed that the thirty minute boiling
time was sufficient to allow those reactions where solutions were
used to reach completion.

THE EFFECT OF pH ON PHOSPHORUS FIXATION

In the "slow titrations" the pH of the equilibrium solutions
and the amount of phosphorus combined in the basic ferric phosphate
were determined. The graph in figure 9 shows the amount of
phosphorus fixed at the various pH values when 3 M.e. of iron were
titrated with sodium hydroxide in the presence of 1 M.e. of
phosphorus. It will be noted that the maximum fixation of
phosphorus occurs in the acid region of pH 2.5 to 3.0; however,
iron is still very active in phosphorus fixation over the pH

FIGURE 8

INFLUENCE OF TIME OF REACTION ON AMOUNT OF PHOSPHORUS
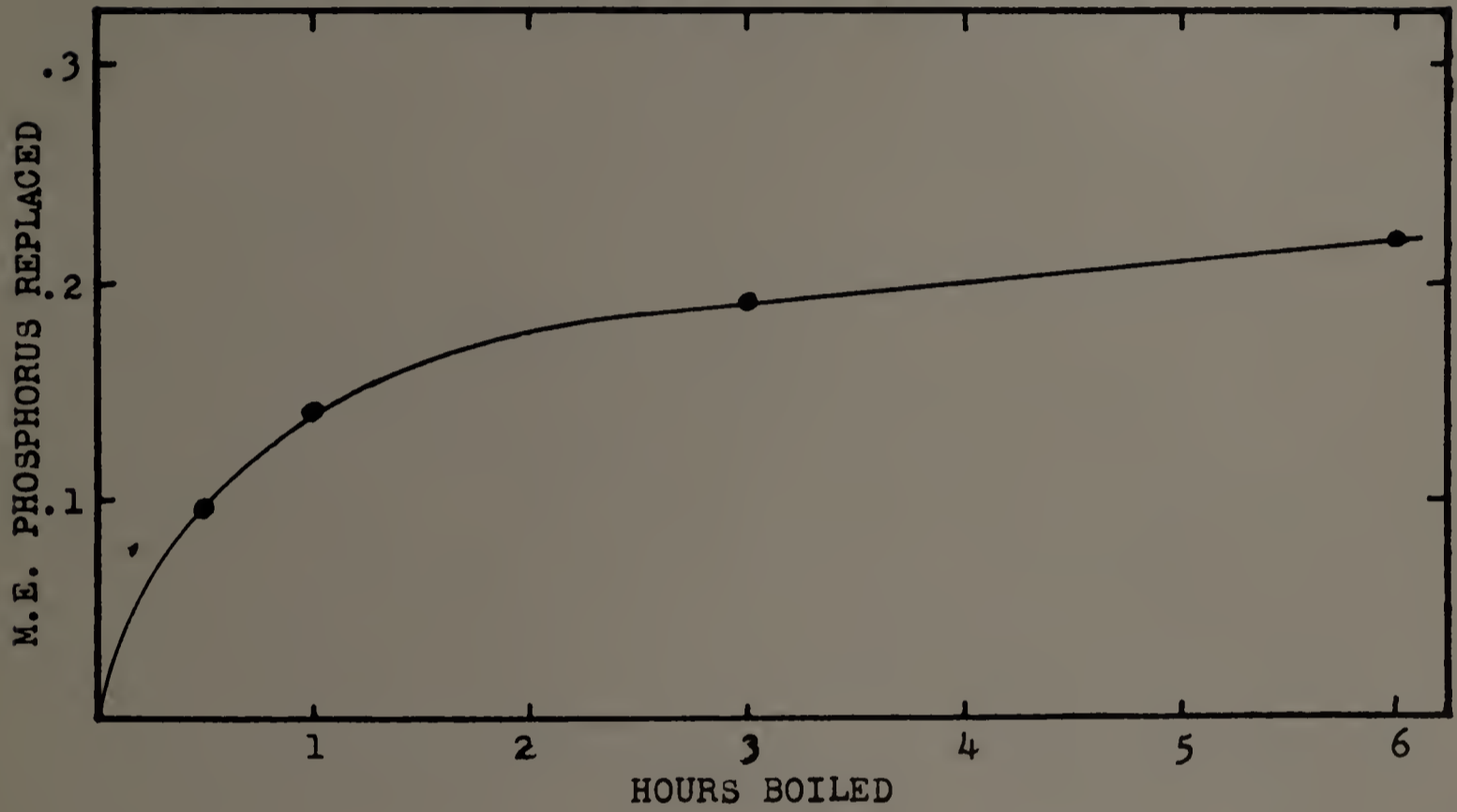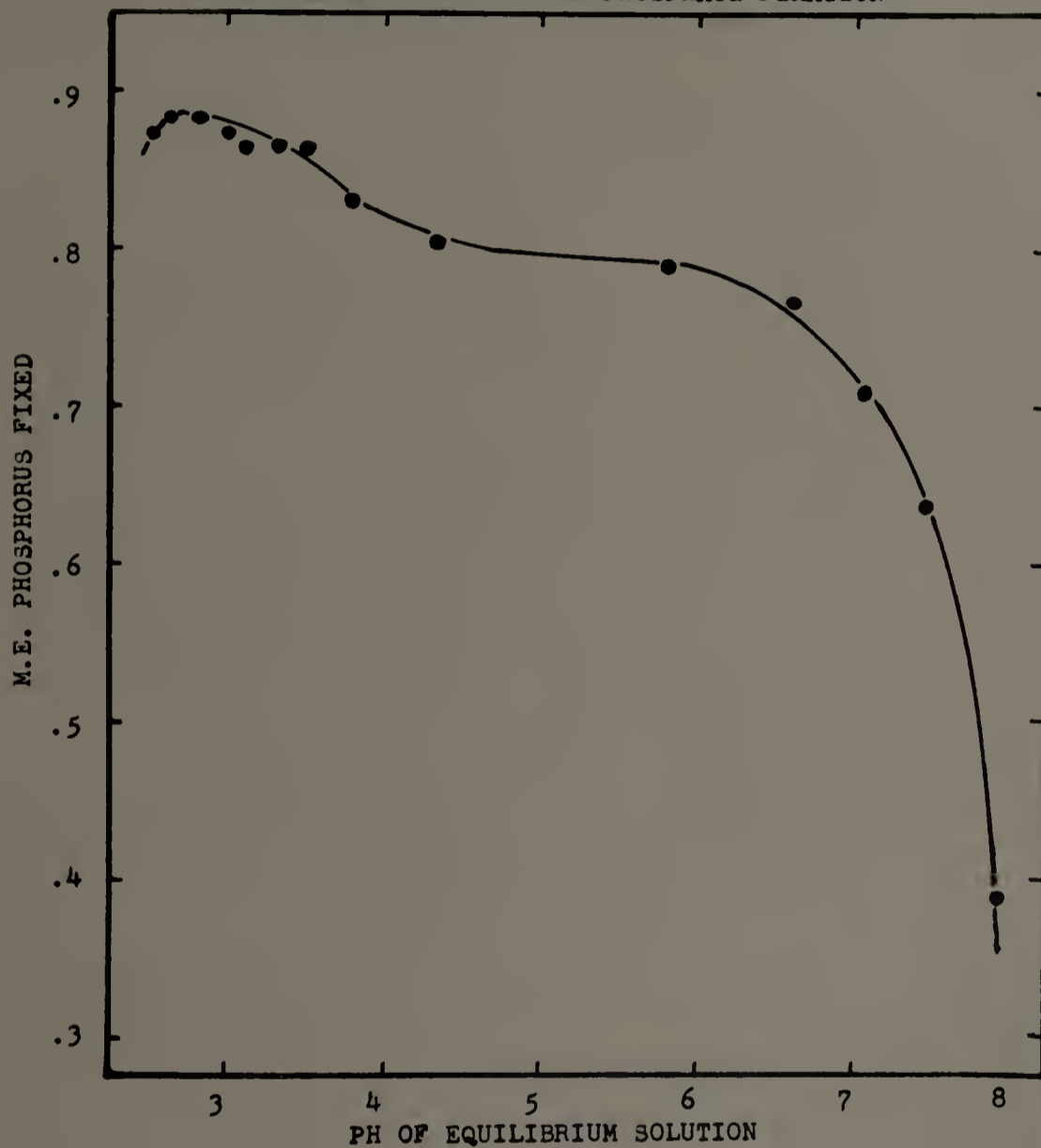REPLACED BY TARTRATE FROM PHOSPHATED GOETHITE

FIGURE 9

INFLUENCE OF PH ON IRON PHOSPHATE FIXATION

range of 3.5 to 6.5. Approximately 90 per cent of the phosphorus is still fixed at pH 6.5. Above pH 6.5 the replacement of $H_2PO_4^-$ by OH^- is very rapid for the following reasons: (a) the stability of the $Fe(OH)_2H_2PO_4$ compound is decreasing, (b) the $H_2PO_4^-$ are dissociating to form $HPO_4^=$, and (c) the concentration of the OH^- is increasing which shifts the equilibrium toward the formation of ferric hydroxide. These three factors explain why iron is not as active in phosphorus fixation above pH 6.5 as it is below that value. At pH 8 only 56 per cent of the fixed phosphorus has been replaced by the OH^-; however, the rate of replacement is such that all the phosphorus would be removed at approximately pH 8.5.

These results indicate that at pH values below 7 most of the organic anions are more active in removing fixed phosphorus than the OH^-; however, at values above pH 8 the OH^- is more active than the organic anions in the replacement of fixed phosphorus (see figure 4).

The results show the inadvisability of depending entirely upon the addition of lime to acid soils for the purpose of making fixed phosphorus available for plant use. The addition of enough lime to release 50 per cent of the phosphorus chemically combined with iron would necessitate raising the pH of the soil to between pH 7 and 8. At pH values as high as 7 and 8 calcium becomes active in phosphorus fixation; therefore, liming cannot be looked upon as the method of preventing phosphorus fixation in acid soils.

DISCUSSION

It has been established by the work of other investigators
that the greatest phosphorus fixation occurs in those soils and
soil horizons having the highest iron content. By this statement
it is not to be inferred that iron is the only phosphorus fixing
agency in the soil; however, it is of major importance in acid
soils. The results obtained in this research show that the
mechanism of iron phosphate fixation is a double decomposition
reaction, there being an equivalent exchange between the OH^- and
the $H_2PO_4^-$ resulting in the formation of the compound $Fe(OH)_2H_2PO_4$.
It is the $H_2PO_4^-$ that reacts with iron since the equivalence point
in the potentiometric titrations was reached at pH values where
virtually only $H_2PO_4^-$ were present, and in all cases only the
theoretical amount of OH required to form this compound was
needed to reach the equivalence point in the reactions.

The equilibrium reaction can be shown as:

$$\overset{OH}{\underset{H_2PO_4}{Fe-OH}} \quad + \quad OH^- \quad \rightleftharpoons \quad \overset{OH}{\underset{OH}{Fe-OH}} \quad + \quad H_2PO_4^-$$
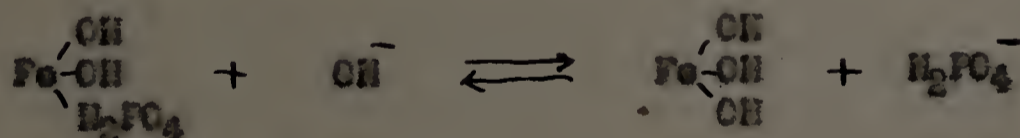
When the concentration of the $H_2PO_4^-$ is increased, the equilibrium
is shifted to the left. Under the conditions of the experiment
it was found that 2 M.e. of H_2PO_4 for each 3 M.e. of iron were
required for 100 per cent[5] formation of the iron-phosphate complex.
When 1 M.e. of phosphorus was added for each 3 M.e. of iron, the

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5 See footnote 4, page 40.

reaction resulted in the formation of only 68 per cent of the iron-phosphate complex. On the addition of OH^- the equilibrium would be shifted to the right. At high pH values, that is in the presence of high concentrations of OH^-, the iron-phosphate complex would not be formed; therefore, iron would not be active in phosphorus fixation. It can be concluded that the addition of lime to an acid soil will tend to increase phosphorus availability.

It was found, on analysis of the amount of H_2PO_4 contained in the iron-phosphate complex, that the P/Fe ratio of the compound formed is unity. The ratio does not exceed that value even though amounts of $H_2PO_4^-$ are present in excess of the amount required for the formation of a compound having a P/Fe ratio greater than one. It is believed that the reason the $H_2PO_4^-$ occupies only one coordinating position of the iron may be due to steric hinderance. Due to the large size of the $H_2PO_4^-$ and the fact that the iron is surrounded by its water of hydration it is thought the spatial arrangement is such that it prevents the attachment of more than one $H_2PO_4^-$. Also, it is possible that the reason an iron-phosphate compound having a P/Fe ratio of 2 or more is not formed is because under the conditions of this experiment $Fe(OH)_2H_2PO_4$ and $Fe(OH)_3$ are more stable than $FeOH(H_2PO_4)_2$. At pH 7 the $Fe(OH)_3$ is more stable than $Fe(OH)_2H_2PO_4$, while at pH 3 the latter is more stable than the former. The addition of OH^- to the di-hydroxy ferric phosphate converts it to ferric hydroxide.

It is known that ferric iron forms complexes with tartaric acid, citric acid, salicylic acid, etc.. In fact, Kolthoff and

Sandell (29) state that most organic acids containing hydroxyl groups form complexes with iron and prevent its precipitation as a hydroxide. It is believed that organic acids and other anions complex with iron by forming five and six membered chelate compounds. Chelate compounds are ring compounds with coordinate valence in the ring. In this type of coordinate valence two electrons are shared as in the covalence bond; however, both electrons are furnished by the same atom. Ephraim (18 p.339) gives the following conditions as being essential for the formation of rings: (a) The radical must contain an acidic group such as OH- or NH-, which can take up one of the primary valencies of the metal in salt formation. (b) Groups must be present which can become co-ordinated with the centeral atom through their lone pair of electrons, e.g. through O as in water, through N as in ammonia, etc. (c) Further, these last radicals must be separated from the replaceable H atom by chains of suitable length for the production of five- or six-membered rings. He also states that it is mostly organic radicals which form these internally complex compounds as they comprise chains of sufficient length to give five or six membered rings.

On the decomposition of organic matter organic acids are formed that complex with iron. Since the $H_2PO_4^-$ is held in the iron-phosphate complex in an exchangeable form, it may be replaced by other anions that possess greater activity for complex formation with iron. It has been shown that several of the organic anions are able to replace phosphorus that is chemically combined with iron. It is believed that the presence of decaying

organic matter in the soil results in the release of fixed phos-
phorus to the soil solution. The fact that organic acids replace
fixed phosphate gives further importance to the maintenance of
soil organic matter in acid soils and also relates phosphorus
availability to soil organic matter.

The reaction of organic acids with iron to form soluble
complexes explains the downward movement of iron in podzolic soils.
This shows a movement of iron in the ferric state; iron also moves
as a ferrous ion, a state of reduction which may be brought about
by organic acids.

It is concluded from this investigation that hydrated iron
compounds, as well as the relative soluble iron compounds of the
soil, have the ability to fix phosphorus in an unavailable form.
Hydration can be interpreted as a degree of solution, thus the
hydrated iron oxides are able to react with soil phosphorus.
This would explain why non-hydrated hematite did not fix phosphorus
as was reported by Ford (20), Weiser (59), and Doughty (17). The
fact that the anions replaced fixed phosphorus from phosphated
goethite and limonite in the same order and magnitude shows that
the same fixation forces are active in both compounds; that is,
there is a quantitative reaction that takes place between iron
and phosphorus. This would indicate that phosphorus fixation by
these compounds is not a simple adsorption system but that there
is a stoichiometric relationship involved.

SUMMARY AND CONCLUSIONS

1. Potentiometric titrations and the reaction of iron in the presence of varying concentrations of KH_2PO_4 were employed as experimental methods to determine the mechanism of phosphorus fixation by iron.

2. The mechanism of iron phosphate fixation is a double decomposition reaction, the compound $Fe(OH)_2H_2PO_4$ being formed.

3. The P/Fe ratio of the iron-phosphate complex is unity.

4. The following reaction exists in equilibrium:

$$
\begin{array}{ccc}
\text{OH} & & \text{OH} \\
\text{Fe-OH} & + \quad \text{OH}^- \rightleftharpoons \quad \text{Fe-OH} & + \quad H_2PO_4^- \\
\text{H}_2\text{PO}_4 & & \text{OH}
\end{array}
$$

2 M.e. of H_2PO_4 for each 3 M.e. of iron must be present for 100 per cent formation of the iron-phosphate complex.

5. The maximum fixation of phosphorus by iron occurs in the pH range 2.5 to 3.0. The isoelectric point of ferric hydroxide occurs at approximately pH 7.

6. The $H_2PO_4^-$ is held by iron in an exchangeable form, being replaced by anions that are more active in complex formation with iron.

7. The following lyotropic series was obtained for the ability of anions to replace fixed phosphate: citrate > isoascorbic acid > gallic acid > pyrocatechin > tartrate > mucic acid > fluoride > gluconic acid > silicate > glycine. Glutamic acid, malic acid, and p hydroxy benzoic acid were found to possess little or no

replacing ability. Below pH 7 most of the organic anions
have greater replacing value than the OH$^-$; however, above
pH 8 the OH$^-$ possesses greater replacing ability than the
other anions studied.

8. Humus and lignin possess the ability to prevent phosphorus
fixation.

9. The amount of phosphorus replaced from the phosphated hydrous
oxides by the anions increases with time of reaction. It
is believed that this results in a slow continual release of
phosphorus to the soil solution.

10. It is believed that the replacement of fixed phosphorus by
organic acids explains the increased solubility of phosphorus
in the presence of organic matter, as noted by other in-
vestigators.

11. The maintenance of organic matter in acid soils is given as
a practical means of increasing phosphorus availability.

12. The hydrated iron compounds, goethite and limonite, are active
in phosphorus fixation.

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