BEHAVIOR OF CLAY FRACTIONS IN THE "FIXATION" OF PHOSPHORUS ON THE EFFECT OF THE BRAY EXTRACTING SOLUTION

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PREFACE

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CHAPTER I

INTRODUCTION

Phosphorus fixation in soil is of considerable agronomic importance because it affects the utilization of soluble phosphate fertilizers by plants. Plant growth requires, on the average, about one-fourth to two-thirds as much phosphate as nitrogen or potassium.

Under cultivation, however, the constant mixing of the organic with inorganic colloidal matter with the soluble phosphate compounds increases the fixation rate (decrease in solubility) and the consequent deficiency of phosphate may be more important than nitrogen and potassium. The phosphate ion is rapidly converted to insoluble compounds by the organic and inorganic soil colloids. This factor is of lesser importance for nitrogen and potassium.

The determination of the readily available phosphate in soil has been investigated by many soil chemists. It is well known that soluble phosphate in fertilizers, when added to the soil becomes relatively insoluble and only very small quantities are lost in drainage water. Soils may show a deficiency in soluble phosphorus although the total phosphorus fertilizer applied each year is in amounts much greater than the crop can remove that year. The residual effect on the following crop will depend upon the degree of fixation of phosphorus by the soil.

The degree to which applied phosphates are "fixed" by the soil is well known as a result of both laboratory and field studies. There are many factors which effect the fixation of phosphorus such as calcium, iron, aluminum, kind and amount of phosphorus applied, soil texture and structure, time, temperature, concentration of solution, ratio of the solvent to soil in the soil test, the reaction of soil, the organic matter content, the silica-sesquioxide ratio and cation exchange capacity.

It has been shown in many cases that less than one-tenth of the phosphate applied in fertilizer is utilized by crop plants. Many research workers have shown the large capacity of soils to absorb soluble phosphates. Phosphates, even the less soluble ones, as well as more soluble ones, nearly always give profitable results, but if fixation could be reduced to some degree, greater profit would be obtained and a valuable natural resource would be conserved.

The clay fraction of the soil has long been known to be one of the most active portions of the soil as far as phosphate fixation is concerned. Toth (110) indicated that colloidal-sized particles of clay minerals are never isoelectric, and must be considered as strongly electronegative colloids. He also considered the soil colloid clay fraction as almost wholly crystalline, or as a central crystalline nuclues surrounded by amorphous precipitates of indefinite composition. There are strong reasons for believing that the importance of the crystalline fraction may in some instances be less important than the precipitates of amorphous materials with respect to such properties as adsorption, fixation, and release of cations.

Earlier workers (28, 30, 34, 36, 68, 86, 101) believed that phosphate was precipitated in acid soil by soluble iron and aluminum but since only small amounts of iron and aluminum are soluble within the reaction range of most soils it was impossible to account for large amounts of phosphate fixed in this manner. The chemical precipitation of phosphate was considered as the primary cause of phosphate fixation although the mechanism was not known.

Phosphate fixation has been defined in different ways. Davis (29) states that phosphate fixation is taken to imply the following phenomenon: "When a solution of orthophosphate is applied to soil, there is a decrease in concentration of phosphate in the solution". Midgley (84) defined phosphate fixation as the conversion of the solution form and further states that "while this fixed phosphate is considered to be insoluble in water, it may or may not be available to plants". Wild (116) states that "phosphate fixation is used to describe any change that phosphate undergoes in contact with the soil, which reduces the amount that the plant roots can absorb." Tisdale and Nelson (108) defined fixation of phosphorus as "a reduction in the solubility of added phosphorus." Kardos (67) defined phosphate fixation as "the process whereby readily soluble phosphates are changed to less soluble forms by reaction with inorganic or organic components in the soil with the result that the phosphates due to their restricted mobility in the soil suffer a decrease in availability to plants." Dean (31) defined fixation of phosphate as the soil phosphorus which has become attached to the solid phase of the soil.

According to these definitions by several investigators, the mechanism of phosphate fixation is due to a variety of factors, however, the main point made is the decrease in phosphate availability or solubility to plants is dependent on some chemical or physical mechanism.

Heck (52) suggested that it was not necessary for iron and aluminum to be in the soil solution in order for them to fix phosphate. He believed that the reaction between phosphate and iron or aluminum was one of simple addition, in which the phosphate was attracted and held by the insoluble iron and aluminum in clay. Scarseth (101) believed that the alumino-silicate minerals were able to hold phosphate on their colloidal surfaces. Murphy (86) concluded that finely ground kaolinite was able to fix large amounts of phosphate. Stout (106) found that the fixation of phosphate by kaolinite was an ion exchange reaction; the phosphate replaced the OH ions on the surface of the kaolinite crystal.

Black (11) and Toth (109) considered that the fixing powers of the clay fraction was attributed to the reaction of phosphate with iron, aluminum, magnesium, manganese and calcium which are present in the soil as exchangeable cations, and the end product of this reaction is insoluble phosphate. They concluded that the main reactions of phosphate "fixed" by soil were:

1) Replacement of clay structure OH ions or "broken bond" OH ions by PO_4.
2) Replacement of silicate ions by phosphate.

Both of these reactions are doubtful explanations.

3) Precipitation on the colloidal surface as insoluble phosphates of iron and aluminum.

Black (11) suggested that not all of the phosphate fixation is confined to the replacement of hydroxyl groups on the surface of clay particles, but in addition some of the phosphate penetrates between the layers of clay minerals and replaces hydroxyl groups inside the clay particle. Coleman (26) and Russell (98) concluded that it is the free hydrous oxides of iron and aluminum that are responsible for the fixation of phosphate by kaolinite clays.

Low and Black (75) reported that the fixation of phosphate by kaolinite was accounted for by the hypothesis that an equilibrium between phosphate and clay may cause the clay to dissolve in accordance with solubility product principles. De Boer (33) considered that phosphate adsorption is a special case of precipitation in which aluminum or iron remains as the constituent of the original phase but reacts with phosphate by use of residual force on the clay mineral surface. Because adsorption of phosphate in soil must be the same mechanism as that involved in the formation of the discrete phase of aluminum or iron. Kittrick (71) has suggested that adsorption and precipitation are the result of the same type of chemical force.

Hsu (53, 54) suggested that the mechanism of fixation basically follows the solubility product principle, but the total activity of all forms of aluminum and iron including amorphous aluminum hydroxides and iron hydroxides should be concerned in governing the concentration of phosphate in solution. From this point of view he considered that the following factors were responsible for the process of adsorption.

1) In the concentration concept of precipitation, the fixation of phosphate will not take place until aluminum or iron is released from the soil minerals. The rate of reaction will be slow unless the experiment is carried out in a strongly acidic medium or when exchangeable Al ions are present.

On the other hand, amorphous aluminum hydroxides and iron oxide are known to be highly absorptive for phosphate and the reaction is rapid. This component of the soil should be able to react with phosphate when it comes in contact with soluble phosphates.

2) The activity of aluminum in solution is limited by pH and is probably negligible at pH 5 and above, but there is no such limitation imposed on the reactivities of phosphate with aluminum hydroxides and iron hydroxides and this process probably dominates the process of fixation.

3) In the conventional concept of precipitation, the rate of availability of the absorbed phosphate may be high for plant growth. On the other hand, the absorbed phosphate may be very difficultly available when a small amount of phosphate is retained by large amounts of insoluble hydroxides or oxides.

Recently, Reeve and Sumner 1970 (96) studied the effect of aluminum toxicity and phosphate fixation on plant growth and concluded that phosphate fixation is the result of an adsorption reaction rather than a precipitation reaction.

The objective of this investigation was to study the behavior of clay fractions in the "fixation" of phosphate and the ability of the Bray Extracting solution (0.03 n NH_4F and .025 n HCL) and/or water to remove phosphorus from the clay suspensions when KH_2PO_4 was added to fine and coarse clay separates variously interlayered with aluminum hydroxide precipitates.

CHAPTER II

LITERATURE REVIEW

The clay fraction of the soil is the most active portion responsible for phosphate fixation according to numerous investigations. But the exact mechanism by which clay is able to fix phosphate is not known.

Midgley (84) studied phosphate fixation and disagrees with other investigators as to whether phosphate fixation is chemical precipitation or absorption by simple addition, or by anion exchange. He agrees with others on alkaline soils with an excess of divalent cations where phosphate may be fixed by being precipitated as calcium and magnesium phosphate, but there is no agreement as to how phosphate is fixed in acid soils.

Early workers believed that phosphate was precipitated in acid soil by solution iron and aluminum which are insoluble in the reaction range of most soils. It was impossible to account for large amounts of phosphate fixed in this manner. Heck (52) believed the reaction between phosphate and aluminum or iron was one of simple addition in which the phosphate was attracted to soluble iron and aluminum.

A consideration of the nature of the substances involved suggests that the difference between the reaction of phosphate with the clay fraction and precipitation of phosphate by some substance in solution may be ascribed mainly to the crystalline condition of the clay fraction because of the non-expanding habit of some clay fractions, for instance kaolinite. The hydroxyl groups on the clay layers inside the crystals are not readily replaced by phosphate ions until they are exposed by fine grinding.

Black (11) and Toth (109) considered that the "fixing" powers of the clay fraction was attributed to the reaction of phosphate with iron, aluminum, magnesium, manganese, and calcium which are present in the soil as exchangeable cations and the end product of the "fixation" reaction is insoluble phosphate. They concluded that the main reaction of phosphates "fixed" by soil clay was replacement of silicate ions by phosphate and precipitation on the colloidal surface as insoluble phosphates of iron and aluminum. The "fixation" of phosphate by replacement of the hydroxyl groups of kaolinite is dependent upon a number of factors which include the degree of subdivision of the clay, the pH of the solution, the length of time of contact and the concentration of the phosphate solution. Black (12) indicates that the "fixation" by hydroxyl group replacement does not take place to any appreciable extent from a very dilute phosphate solution unless the clay has a large amount of surface accessible to the phosphate in the solution. More concentrated phosphate solutions cause fixation by hydroxyl replacement in kaolinite clays, even though the clays may not have a large amount of surface exposed. A long period of contact with the concentrated solution produces increased "fixation" of phosphate by hydroxyl replacement because of the slow penetration of phosphate between the clay layers and replacement of hydroxyl ions directly exposed to the solution. Fisher (41) and Boyd et al. (13) proposed as a mechanism; physical adsorption by clay while chemical absorption is usually applied to phosphate reactions in the soil, however, the reaction has temperature sensitivity characteristics of chemical reactions.

Chemical precipitation of phosphate refers to the removal of phosphate ions from solution and their chemical bonding to the solid phase of the soil. The phosphate formed may be a monolayer addition to the solid soil phase, but it may also be in the form of discrete particles. The rate of reaction of phosphate with soil minerals increases with increase in temperature according to Haseman et al. (51) and Law and Black (75) which occurs both during the initial rapid reaction and during the subsequent slower reaction, indicating that chemical forces, Glasstone (46), are involved in both reaction rates. According to this theory they suggested that the formation and growth of separate phases of phosphate precipitates of varying composition were dependent on the dominent cations, and the varying reactivity depending on the amount of specific surface formed by the mechanism of chemical-precipitation. Others (51, 53, 54, 116) discribed an original model of decomposition and precipitation "to-fix" phosphate by aluminum and iron in acidic soils by precipitation and adsorption which resulted from the interaction of these two forces. Whether precipitation or adsorption occurs is dependent on the form of aluminum and/or iron present at the moment of reaction in soils, because the effect of pH dependent surface-reactive amorphous aluminum hydroxides actually dominate the process of phosphate fixation rather than the aluminum and iron ions present in the solution.

Hsu (55) found that when a slightly acidic soil was aged, aluminum hydroxide formed as a separate phase which reacted with phosphate. He explained that the mechanism of the fixation from the concentrated phosphate solution near a fertilizer particle was due to the kaolinite clay component, as well as free oxides when a soil is fertilized with superphosphate. Each fertilizer particle acts as a center around which the soluble phosphate reacts with the soil. The soil solution at the immediate surface of the fertilizer particle contains a high concentration of phosphate, but the concentration drops off very rapidly away from the phosphate particle due to "fixation" by the soil.

Kittrick and Jackson (71) have proposed a unified theory of phosphate fixation or a fixing mechanism based on the formation and growth of a separate phase of varying specific surface precipitated by ions from solution or at the surface of mineral particles into three main phosphate fixation mechanisms as follows:

A) Isomorphous substitution, is a mechanism where theoretically there is replacement of P for Si in tetrahedral structural units or PO_4 for OH in octahedral structural units in the sol alumino-silicate mineral. Either P for Si or PO_4 for OH is a mechanism which is neither wholly tenable nor of general applicability where positive surface charges may possibly be neutralized by hydroxyl. These minerals may exist in soil, (Russell (98), associated with edges of layer silicate clay particles and iron and aluminum compounds and the hydroxyl might exchange for phosphate, however, this surface phenomena can best be considered as adsorption.

B) Adsorption of phosphate refers to the process of concentration at surfaces of a solid phase of phosphate ions from solution, in forms that are exchangeable or replaceable. It is known that so-called "adsorption isotherms" are not specific as to a reaction mechanism. The process of chemical precipitation from dilute phosphate solution aged for one year with clay, showed that fresh ferric hydroxide formed as a separate phase and retained most of the phosphate removed from the solution. This process can be called precipitation because a distinctly new phase is formed, it can also be called adsorption because Fe^{+3} is not able to fix phosphate under this condition unless it is first precipitated as a surface reactive ferric hydroxide. Whenever phosphate fixation occurs, it must be due to the attraction between phosphate and aluminum or iron. Precipitation occurs when phosphate removes aluminum or iron completely from the clay mineral and it is reprecipitated as a new phase. Adsorption occurs when phosphate can break only part of the Si-O-Al bonds or Al-OH linkages. Leaving aluminum or iron still in the clay mineral structure. This latter process is then so-called "isomorphous substitution". Russell suggested that adsorption is one of the mechanisms responsible for the fixation of phosphate by soil, but there is little conclusive evidence to substantiate the existance of this reaction, nor has the mechanism of adsorption been clearly defined or described.

In a study of phosphate fixation by soils Hsu (54) and Wild (116) and Haseman (51) explained that there are two stages of reaction which have been recognized.

Reaction 1. Progresses at a rapid rate and reaction is at completion in a matter of hours or even minutes.

Reaction 2. This reaction occurs at a much slower rate, because all phases of phosphate fixation are due to the attraction between phosphate and aluminum or iron, the difference in reaction rate can be attributed only to the difference in the readiness of aluminum or iron available for the reaction. Amorphous aluminum hydroxides and iron oxides are very highly adsorptive for phosphate and the reaction is very rapid, therefore, the initial rapid fixation is probably a surface adsorption due to these compounds.

According to Hsu (54) the concept of adsorption is the mechanism where phosphate is retained in the structural layers of clay particles. Adsorption is defined as a process in which phosphate is chemically held on the surface of amorphous aluminum hydroxides or iron oxides. De Boer (34) defined adsorption as the various forces that hold a molecule or ion at the surface of another phase or it is exactly the same as those forces occurring between bound atoms in molecules or between molecules in compounds. Physical adsorption should not be significant as far as the fixation of phosphate is concerned. Adsorption is a special case of precipitation in which aluminum or iron remains as the main constituent of the original phase but reacts with phosphate by the use of residual force on the surface.

This concept is particularly clear for the mechanism for the formation of $Al(OH)_3$ as proposed by Hsu and Bates (56). According to their model when NaOH is added to an aluminum salt solution, the hydroxyl ion tends to link aluminum ions together with the resulting formation of continuous series of positively charged polymers where the aluminum atom on the surface is not fully neutralized and is able to react with phosphate without the necessity of leaving the original dependent on the size of the polymers which is dependent on pH and the solution phosphate concentration. In a moderately acidic medium (such as pH 4) with a high phosphate concentration, the reaction process may be a typical precipitation following either equation 1 or 2.

(1) $6\ Al^{3+} + 6H_2PO_4 \qquad Al_6(OH)_{12}(H_2PO_4)_6 + 12H^+$

(2) $Al_6(OH)_{12}^{+6} + 6H_2PO_4 \qquad Al_6(OH)_{12}(H_2PO_4)_6$

Kardos (67) concluded that the type of reactions by which phosphorus becomes "fixed" can be placed in three general groups: adsorption, isomorphous replacement, and double decomposition involving solubility-product relations. In all these reactions phosphorus is involved as one or more of ionic forms into which orthophosphoric acid may dissociate.

Kolthoff (66) suggested that the adsorption reaction is an exchange reaction between phosphate and hydroxyl ions. Law and Black (75) found that the degree of adsorption was increased by increasing temperature and concluded that adsorption was a chemical reaction at low concentrations (up to 0.001M) and short time intervals (1 to 3 hours) to complete the reaction. Other reactions may dominate at higher concentrations (1.0M) and after more prolonged contact (8 to 10 days).

Toth (109) indicated that the anion adsorptive powers of soil clays are associated with the presence of Fe and Al compounds, since removal of these substances by various methods tends either to destroy completely or markedly to reduce anion adsorption.

Studies (109) of phosphate fixation by clay minerals indicate that the retention may be the result of fixation between free oxides of Fe, Al or Ca as well as fixation by clay minerals. Fixed PO_4 ions can be replaced or released from soil clay by divalent arsenate, silicate, citrate, oxalate, hydroxyl, and fluoride ions.

Kardos (67) regarded isomorphous replacement reactions as "adsorption-plus" reactions of three general types.

1) Continuation of the adsorption reaction through intercrystalline adsorption.
2) Transformation of the adsorption reaction to one of isomorphous replacement of hydroxyl or silicate anions from the crystal structure.
3) Decomposition due to isomorphous replacement, followed by recrystallization as a new mineral compound.

Stout (106) believed that the reaction was primarily a displacement of hydroxyl by phosphate from a determination of the water loss in a system. Clay mineral + KH_2PO_4 alone, was approximately equivalent to the millequivalents of phosphate fixed. Additional support of the hydroxyl replacement mechanism was given by Kelly and Midgley (68) who found a direct relation between the amount of phosphate fixed and the increase in pH obtained when isohydric suspensions of various solid phases and phosphate solutions were mixed.

Although the theory of a hydroxyl replacement mechanism is strongly supported, there is also evidence that silicate replacement by phosphate may be important in phosphate fixation. For instance, Mattson (80) prepared phosphosilicates of Al and Fe, and found the combining capacity of the phosphate to be much greater than that of the silicate. He suggested that desilification due to weathering of silicates takes place when phosphatic solutions such as leachate from guano beds, react with silicates.

Rose and Hendricks (97) discussed the minor constituents in clay minerals, and suggested that some proxying of Si by P may occur, as shown by Toth (109) who studied the displacement of silicate from soil colloids by phosphate. He found that as the phosphate fixation on each of four soil colloids increased, the amount of silica in the supernatant liquid increased.

Law and Black (75) treated kaolinite with phosphate at 60^0C, and observed that considerable silica was released within 48 hours, but when the reaction was carried out at 45^oC very little silica continued to be released up to 35 days. They suggested that the silica release was the result of isomorphous replacement of silicon tetrahedrons up to about the fourteenth day, or when about 24 millimoles of SiO_2 were released for each 100 g. of clay. They described this phenomena as resulting in an unstable phosphate compound, because of an infraction of the electrostatic valence rule where two phosphorus tetrahedrons share a common oxygen ion. He pointed out that silicon tetrahedrons on the edges and corners of the crystal, which have two corners unshared along the edge, may be proxied by phosphorus tetrahedrons without infraction of the electrostatic valence rule. Of the two shared corners, one would be shared with an adjacent silicon tetrahedron and the other with an aluminum octahedron. It may be true from these considerations that, when more edges and corners are present for each unit mass by virtue of finer natural particle size or grinding of the coarser particles, a larger amount of stable isomorphous replacement of silicon by phosphorus would occur.

Kardos (67) considered double decomposition reactions as solubility product relations, where several reactions may be regarded as significant in the fixation (precipitation) of soluble phosphates. Broadly, these reactions fall into two categories: those involving Fe and Al; and second, those involving Ca. The Fe^{3+} and Al^{3+} are similar reactions, however, only the Al^{3+} will be considered here in detail. The aluminosilicates and free sesquioxides may be regarded as the primary compounds supplying the Al^{3+} ion. Kardos (67) used kaolinite and gibbsite as typical examples of these two classes of compounds and he studied the relationship between hydroxyl ion concentration and the solubility product.

Kaolinite $Al_7(OH)_4Si_2O_5$ or $Al\ (HO)_2(HSIO_3)$
$Al^{3+}\ {}_2OH^- + HSIO_3^-$
$Ksp = Al^{3+} + OH^{-2} HSIO_3^-$
Gibbsite $Al(OH)_3 = Al^{3+} + {}_3OH^-$
$Ksp = Al^{+3}\ OH^{-3}$

From the solubility product of gibbsite 1.9×10^{-33}, he calculated that at pH 5.0 the Al^{3+} concentration will not exceed 1.9×10^{-6}M. At pH 6.0 it drops to 1.9×10^{-4}, whereas at pH 4.0 it increases a thousand fold to 1.9×10^{-3}. If phosphate ions are added to a soil system in the form of a soluble fertilizer, the quantities added at any one time do not usually exceed 200 pounds of P_2O_5 per acre. If the phosphates were dissolved uniformly throughout the soil water the resulting phosphate concentration would be 0.007M.

Now, assuming that the phosphate will form a variscite-like compound, $Al(OH)_2H_2PO_4$, having a solubility product of 2.8×10^{-29} according to the equation $Al(OH)_2H_2PO_4 = Al^{3+} + 2OH^- + H_2PO_4^-$, then he calculated the extent by which the aforementioned phosphate concentration (0.007M) exceeds the equilibrium concentration at pH 4.0 when Al^{3+} is maintained at 1.9×10^{-3}M by an excess of solid phase $Al(OH)_3$.

$$H_2PO^-{}_4 = \frac{2.8 \times 10^{-29}}{1.9 \times 10^{-3}\ 10^{-10\ 2}} = 1.5 \times 10^{-6}$$

Thus the phosphate concentration would be reduced from $7 \times 10^{-3}M$ to $1.5 \times 10^{-6}M$; or a reduction in concentration of 99.98 percent.

Lindsay and Moreno (76) developed a solubility diagram for variscite $AlPO_4 \cdot {}_2H_2O^-$, strengite $Fe\ PO_4 \cdot {}_2H_2O$, fluorapatite $Ca_{10}(PO_4)_6F_2$, hydroxy apatite $Ca_{10}(PO_4)_6(OH)_2$ and octacalcium phosphate $Ca_4H(PO_4)_3 \cdot {}_3H_2O$. In constructing the diagram they assumed that Al^{3+} activity was limited by the solubility of gibbsite, Fe^{3+} activity by the solubility of geothite, F^- activity by the solubility of fluorite, and Ca^{2+} activity was arbitrarily that of a 0.005M solution, and the activity of H_2O was unity. The resulting solubility diagram indicated the importance of the effect of pH on this reaction. It shows that variscite and strengite increase in solubility with a decrease in pH, but fluorapatite, hydroxyapatite, octacalcium phosphate and dicalcium phosphate dyhydrate are decreased in solubility with a decrease pH.

Frink and Peech (43) later showed that crystalline gibbsite was extremely slow in dissolution in 0.01 M $Cacl_2$ soil extracts, and that such extracts to which gibbsite has been added remained undersaturated with respect to gibbsite, even after one month of equilibration.

It may be true that the supply of aluminum in soils for reaction with phosphate may be controlled as much by the aluminosilicates and the aluminum on exchange sites as by gibbsitic aluminum. The complexity of the aluminum hexahydronium ion with its monomeric and polymeric hydroxy forms as absorbed by vermiculite, is described by Jackson (62) as the solubility-product phenomena, particularly in soils containing clays. With large layer charge densities there is increased difficulty of interpretation. Further, as Huffman (59) pointed out, all of the complex phosphates (K and NH_4 taranakites, acid NH_4 and K ferric phosphates, and Ca ferric phosphate dissolve incongruently in water, leaving solid residues which behaved like tertiary phosphates of Fe and Al in which the P:Al or P:Fe ratio approached 1.0.

Since the availability of Al^{3+} and Fe^{3+} for reaction with phosphate is controlled by the hydroxyl ion concentrations, phosphorus precipitation (fixation) can be decreased by increasing pH of the soil but when calcium compounds, such as $Ca(OH)_2$ and $CaCO_3$ are responsible for the increase in pH, other reactions may take place to precipitate phosphorus.

From the literature there are three types of reaction mechanisms of phosphate fixation and one may conclude that no one type of reaction can account for all of the phosphorus fixation in a complex chemical medium like the soil.

It has been shown by many investigators (9, 10, 11, 14, 17, 23, 41, 42, 44, 119) who have studied and attempted to fractionate phosphorus in soil, that was extraction may be based on any one of many models. These models may be based on solubility product, available forms, and ability of phosphate compounds to be resistant to different kinds of extracting reagents. Any method to separate different forms of phosphorus in soils probably has many weak and strong theoretical considerations. Dean (32), Chang and Jackson (17) separated phosphorus in soil into two main groups which were organic phosphorus and inorganic phosphate (calcium phosphate, aluminum phosphate and iron phosphate). Ghani (44) separated phosphorus forms into five soil phosphate fractions. (a) Mono, di, and tricalcium phosphate, soluble in acetic acid; (b) Iron and aluminum phosphate, soluble in alkali solutions; (c) organic phosphorus, soluble in ammonia; (d) apatite, soluble in sulfuric acid and (e) insoluble phosphate, or phosphorus permanently "fixed" in the clay particles. Fisher and Thomas (41) developed a method to differentiate groups of phosphate compounds with buffered acid extractants and separated them into four groups:

1). Phosphate adsorbed upon hydrous oxides and those present in the form of apatite. This phosphorus was extracted with 0.007N sulfuric acid at a pH of 2.

2). Amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese.

3). Amorphous phosphates of aluminum and iron.

4). By difference, phosphates present as crystalline phosphates of aluminum and iron. #2 and 3 were extracted with acetic acid of pH 5 and they were appreciably soluble.

Cherikov and Volkova (23) fractioned the soil phosphorus into five groups based upon extraction reagents as follows:

a) Group of compounds soluble in a CO_2 saturated water, consisting of alkali phosphates; di-phosphates of calcium and magnesium, tri-magnesium phosphate.

b) Group of compounds soluble in 0.5 N acetie acid, which includes some apatite, phosphorite; salts of alcohol-phosphoric acids and sugar phosphoric acids.

c) Group of compounds soluble in 0.5 N Nacl which included apatite, aluminum phosphate, iron phosphate, some of the more basic phosphates of iron and phytin.

d) A fraction soluble in 0.5N NaOH, which includes nucleins, nucleoproteins, and compounds of humic acid.

e) Insoluble phosphate compounds, which are not dissolved in any of these extractants and may consist of titanium phosphate and phosphorus compounds of no availability to plants.

Bhangoo and Smith (10) studied the distribution of phosphorus in virgin soils of Kansas, and partitioned phosphorus into (a) soluble phosphorus fraction in 0.1N HCl (calcium-phosphate), (b) cold alkali soluble phosphorus after removal of acid soluble (adsorbed phosphorus), (c) hot-alkali soluble phosphorus, after removal of (a) and (b), which includes iron and aluminum phosphate, and (d) organic phosphorus.

Williams (119) classified the phosphorus compounds of the soil, on the basis of their solubility in sodium hydroxide, as follows: (a) soluble-phosphorus in combination with sesquioxides, organic phosphorus, exchangeable phosphorus of the clay complex, phosphorus of calcium compounds such as $CaHPO_4$, phosphorus of water soluble compounds; (b) insoluble phosphorus in compounds of the apatite class; (c) unclassified phosphorus in the interior of the clay mineral structure and phosphorus of titanium compounds.

In the method of determining available or soluble phosphorus in soils not only the technique of extraction is important by itself but the extracting reagents also varies widely in their ability to remove phosphorus from phosphate compounds. Tisdale and Nelson (108) defined "available phosphorus" as the sum of water-soluble and citrate-soluble phosphate in the soil.

The fractionation procedure for total phosphorus is sequential in order to obtain the complete separation of the different chemical forms of phosphorus. Chang and Jackson (17) developed a procedure in an attempt to differentiate groups of phosphates in various extractants. Ammonium fluoride dissolves the aluminum phosphate and a small amount of iron phosphate. After extraction of aluminum phosphate a treatment with sodium hydroxide dissolves iron phosphate but not calcium phosphate. The residual sample is extracted with sulfuric acid to dissolve apatite and other forms of calcium phosphate. Finally, after the extraction of these three forms, the "reductant-soluble-iron-phosphate" is dissolved by reducing the ferric iron and chelating it with a citrate-dithionite treatment. After the reduction-chelation of the soil phosphorus, the occluded aluminum phosphate is usually extracted with ammonium fluoride. This fractionation procedure has been an important contribution to soil science and very helpful in studies of soil fertility because the chemical properties and especially the solubility of each form of soil phosphorus is a factor in determining the total availability of this element to plants.

In the last few years, Chang and Jackson's method for fractionation of soil phosphorus has been widely used in the field of soil chemistry, fertility and soil genesis by many investigators (20, 21, 42, 49, 57, 69, 79, 95, 115, 121, 122).

The methods presently receiving the widest use for fractionation of inorganic phosphorus are those of Chang and Jackson or a modification of their procedure. Glenn, et al. (47) studied the selectivity of different extraction solutions used by Chang and Jackson (17) for fractionation of discrete compounds in the soil using natural soil samples and synthetic and natural phosphate minerals. They found iron phosphate could be extracted with 0.7N sodium hydroxide, after extraction of aluminum phosphate, to be a complete extraction during a nine-hour or longer extracted period, the reductant-soluble iron phosphate and occluded aluminum phosphate are extracted after sodium hydroxide extraction of iron phosphate and before extraction of calcium phosphate with 0.5N sulfuric acid. (This reagent was otherwise found to extract appreciable amounts of occulded iron and aluminum phosphate). Chang (20) after reviewing the criticism of other investigators made the following modifications:

1. Extractions of aluminum phosphate with 0.5N ammonium fluoride at a pH of 7 for one hour for paddy soils and extraction at a pH of 8.2 for one hour for upland soils.
2. Extraction of iron phosphate with 0.1N sodium hydroxide for nine to twelve hours.
3. Extraction of calcium phosphate with 0.5N sulfuric acid for one hour after the extraction of occluded phosphate.

This modification differs from that of Chang and Jackson only in the order to the different forms and the pH of the ammonium fluoride solution used to extract aluminum phosphate.

Mehta, et al. (82) determined organic phosphorus in soils which consisted of successive extractions with concentrated HCl and 0.5N, sodium hydroxide at room temperature, and 0.5N sodium hydroxide at 90°C. The difference in content of inorganic and total phosphorus in the combined extract was taken as the total organic phosphorus in the soil.

Russell (99) pointed out the various chemical methods have been used for determining the properties of the principle inorganic phosphates present in the soil and these are based on the following assumptions:

a) Dilute acid dissolves all of the calcium phosphates present except the apatites.

b) Concentrated solutions of acids dissolves a apatite.

c) Fluoride displaces phosphate from the surface of hydrated aluminum oxides and subsequent treatment with alkali displaces phosphates from the surface of hydrated ferric oxides.

d) Reducing solutions containing an iron chelating agent will remove phosphate present below the surface of iron oxide films, and in particular, the phosphate present in nodules of hydrated ferric oxides.

Olsen, et al. (89) used an extraction solution of 0.5N sodium bicarbonate which extracted available phosphorus from calcareous of alkali soils. Watanabe and Olsen (113) recommended the Murphy and Riley (87) procedure which used a single reagent for determining phosphorus. They also reported that this method was accurate for determining phosphorus in the soil extract. The Murphy and Riley method is based on the reduction of the ammonium molybd-phosphate complex by ascorbic acid in the presence of antimony. The color produced is stable for 24 hours and it is less subject to interfering substances than are other methods involving reduction by stannous chloride. A disadvantage of ascorbic acid is the hydrolysis reaction may produce inorganic ortho-phosphate during the long period required for development of the molybdenm blue color. They concluded that phosphorus determination in water extracts of soil may be inaccurate due to the interference from dissolved organic matter or some material sorbed by carbon black. For their study which involved large soil water ratios or large concentrations of phosphorus the isobutyl alcohol method of concentration by Pons and Guthrie (93) was recommended, furthermore the isobutyl alcohol method is suitable but undesirable for routine analyses. Stannous chloride has not been entirely satisfactory for reducing the molybdo-phosphate complex because organic matter in the soil extract causes instability of the blue color, but ascorbic acid as a reducing agent appears to overcome these objections.

Caldwell (24) used the Murphy and Riley method on sodium bicarbonate extracts with a favorable result in estimating the phosphorus requirement of wheat soils. He suggested from the experimental results that phosphorus fractions associated with aluminum in acid pasture soils under clover were more available than those associated with iron and organic phosphorus.

Saunder (100) developed a method in which the extracting solution was hot 0.1N. sodium hydroxide for extracting available phosphorus from tropical soils, particularly red soils, where phosphorus was present in strongly sorbed forms.

Plessis and Burger (92) extracted soil samples with eight reagents for available phosphorus. They found a relationship between phosphorus and aluminum phosphate, iron phosphate and calcium phosphate. Weir (114) used a similar procedure in order to increase the precision of the estimation of the available phosphorus in the soil as follows: first, 0.002N. sulfuric acid method by Truog (111); second, 0.1N. hydrochloric acid method by Bray (15); third, 0.5N. sodium bicarbonate method by Olsen, et al. (89); fourth, 10 percent sodium acetate method by Morgan (85); and fifth, the 0.1N. sodium hydroxide method of Saunder (100). He concluded that the 0.002N. sulfuric acid extractable phosphorus test was well correlated with the calcium phosphate content but not with the iron phosphate or aluminum phosphates contents.

Jackson and Paterson (64) extracted available soil phosphorus with 0.025N hydrochloric acid and 0.03N. ammonium fluoride (modified Bray procedure). The extracted phosphorus was correlated with the phosphorus uptake and yield of lucerne in the field. They concluded that no method was found to be significantly superior to any other in predicting the phosphorus status of the soil. However, the Olsen method (89) was the least effected by soil pH and generally yielded the highest correlation coefficient. Kaila (65) compared the Bray #1 (14) test and the Olsen (89) test with an acetic acid extraction for 346 mineral soils. He determined the inorganic phosphate fraction extracted by ammonium chloride, ammonium fluoride, sodium hydroxide, and sulfuric acid and concluded that the Bray #1 and Olsen tests on the average extracted equal amounts of phosphorus and were closely correlated with each other and were poorly correlated with acetic acid values.

McGeorge (77) suggested a carbonic acid extraction for alkaline Arizona soils, because the acid was weak and was similar to the mechanism which he believed was operative at plant root surface.

CHAPTER III

MATERIALS AND METHODS

Three clay fractions used in this study were, Camargo Bentonite collected from a open-pit mine site near Camargo, Oklahoma. Panther Creek Bentonite, collected near Panther Creek, Mississippi and Miller silty clay loam which was collected from the Fort Reno Livestock Research Station. The Miller soil (Vertic Haplustoll) develops in a Pliestocene mantle bordering the flood-plain of the North Canadian river (120). Williams (120) studied the shrink-swell characteristics of the Miller soil and collected and separated the Miller silty clay loam into fine and coarse clay. Williams (120) discussed the results of his x-ray diffraction studies of the Miller silty clay loam and the sand fraction was composed largely of quartz and feldspars which were present throughout all depths. No montmorillonite, illite or kaolinite were found in the silt fraction. The clay fraction was composed primarily of montmorillonite and was stored in the Mg. saturated form. Both coarse and fine silt fractions were quite similar throughout the profile.

The Camargo and Panther Creek bentonite were collected and fractioned by Kidder (72) into coarse clay and fine clay, and the samples were stored as Mg clay saturated suspension since 1969.

Some physical and chemical properties of clay fractions used in this study are reported in Table I.

TABLE I

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE MILLER SOIL AND TWO PURE CLAYS STUDIED

Clay Sample	CEC Meq/100g	Surface Area N^2/gm	pH of Solutions		Total Al %	Free Fe_2O_3%
			Original	Added KH_2PO_4		
MILLER SOIL PROFILE Depth CM						
B_1 20.3 - 30.5	23.8	131.67	7.1	7	4.66	0.03
B_2 30.5 - 40.6	22.4	168.49	7.4	7.5	5.46	0.03
B_3 40.6 - 58.4	22.6	148.35	7.8	7.8	6.04	0.04
B_4 48.3 - 58.4	23.8	283.42	7.6	7.7	6.58	0.03
B_5 58.4 - 89.0	15.4	194.05	7.7	7.7	5.32	0.02
B_6 91.4 - 121.9	10.6	111.02	7.3	7.4	6.68	0.03
B_7 121.9 - 152.4	10.0	75.04	7.25	7.4	5.78	0.02
Camargo Coarse (CC)	129.0	937.00	8.1	8.0	-	-
Camargo Fine (CF)	131.0	943.00	7.9	8.4	-	-
Panther Creek Coarse (PC)	91.0	740.00	9.15	9.0	-	-
Panther Creek Fine (PF)	108.0	868.00	7.4	7.65	-	-

Several methods of studying phosphate fixation have been outlined in the literature. They differ in detail, in results produced, and information obtained. That there are many questions about the mechanism of phosphate fixation in the clay fraction of soils is evident by the literature on the subject.

The procedures used in this study of the amount of phosphate held by the clay fraction of soils (fixed phosphorus) and the effect of the Bray Extracting reagent treatment were as follows:

The clay fraction was divided into two groups.

A0 Extracted group. 2 ml of clay suspension (0.0193-0.0909g) was pipeted into 15 ml test tubes and extracted with 2 ml. of the Bray Extracting reagent for (63) about 30 minutes then centrifuged at 5000 rpm on a Sorvall Rc-z centrifuge for 15 minutes. Phosphorus was determined on the supernatant by the Bray and Kurtz method (14) and reported as the Bray reagent extractable phosphate of the original clay fraction. The results of these analyses are reported in Table II and Table III.

The remainder of the clay in the centrifuge tube was kept for the phosphate fixation study.

B) Non Extracted group. The same clay fraction (suspension) was centrifuged at 5000 rpm for 15 minutes. The supernatent was discarded and the clay was saved for the phosphate fixation treatment. Note: this clay fraction was not extracted with the Bray reagent. It was only extracted with water.

The procedure used in the fixation experiment was to add 5 micrograms of a standard phosphate solution (5 ml. of 1 ppm KH_2PO_4) to both groups of samples. The containers were stoppered and shaken about five minutes. The clay phosphate suspension was allowed to stand for 24 hours and then centrifuged at 5000 rpm for 15 minutes. The clay was all centrifuged to the bottom of the tube and clear supernatent solution was obtained. An aliquot of the supernatent solution was taken for phosphate determination by the Bray and Kurtz method (14) and reported as water soluble phosphate of the clay fraction. The results are reported in Tables II and III.

The clay was then extracted with 2 ml. of the Bray extracting solution by shaking for 30 minutes and then centrifuged at 5000 rpm for 15 minutes. The supernatant was removed and phosphorus determined was by the Bray and Kurtz (14) method and report as Bray extractable phosphate. The clay fraction was repeatedly re-extracted with Bray reagent until no more phosphate was removed from the clay. The removal of phosphorus was completed within five times of successive extraction with the Bray reagent. The amount of Bray reagent extractable phosphate was reported for each extraction. The results are shown in Tables II and III.

The clay remaining was washed three times by shaking and distilled water followed by centrifugation at 5000 rpm for 15 minutes. The standard phosphate solution was added for the second phosphate fixation experiment at the same amount and the procedure was repeated as in the first phosphate fixation experiment. The water soluble phosphate and the Bray reagent extractable phosphate were determined as in the previous phosphate determination. The results of the second phosphate fixation treatment are reported in Tables IV and V. A flow diagram shows the steps and procedures used for this study in Figure 1.

Total phosphate was determined by Harper's method (50) of digesting a soil sample with 72% perchloric acid. Color was developed by reducing the molydenum which combined with the phosphate ion and was reduced with hydrazine sulphate. 10 ml of clay suspension (0.0665 - 0.4545g) was used. The extracted clay fraction was observed by x-ray diffraction with two different treatments.

1. The digested clay samples were saturated with Glycerol
2. The clay samples were saturated with Ethylene Glycerol

The results of the x-ray diffraction study are shown in Figure 9.

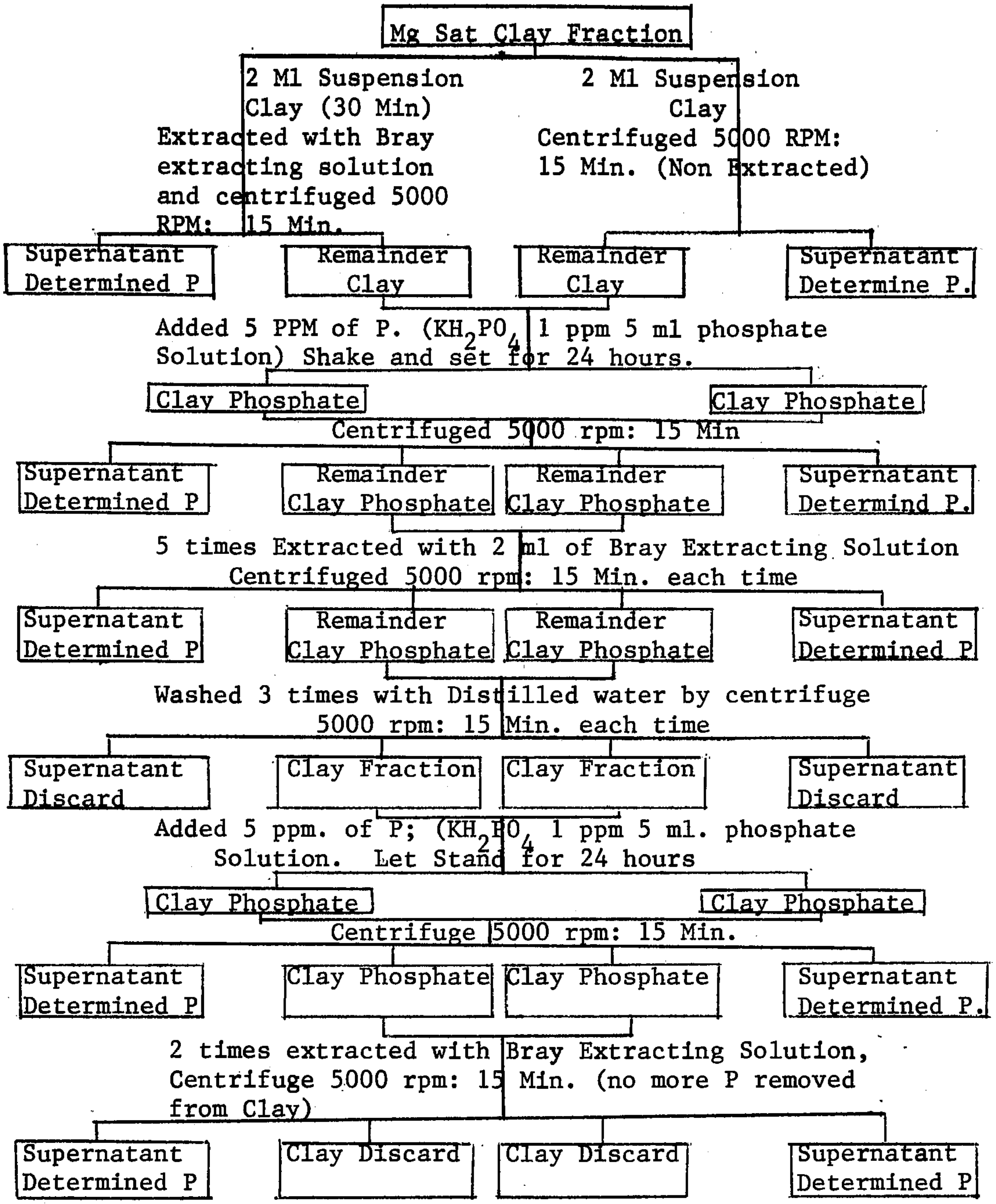

Figure 1. Flow Diagram Showing Steps in Procedure of the Methods

CHAPTER IV

RESULTS AND DISCUSSION

The fixation of phosphorus in this investigation refers to the amounts of non-extractable phosphate by the Bray extracting reagent. The fixation may be the result of some chemical reaction between the clay suspension and phosphate or it may be due to reactions between phosphate and other compounds, such as, oxides and hydroxides of aluminum and iron. The mechanisms of "fixing" and of phosphate fixed have many possibilities. Reports by many investigators (28, 30, 34, 36, 68, 86, 101) have shown that the active aluminum and iron oxides in soils are the main factor concerned in chemical reaction of soluble soil phosphate and conversion to insoluble phosphate forms.

The total phosphorus added and fixed (not soluble in water or Bray solution) by the several clay fractions is reported in Tables II, III, IV and V.

The results show that the Bray extracted group of samples (a) have a P fixing range from 75.40 to 12.00 percent. The non Bray extracted group of clay samples (b) have a phosphate fixing range from 63.5 to 0.00 percent.

The phosphate fixing properties of the several clay fractions is also shown in Figure 2. Both the Bray extracted clay samples and non-extracted clay samples of the second phosphate addition appeared to fix more phosphorus after the second P addition than the first, however,

TABLE II

SUMMARY OF PHOSPHORUS DETERMINED FROM SAMPLES OF MILLER SILTY CLAY LOAM OF THE FIRST PHOSPHATE ADDITION

Treatment[1]	Phosphorus in Miller Samples						
	B_1	B_2	B_3	B_4	B_5	B_6	B_7
(1) Total Phosphorus μgm/gm	86.20	87.75	92.36	77.53	27.83	99.94	121.00
(2) Bray Phosphorus in Original Clay μgm/gm	4.79	3.51	4.61	5.16	13.12	8.92	7.42
P Added As KH_2PO_4 μgm P/gm	95.78	87.75	153.94	258.45	79.51	71.38	55.00
(3) % P Removed by Water Extract							
(a)	24.94	20.00	13.99	40.49	27.92	31.00	18.00
(b)	4.99	9.99	5.99	4.99	20.61	16.48	13.49
(4) P Removed by 5 μgm/gm Successive Bray Extractions							
(a)	7.2	8.96	5.99	4.89	14.99	14.99	21.49
(b)	20.99	22.99	21.99	16.49	45.00	40.90	40.00
(a)	3.99	4.00	1.99	0.09	6.51	5.99	10.00
(b)	12.49	9.91	12.29	14.99	15.99	15.99	20.00
(a)	2.99	3.35	2.09	-	4.47	4.98	4.98
(b)	8.99	8.99	6.99	-	14.99	10.99	15.00
(a)	1.99	1.99	0.49	-	1.99	1.49	3.00
(b)	4.99	5.99	5.99	-	6.99	7.99	9.00
(a)	0.90	-	-	-	-	-	1.94
(b)	-	0.09	-	-	0.08	-	-
% Total Bray Extractable P.							
(a)	16.05	19.35	10.59	5.09	27.99	27.50	40.94
(b)	47.79	48.12	47.29	31.49	83.09	76.00	83.38
% Total P Recovered							
(a)	41.06	39.36	24.59	45.59	55.91	58.50	79.43
(b)	52.49	58.09	53.29	36.49	103.72	92.50	97.49
% Total P Not Recovered							
(a)	58.93	60.63	75.40	54.40	44.08	41.49	20.56
(b)	47.50	41.90	46.70	63.50	6.00	7.49	2.50

[1] (1)Total phosphorus in Miller Silty Clay Loam, (2) Bray Extractable phosphorus in original clay, (3) Water Extractable phosphorus, (4) Five successive extractions of Bray Extractable phosphorus (a) Sample Bray Extracted before KH_2PO_4 addition, (b) Samples no previous P. extraction.

TABLE III

SUMMARY OF PHOSPHORUS DETERMINED FROM SAMPLES OF CAMARGO AND PANTHER CREEK CLAY, COARSE (C) (2-.2μm) AND FINE (F) ($<$.2 m) OF THE FIRST PHOSPHATE ADDITION)

Treatment[1]	Phosphorus In Camargo and Panther Creek Clay			
	CC	CF	PC	PF
(1) Total Phosphorus μgm/gm	74.73	102.02	51.46	17.29
(2) P in μgm/gm Clay	30.64	47.64	14.11	63.96
P added as KH_2PO_4 μgmP/gm	93.42	128.77	83.00	172.89
(3) % P Removed by Water Extract				
(a)	39.99	40.00	25.00	20.99
(b)	32.49	36.99	17.00	36.99
(4) P Removed by 5 μgm/gm Successive Bray Extractions				
1 (a)	5.99	4.99	38.49	4.98
(b)	22.99	4.99	41.00	12.49
2 (a)	0.99	0.09	41.00	0.99
(b)	1.99	-	41.00	3.99
3 (a)	-	-	5.79	0.09
(b)	-	-	8.00	0.09
4 (a)	-	-	0.09	-
(b)	-	-	6.00	-
5 (a)	-	-	-	-
(b)	-	-	0.09	-
% Total Bray Extractable P.				
(a)	7.05	5.11	57.89	6.09
(b)	24.99	4.99	71.59	16.59
% Total P Recovered				
(a)	46.76	45.09	82.89	27.09
(b)	57.49	61.99	88.59	53.59
% Total P Not Recovered				
(a)	53.23	54.90	12.0	72.90
(b)	42.50	58.00	11.4	46.40

[1] (1) total phosphorus in the samples, (2) Bray Extractable Phosphorus in original clay, (3) water extractable phosphorus, (4) Five successive extractions of Bray extractable Phosphorus, (a) Sample Bray Extracted Before KH_2PO_4 addition, (b) Sample no previous P extraction.

TABLE IV

SUMMARY OF PHOSPHORUS DETERMINED FROM SAMPLES OF MILLER SILTY CLAY LOAM OF THE SECOND PHOSPHATE ADDITION. (a) SAMPLES BRAY EXTRACTED BEFORE KH_2PO_4 ADDITION (b) SAMPLES NO PREVIOUS P EXTRACTION

Treatment		Phosphorus in Miller Samples						
		B_1	B_2	B_3	B_4	B_5	B_6	B_7
KH_2PO_4 added in μgm/gm of (a) and (b) clay samples		95.78	87.75	153.94	258.45	79.51	71.38	55.00
<u>% Water Extractable P</u>								
	(a)	28.73	26.67	47.72	90.45	23.85	26.77	16.22
	(b)	25.38	26.67	46.18	90.45	22.26	20.90	18.70
<u>Bray Extractable P μgm/gm</u>								
1	(a)	4.78	4.38	6.92	6.46	3.97	2.85	3.30
	(b)	5.78	4.38	6.15	6.46	2.38	2.14	1.64
2	(a)	0.035	0.027	-	0.019	0.019	0.09	0.012
	(b)	0.022	0.024	-	0.021	0.019	-	0.012
<u>% Total Bray Extractable P</u>								
	(a)	4.81	4.40	6.92	6.42	4.07	2.94	3.71
	(b)	5.76	4.46	6.15	6.48	2.46	2.14	1.16
<u>% Total P Recovered</u>								
	(a)	64.99	64.60	64.51	64.05	64.89	58.38	64.50
	(b)	67.51	64.57	66.01	62.50	68.90	67.66	35.10
<u>% Total P Not Recovered</u>								
	(a)	35.01	35.40	35.49	35.95	35.11	41.62	35.50
	(b)	32.50	35.43	33.99	37.50	31.10	32.34	36.90

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[1] Phosphorus as (KH_2PO_4) was added to the (a) and (b) samples.

TABLE V

SUMMARY OF PHOSPHORUS DETERMINED FROM SAMPLES OF CAMARGO AND PANTHER CREEK CLAY, COARSE (c) (2-. 2μm) AND FINE (F) (<2μm) OF THE SECOND PHOSPHATE ADDITION. (a) SAMPLES BRAY EXTRACTED BEFORE KH_2PO_4 ADDITION, (b) SAMPLES NO PREVIOUS P. EXTRACTION

Treatment	P. in Camargo & Panther Creek Samples			
	CC	CF	PC	PG
KH_2PO_4 added in μgm/gm of (a) and (b) clay sample[1]	93.42	128.77	83.00	172.89
% Water Extractable P				
(a)	35.03	50.22	34.03	64.83
(b)	38.30	51.51	31.95	69.15
Bray Extractable P gm/gm				
1 (a)	3.25	5.15	8.30	7.77
1 (b)	2.80	4.50	9.13	4.32
2 (a)	-	-	0.11	-
2 (b)	-	-	0.14	-
% Total Bray Extractable P				
(a)	3.26	5.15	8.41	7.77
(b)	2.80	4.50	9.27	4.32
% Total P Recovered				
(a)	59.02	44.63	48.87	62.51
(b)	56.01	43.99	40.34	57.51
% Total P Not Recovered				
(a)	40.98	42.99	51.13	37.49
(b)	43.99	43.49	49.66	42.49

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[1] Phosphorus (KH_2PO_4) was added to the (a) and (b) Samples

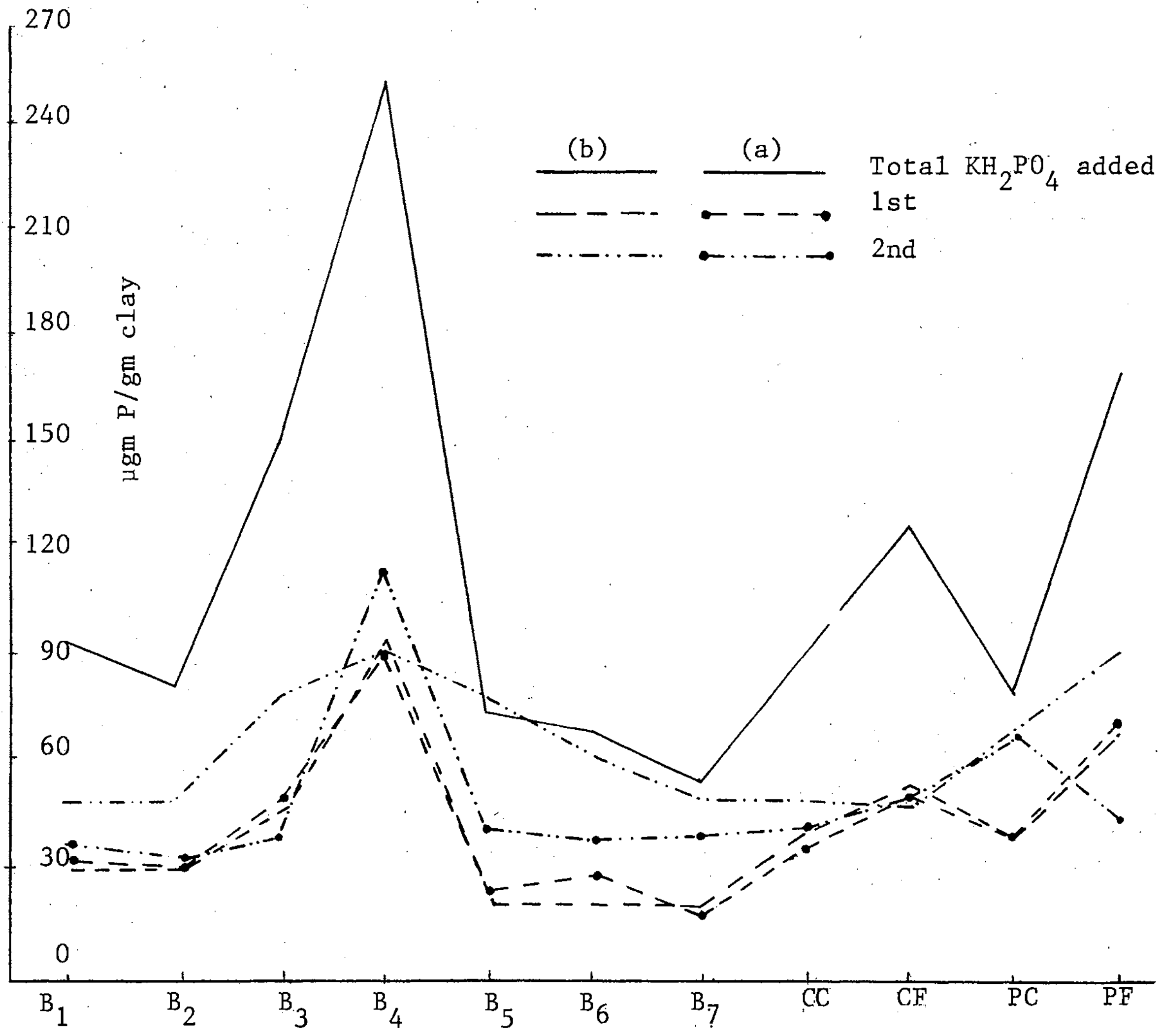

Figure 2. Total Phosphorus Removed from Clay Fractions after Twice Adding Known Quantities of Phosphorus to Both Groups

the Bray extracted group of samples of the first P addition is quite similar to the P fixation of both groups of the second P addition.

These results indicate that the ability of a clay to fix phosphorus was affected by the Bray reagent. The increasing activity of clay when extracted with the Bray reagent might be a factor responsible for an increase in the activity of aluminum and iron oxides in the clay suspension. Soluble aluminum and iron might be expected to react with phosphate with concomitant precipitation or absorption of more phosphate ion by the clay.

Since the clay crystal system has several atoms of aluminum and/or iron present per unit cell it should react with phosphorus to form insoluble compounds. However, a constant product of the sum of aluminum and/or iron oxide activity and phosphorus would not be expected, because compounds of different compositions and structures are formed. This concept can be further extended to cover the mixed system containing various phosphate fixing cations such as aluminum, iron and calcium; although given amounts of aluminum and iron may not precipitate phosphate separately. Another possibility of phosphate fixation observed in this experiment could be due to soil minerals being decomposed during aging and therefore provide reactive aluminum and iron to the clay system thereby fixing more phosphate. The fixation in this case may be the result of isomorphous substitution of phosphate for the silica tetrahedron or hydroxyl substitution on the octahedral of the clay mineral structure as a special case of the fixation process (98) in which the aluminum-phosphate attraction may break only a part of the Al-O-Si or Al-OH linkage.

Water soluble phosphate or retained phosphorus determined in an aliquot of clay suspension was regarded as available (soluble) phosphate. The results of this investigation show that most Bray extracted clay samples gave high water soluble phosphate over non-extracted groups, except Panther Creek fine clay. However, the results obtained between the Bray extracted and non-extracted were quite similar. A comparison of the water extractable phosphate between the two groups: Bray extracted clay fractions and non-extracted clay fractions and the first and second soluble phosphorus treatments is shown in Figure 3.

Both groups gave similar amounts of the water extractable phosphate and a slightly higher quantity of phosphorus extracted from the first phosphorus than from the second. The Bray non-extracted group of clay samples of the first phosphorus addition gave the lowest water extractable quantity of phosphorus regardless of type and texture of the clay.

The difference in the water extractable phosphate may be due to the weathering of the clay particles by the Bray reagent. This may be observed in the results as indicated in Figure 3 which shows that the Miller soil has a similar clay throughout the soil profile but the variation of the clay in the soil profile as shown by surface area and CEC (120) for sample B_4 was 283.42 M^2/gm of surface area and a CEC of 23.8 M.e.q./100 gm. This sample had the highest water extractable phosphate in the Bray extracted group of the second phosphorus treatment while B_7 had 75.06 M^2/gm of surface area and 10.0 M.E.Q./100 gm of CEC gave the lowest water extractable phosphate. Camargo bentonite coarse clay and Panther Creek bentonite coarse clay gave lower water extractable phosphate than Camargo or Panther Creek fine clay. The effect of the Bray reagent also increases the water extractable

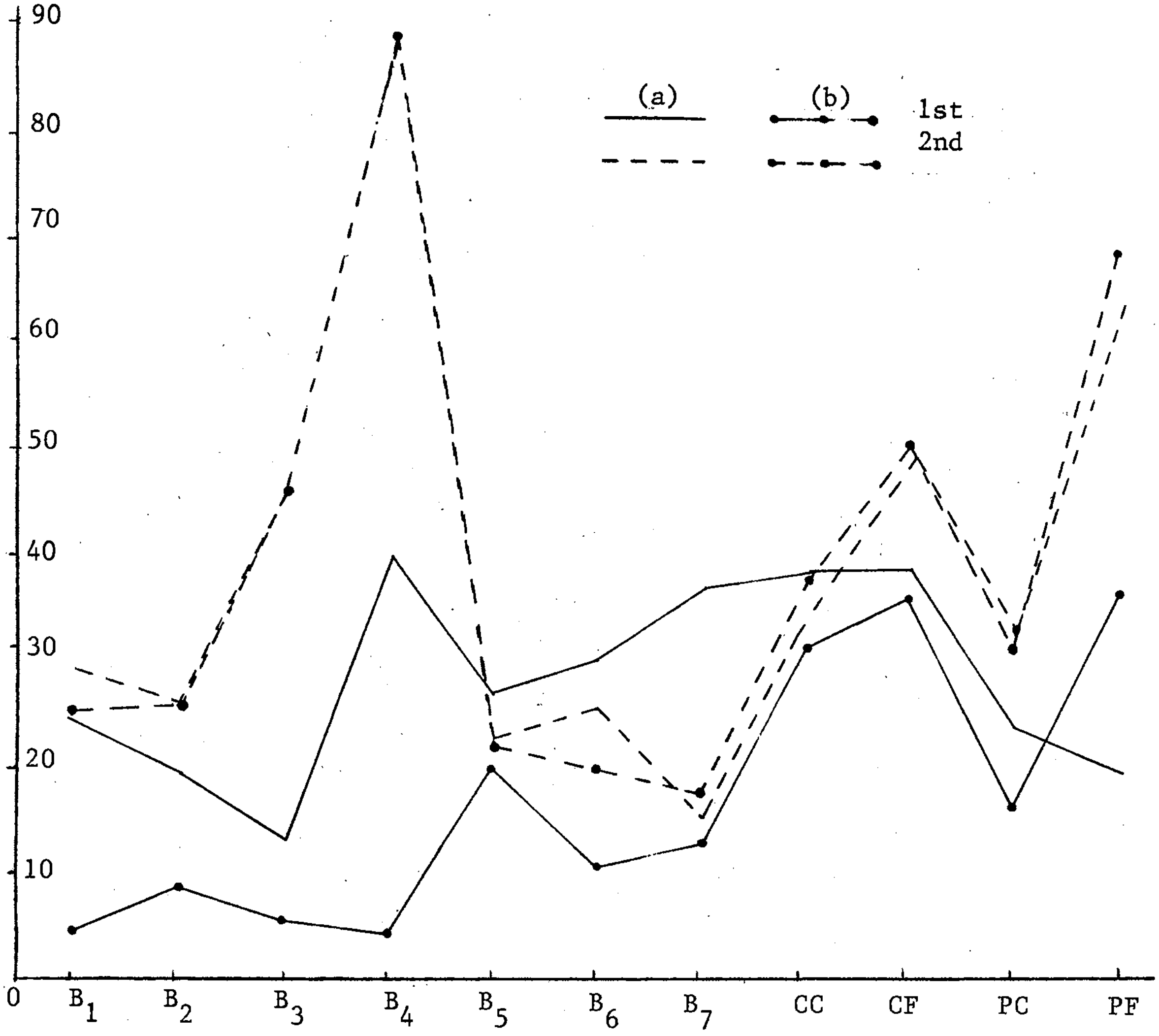

Figure 3. Total Water Extractable P as % of That Added After Twice Treatments with KH_2PO_4 of Both Groups

phosphate of the Bray extracted clay fraction of both the first and second addition of soluble phosphate. This result may be due to reactions between NH_4F in the Bray reagent and the aluminum of the clay. Many investigators believe that the Free Al and Fe oxides are responsible for phosphorus fixation (11, 29, 32, 35, 67, 99, 11, 109).

Soluble phosphorus added as KH_2PO_6 to the clay fractions will react with any free aluminum and iron to form insoluble AlPO and $FePO_4$ in the clay suspension. Soluble phosphate may also react with the clay particle to form insoluble precipitates of $AlPO_4$ on the particle. It is almost impossible to remove all of the free iron and aluminum oxides from clay suspensions without breaking down the crystal structure (25) of the clay.

Jackson (1967) interpreted the chemistry of soil phosphate by studying the reactions of soil with NH_4F and the formation of $AlPO_4$ and $FePO_4$ in acid solution as follows:

$$3\ NH_4F + 3\ HF + AlPO_4 \qquad H_3PO_4 + (NH_4)AlF_6$$

$$3\ NH_4F + 3\ HF + FePO_6 \qquad H_3PO_6 + (NH_4)_3FeF_6$$

The compounds $AlPO_4$ and $FePO_4$ actually represent hydrated and hydroxyl phosphates of aluminum and iron including adsorbed or precipitated phosphates on the surface layers of alumino-silicates and on the surface of iron oxides. The reaction which might form $FePO_4$ does not go to completion iron oxide coated iron phosphate and the fluoroferrate is unstable in neutral or alkaline systems. Phosphorus from $AlPO_4$ can be fractionated by 1 Normal NH_4F extraction. The $(NH_4)_3\ AlF_6$ and $(NH_4)_3\ FeF_6$ may precipitate as insoluble compounds in the presence of a large excess of fluoride. KH_2PO_4 was added to the clay suspension which had been extracted with the Bray solution and

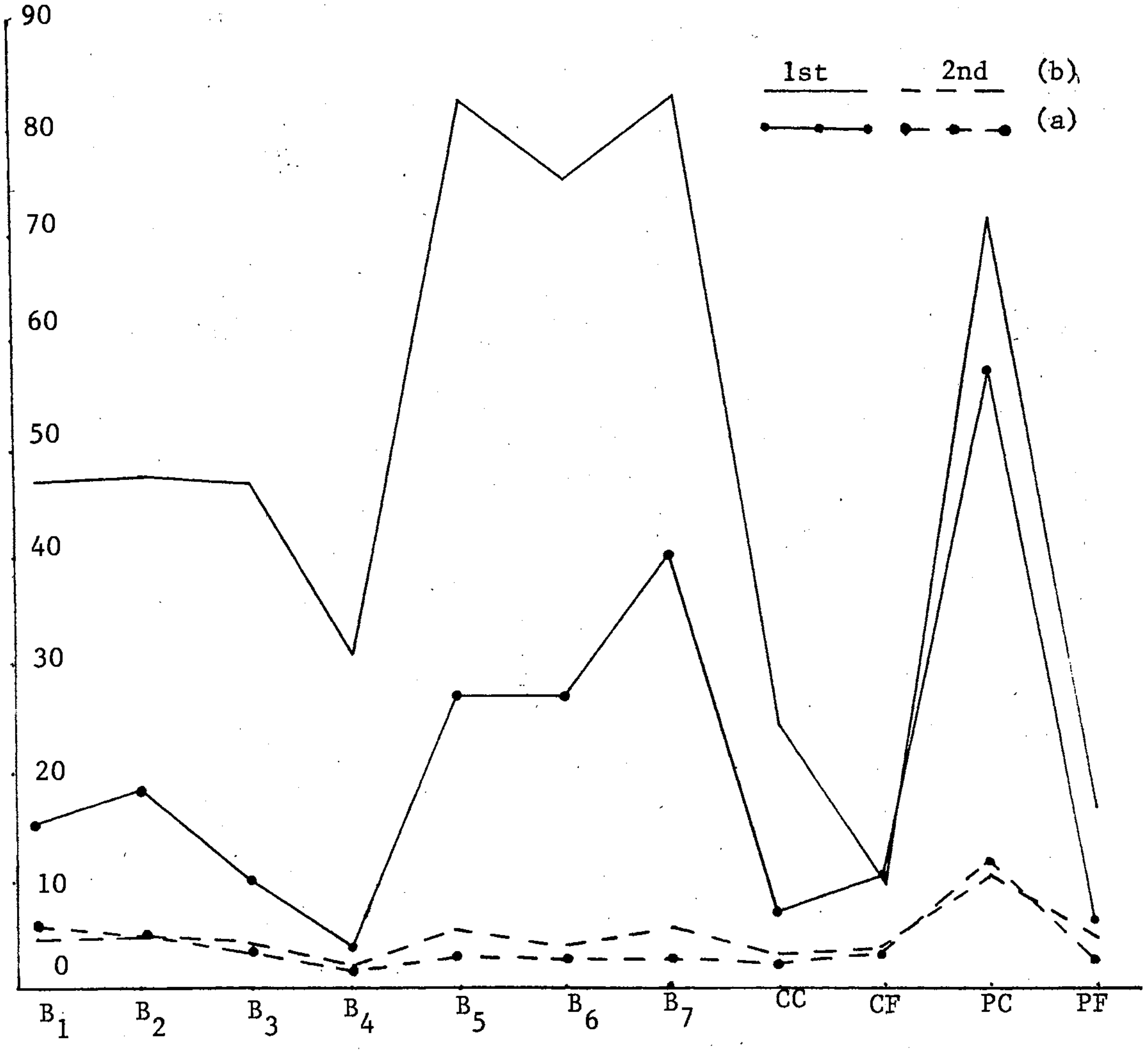

Figure 4. Total Bray reagent extractable P as % of that Added after the First and Second Treatments with KH_2PO_4 of Both Groups

some Al and iron reacted with the soluble phosphate to form insoluble Fe and $AlPO_4$. However, the amount of Al and Fe in the clay suspension may have been decreased because the clay suspension probably retained a small amount of free Al and Fe to react with NH_4F in the Bray reagent and the free Al and Fe thus retained in the clay fraction was precipitated as $(NH_6)_3AlF_6$ and $(NH_4)_3FeF_6$. This may account for the large amount of phosphorus which remained in the supernatant of the Bray extracted clay fraction on the first addition of soluble phosphate and in the second addition of soluble phosphate to the clay suspension.

Bray extractable phosphate may be considered as a phosphorus fraction which is slowly available to the plant. Both groups of clay suspensions previously extracted with water or Bray solution and then extracted 5 times with Bray solution is shown in Tables II, III, IV, and V. Most of the phosphorus removed was removed in the first two extractions.

The amount of Bray extractable phosphate removed by Bray reagent was considered as a part of the total phosphorus which was the soluble part of the native phosphorus in the sample. The results shown in Figure 4 show that the non Bray extracted group (b) of clay suspension samples were higher in amounts of phosphorus extracted by the Bray reagent after addition of soluble P to the clay samples than the extracted group (a), however, both groups were lower in Bray extractable phosphate when treated for a second time with soluble phosphate. The Bray extractable phosphate, however, of both groups of samples was quite similar.

The main factor which might have affected the removal of soluble phosphate between the two groups of clay fraction samples, i.e., water and Bray extracted and between two addition of soluble phosphates to the clay might be due to NH_4F in the Bray reagent. The $AlPO_4$ and $FePO_4$ form of phosphorus in the clay suspension may not be capable of fractionation due to an excess of NH_4F. That is, Al and Fe might be precipitated as $(NH_4)_3ALF_6$ and $(NH_4)_3$ FeF_6 after the clay suspension exceeds its ability to absorb NH_3F (Jackson 1967). This is a doubtful chemical reaction phenomenon in the behavior between the clay fraction and the Bray extracting solution.

Total phosphorus in the original clay fractions shown in Table II and III varies from 17.29 to 121.00 μgm/gm. These results may be due to the primary composition of the clay or due to the release of ionized iron and aluminum present as non-clay material due to exposure to acid in the Bray extracting solution and subsequent ionization.

Clay suspension samples used in this study were studied by x-ray diffraction in an attempt to learn something about the effect of soluble phosphate solutions, Bray extracting solutions and perchloric acid digestion on the integrity of the clay particle. The x-ray diffraction pattern of clay samples digested with perchloric acid and solvated with polyalcohols show that the Panther Creek coarse and fine clay and Camargo coarse clay (Figure 5, 6, and 7) have strong diffraction peaks with both glycerol and ethylene glycol solvation of calcium saturated samples and the spacing was similar to the original clay which was treated with glycerol. These results indicated that Panther Creek coarse and fine clay, and Camargo coarse clay were resistant to Perchloric acid digestion, however, the basal spacings were slightly changed from the original clay. This effect might have

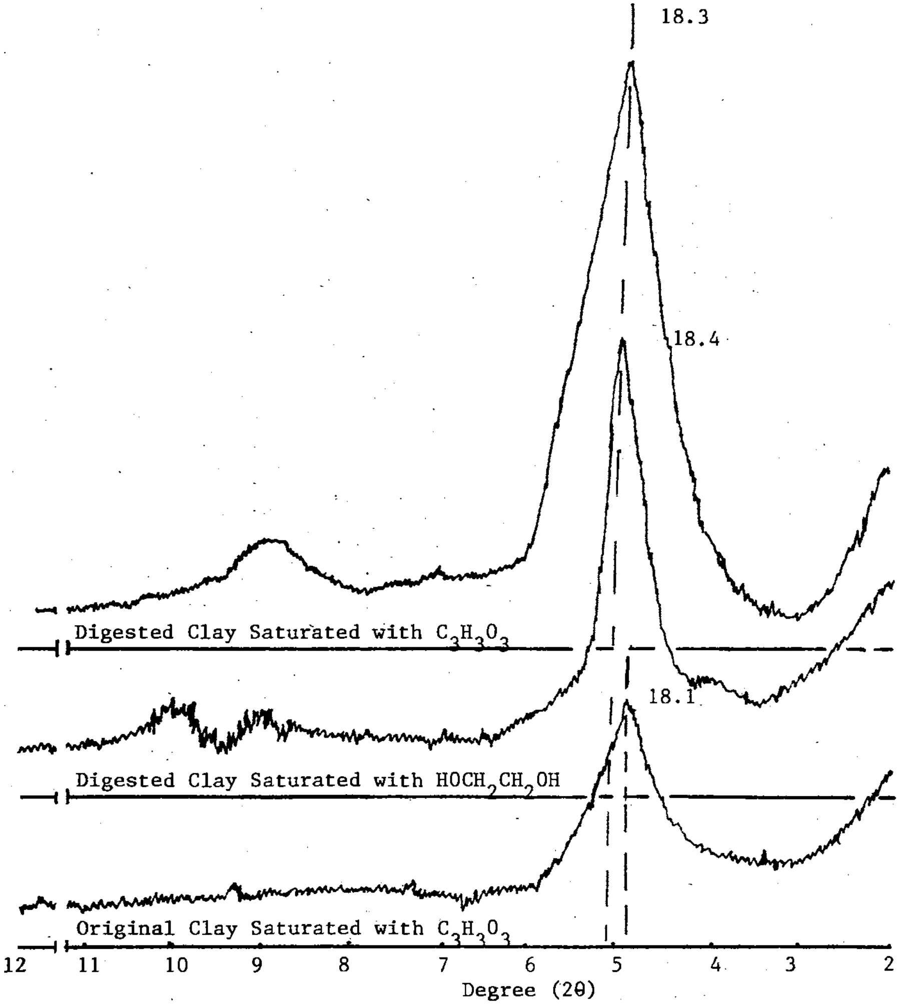

Figure 5. X-ray Pattern of Panther Creek Coarse Clay Digested with $HCLO_4$ Treated with $C_3H_3O_3$ and $HOCH_2CH_2OH$

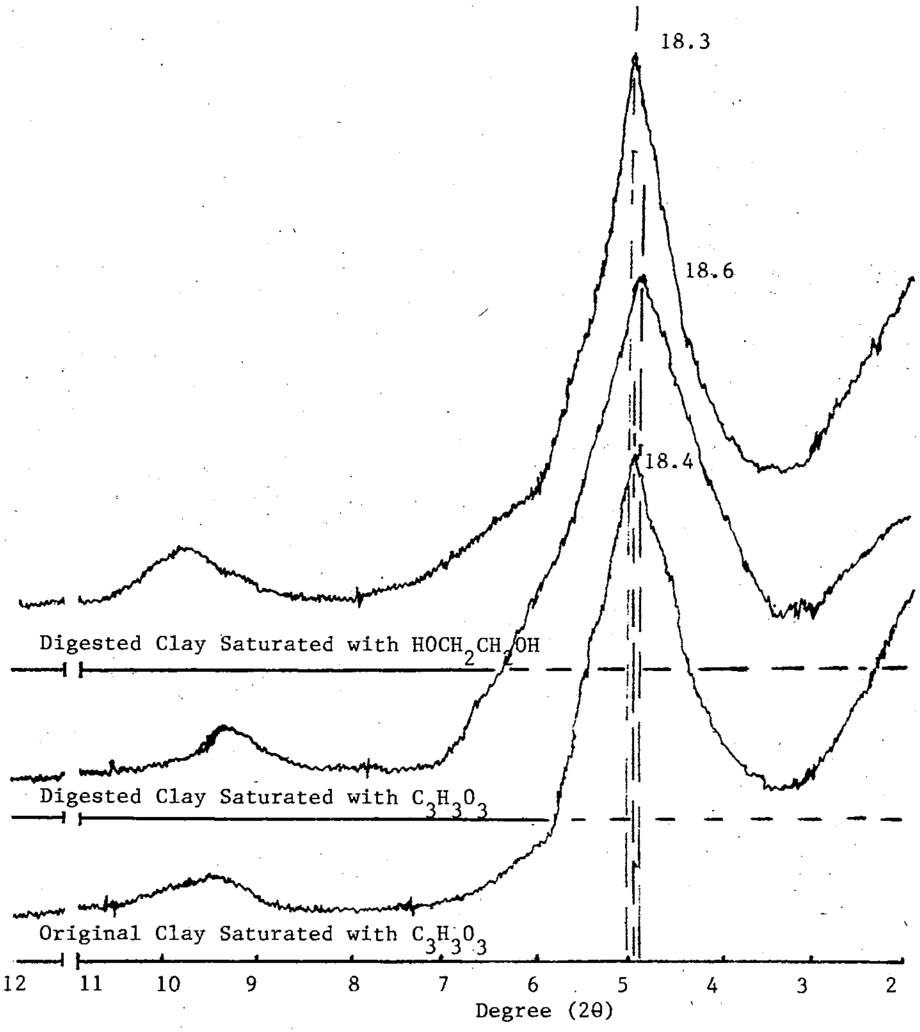

Figure 6. X-ray Pattern of Panther Creek Fine CLay Digested with $HCLO_4$ and Treated with $C_3H_3O_3$ and $HOCH_2CH_2OH$

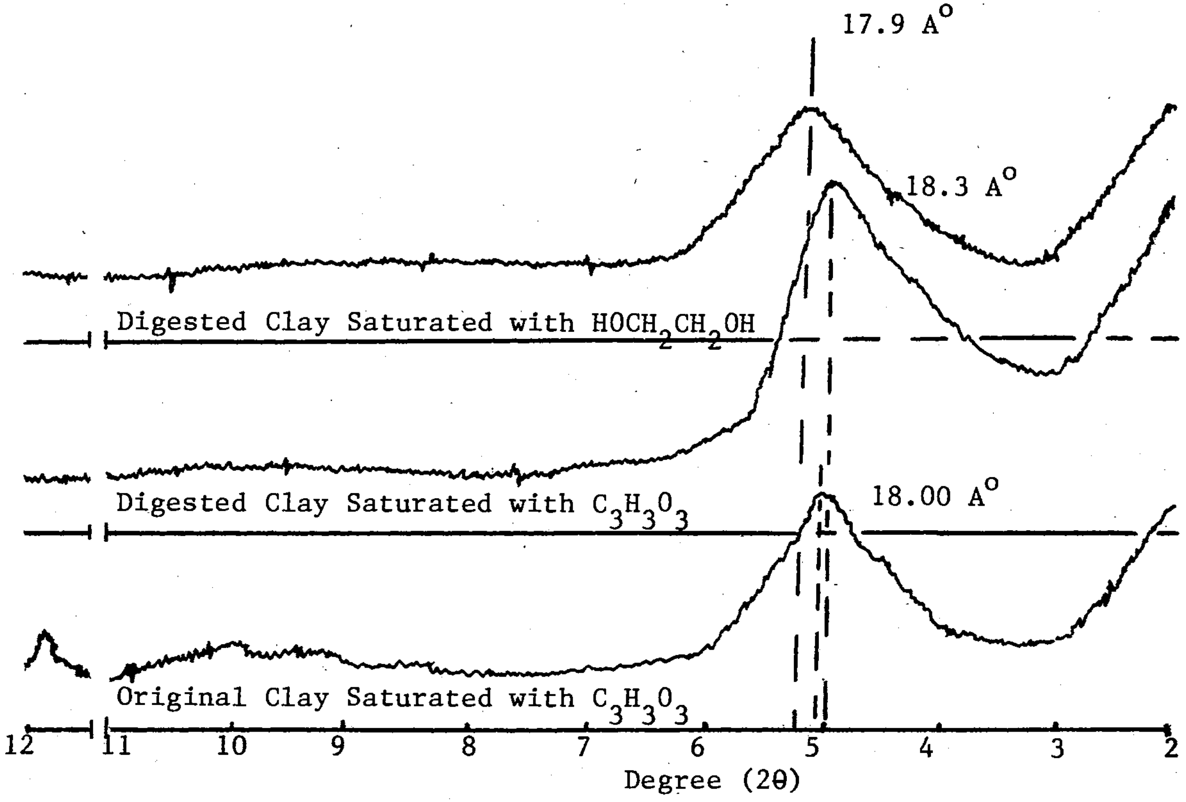

Figure 7. X-ray Pattern of Camargo Coarse Clay Digested with $HClO_4$ and Treated with $C_3H_3O_3$ and $HOCH_2CH_2OH$

been due to the removal of phosphorus and silica or alumina interlayers removed by the $HClO_4$ treatment (Jackson 1957).

Camargo fine clay (Figure 8), however, does not show diffraction peaks with either treatment and the crystal structure appears to be completely destroyed by $HClO_4$ digestion. These results seem to agree with Jackson (1957) who suggested that bentonite clay is not resistant to chemical degradation and is often destroyed in the laboratory preparations designed for the study of clay minerals.

Miller clay (Figure 9) does not show a diffraction peak when treated with glycerol but gave very strong and sharp peaks with a first order spacing of $18A^o$ when treated with ethylene glycol.

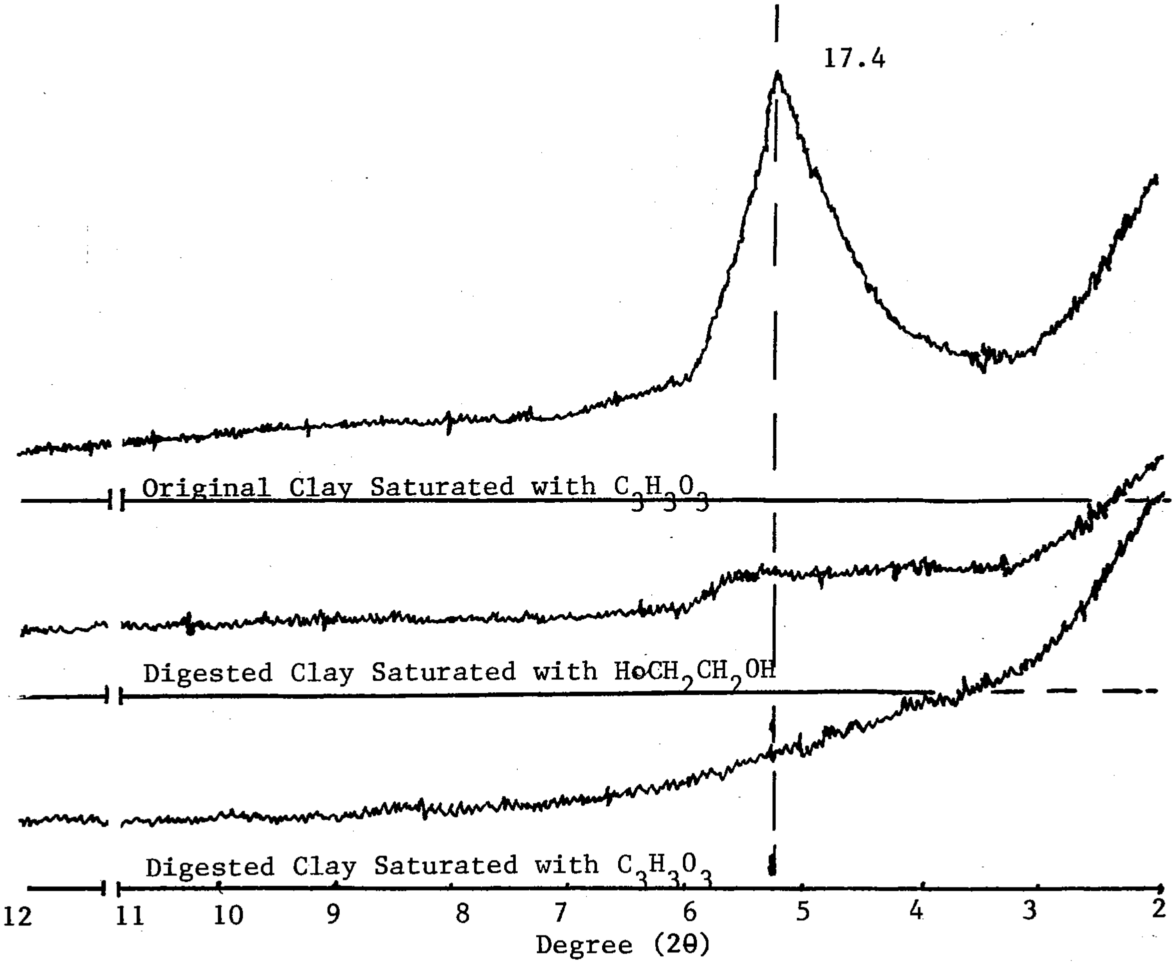

Figure 8. X-ray Pattern of Camargo Fine Clay were Digested with $HCLO_4$ and Treated with $HOCH_2CH_2OH$ and $C_3H_3O_3$

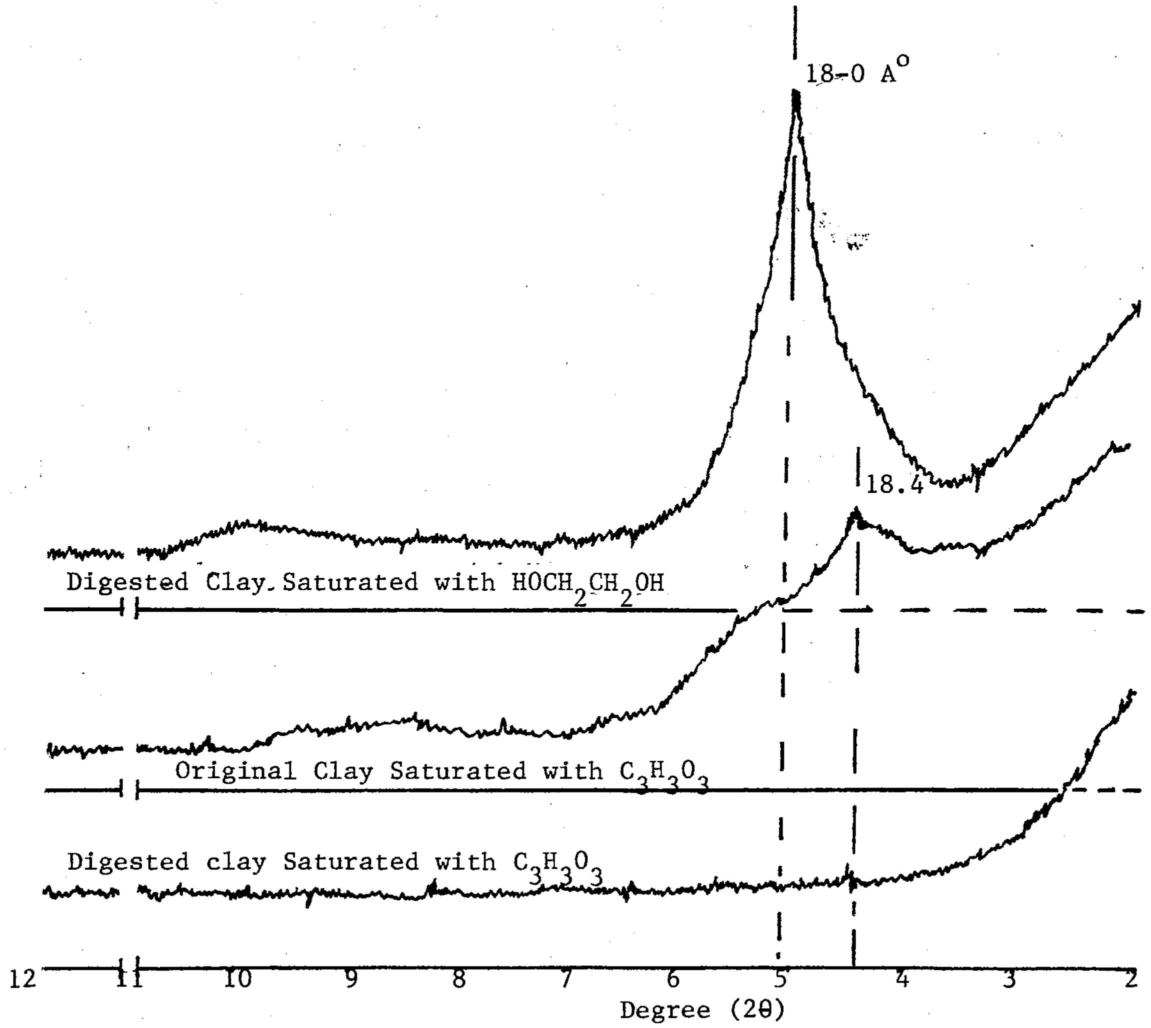

Figure 9. X-ray Pattern of Miller Clay Horizon (B_2) which were Digested with $HCLO_4$ and Treated with $C_3H_3O_3$ and $HOCH_2CH_3OH$

CHAPTER V

SUMMARY AND CONCLUSION

Two groups of clay samples were examined. Both groups of clay samples were extracted with water and the Bray solution and the phosphorus extracted was determined. Then all of the samples were treated with a standard phosphorus solution of KH_2PO_4. All samples were extracted first with water to determine water soluble phosphate before extraction with the Bray solution.

The original clay samples as prepared were extracted with water and none of the samples contained water soluble phosphorus. One set of samples were extracted with the Bray solution and the phosphorus extracted was found to vary from 5 to 37 ppm. Next, the water extracted (or non Bray extracted samples) and the Bray extracted samples were treated with known quantities of phosphorus as a KH_2PO_4 solution. All phosphate clay suspension samples were then shaken and allowed to equilibrate for 24 hours and then extracted with water and the phosphorus extracted was determined, and found to vary from 13.99 ppm to 40.49 ppm. in the Bray extracted group and 4.99 to 36.99 ppm in the non Bray extracted group. Both groups of samples were then extracted with the Bray solution for 5 successive extractions. In each extraction the samples that had been previously extracted with the Bray solution yielded less phosphorus than those that had not been previously extracted through five extractions. The net result was that clay samples initially extracted with the Bray solution resulted in more of the added phosphorus rendered insoluble or "fixed" than the non-previously Bray extracted samples.

All samples were then washed three times with distilled water to remove the Bray reagent and then known quantities of a standard phosphorus solution of KH_2PO_4 was added to all samples. After the second addition of the standard phosphorus solution, the samples were shaken and allowed to stand for 24 hours and then extracted twice with the Bray reagent. The phosphorus removed by this Bray extraction of both groups of clay samples was less than that extracted with water, but both groups had similar amounts of Bray extractable phosphorus when extracted for the second time. In comparing between the first and second extraction of soluble phosphate treated samples more phosphorus was fixed or rendered insoluble in the second extraction than in the first extraction regardless of whether the sample had only been extracted once or twice with the Bray reagent previously. These results would seem to indicate that most clays would increase their ability to fix phosphate or be low in Bray soluble phosphate and water soluble phosphate with continued extraction of clay with the Bray solution.

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APPENDIX

X-ray Instrument and Operation

Samples were X-rayed on General Electric XRD6

Cu K2 radiation generated

50 KVP, MA 20

Soller Slit - HR

Tub Slit - 1° MR

Detector Slit 0.2°

Detector Vollage 1500

EPB Range 1000

Amplifier - Full coarse Full Line

Sean Rate 2°/minute

Time constant 1

VITA

Sungwal Colatat

Candidate for the Degree of

Master of Science

Thesis: BEHAVIOR OF CLAY FRACTIONS IN THE "FIXATION" OF PHOSPHORUS ON THE EFFECT OF THE BRAY EXTRACTING SOLUTION

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