

CHAPTER I



INTRODUCTION

Scientific informations about soils, in Thailand, have been collected and measured since 1935, the first year that soil science was introduced to the country by Dr. Robert L. Pendelton. At the first stage of scientific soil study; it appears, from the author's opinion, to emphasize on soil testing which is generally looked upon as a test to determine fertilizer and lime needs for the crop under consideration. There has been a soil testing programme by the Agricultural Chemistry Division Laboratory, Ministry of Agriculture and Co-Operative provided free of charge for fertilizer and lime recommendations for farmers until today. However, it is generally known now that the validity of soil testing is based on the relevance of correlations provided by research with emphasis on the associated crop production. The data collected, at the following stage, are more on the country soil classification and some from research work on Agronomy.

Cation and anion adsorptions, which depend directly on signs and magnitudes of charges associated with various soil constituents, are the dominant interest to soil chemist especially when the soil is considered as a reservoir for plant nutrients. While cation adsorption or retention has long been generally known in soil science literature, anion adsorption has received only scant attention in the literature until recently when papers on anion effects on soil physical properties became more abundant (1). It should be noted that papers on anion adsorption laid special emphasis on tropical soils (2,3,4,5).

Since anion adsorption is quite a new field of soil study especially in Thailand it is, therefore, the author's intention to study on this subject. The objective of this study is to determine the magnitude of anion adsorption on three Thai red soils and to study the influence of pH and concentration of different anions on adsorption mechanism on these soils and also to make a comparative study of the adsorption characteristics of Thai red soils with varying anion species.

Adsorption of anions at mineral surfaces is important for soils with respect to the availability of plant nutrients which may occur naturally as anions or as cations or may be added in the form of fertilizers.

1.1 Essential Elements from the Soils

There are many elements that are generally known to be essential for plant growth. There are of two types, macro-and micro-nutrients. Macro-nutrients are nitrogen, phosphorus, potassium, calcium, magnesium and sulphur which are used in relatively large quantities by higher plants. The others, on the other hand are used in very small amounts, i.e., iron, manganese, copper, zinc, boron, molybdenum, chlorine and cobalt. Plant can absorb Ca, Mg, K, Zn, Cu, Mn, Fe in cationic form and P, S, Cl, Mo, B in anionic form and N both in cationic and anionic forms.

1.1.1 Forms of Sulphur in Soil

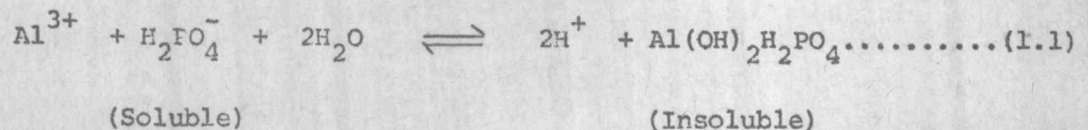
Soils contain both organic and inorganic forms of sulphur. In the surface layer of most soils, over half of sulphur occurs in the organic fraction as a constituent of certain amino acids in plant parts. Most of the inorganic sulphur occurs as sulphate ion in well aerated soils, and

sulphide ion in reduced condition, for example, in places where acid sulphate soil is located. However, upon oxidation it becomes sulphuric acid and sulphate compounds of some minerals. The sulphate compounds are the source of most sulphur acquired by higher plant. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is also the most common sulphate mineral in soils. The retention of sulphate ion by soils has not received much consideration until recently (6). With greater attention being focused on sulphur as a nutrient element, more information related to the factor affecting sulphate retention in soils is desirable.

1.1.2 Forms of Phosphorus in Soil

Most of phosphorus absorbed by plants, and the "available phosphorus" in soils both present in the form of phosphate ions. The orthophosphates are the most stable forms of phosphate in soils, the kind of orthophosphate ion present varies with pH of the soil solution. When pH is distinctly alkaline, the HPO_4^{2-} is the form in which soluble phosphorus occurs. If the pH is lowered or the soil becomes slightly to moderate acid, both HPO_4^{2-} and H_2PO_4^- prevail; at the high acidities phosphorus is commonly present as H_2PO_4^- (7). The phosphate availability to plant is maximum at soil pH about 6.7-7.0 (Fig.1.1) since at higher or lower pH than this range the fixation and precipitation of phosphate occur (8) as illustrated below :-

In acid condition. Soluble iron, aluminum, and manganese in mineral soils will react immediately with H_2PO_4^- , rendering the insoluble phosphorus and also unavailable for plant growth. The reaction is called precipitation.



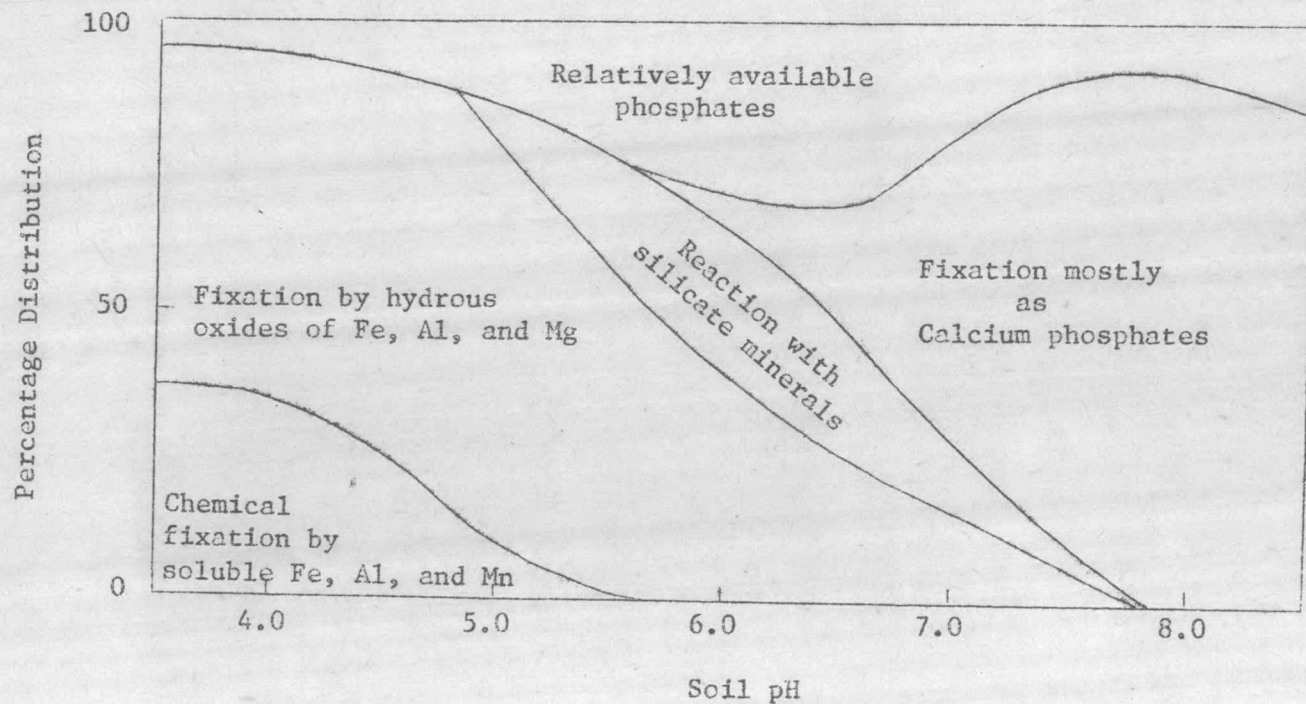


Figure 1.1 Inorganic Fixation of Added Phosphates at Various Soil pH values.



1.1.3 Form of Chlorine in Soil.

Chlorine has only recently been found to be essential for plant growth, in spite of the fact that it is used in larger quantities by most plants than any of the micronutrients except iron. Most of chlorine found in soils is in the form of simple soluble chloride salts such as potassium chloride.

1.2 Surface Charge on Soil Colloidal System.

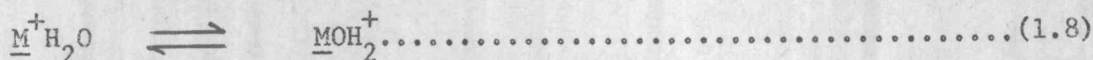
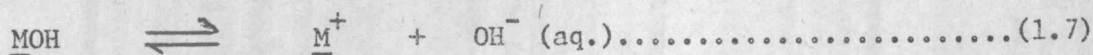
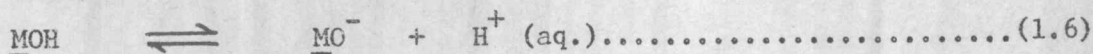
Soil colloidal systems are composed of two distinct types, inorganic and organic, which exist in intimate intermixture. The inorganic component is present almost exclusively as clay minerals of various kinds. Two groups of inorganic clays are recognized as silicate clays and iron and aluminum oxides. The organic fraction is represented by humus. Since the soils in the tropics contain very small amount of organic colloids, the attention will be focused initially on inorganic fraction. It may be classified as weathered fragments of original soil minerals and as new formations. These new formations exist as more or less dehydrated gels inclosing the original mineral particles. The gels do not obey the law of definite chemical composition but should be pictured as complexes of variable compositions altering in structure and behaviour with the ions in the soil solution. The gels may be hydrous oxides of iron, aluminum or silica. The first two oxides do not possess any appreciable cation exchange power, but do retain certain anions over a wide range of hydrogen ion concentration (9). The adsorption of anions by the oxide gels, which can function as acidoids, imparts to the gels new properties. Surface charge characteristics of soil colloids fall into two types, these are the constant charge or permanent charge and constant potential or pH-dependent charge types.

1.2.1 Characteristics of Constant Charge, Variable Potential Surfaces.

The charges on soil colloids may result from either structural imperfections in the interior of the crystal structure or preferential adsorption of certain ions on particle surfaces. Structural imperfections, due to isomorphous ion substitutions of tetrahedrally or octahedrally coordinated cations or site vacancies, frequently result in a permanent charge on soil colloid particles. This type of colloid, which has a completely polarizable interface, is considered to have a constant charge-variable potential surface. Such colloids occur frequently in 2:1 type clay minerals such as montmorillonite, micas, etc. The charge resulting from a given ion substitution may, theoretically, be either positive or negative. However, in the case of 2:1 type clay minerals which consist largely of Si^{4+} or Al^{3+} in tetrahedral coordination, and Fe^{3+} , Fe^{2+} , Al^{3+} and Mg^{2+} in octahedral coordination, ion size limitations generally result in a substitution of cations of lower valence for those of higher valence resulting in a net negative charge on the clay structure (10,11).

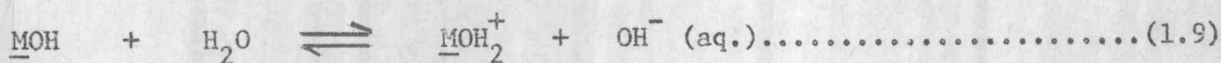
1.2.2 Characteristics of Constant Potential, Variable Charge Surfaces.

Constant potential or variable charge surface of soil colloid usually occurs in 1:1 type clay minerals, amorphous colloids, and hydrous oxides of iron or aluminum. Hydroxylated surfaces, resulting from chemical adsorption of water as it is dissociated into H^+ and OH^- during adsorption, can be expected on all oxide minerals at equilibrium with an aqueous environment. Charge can develop on these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- . These reactions, according to Parks (12), can be shown as follows :



where under-scored symbols refer to species forming part of the surface.

Since the probability of $\underline{\text{M}}^+$ existing at the surface is small, the basic dissociation or formation of a positively charged site probably occurs through a combination of the reactions shown in Eq. (1.7) and (1.8)



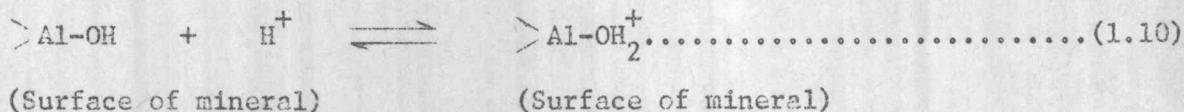
In both of the above mechanisms (Eq. (1.6), (1.9)), the H^+ and OH^- which establish the surface charges are also those which would establish the potential of a reversible oxide and hydroxide electrodes and hence are referred to as potential determining ions (PDI). Concentrations of the PDI and the net surface charge are obviously pH dependent and there will be a pH value at which the net surface charge is zero, that is when the amounts of positive and negative charges are equal. This pH is referred to as the isoelectric point (IEP) or zero point of charge (ZPC) of the solid. Since the net charge on such surfaces is dependent on the H^+ or OH^- activities, it can be made positive or negative by raising or lowering the pH. The charge developed by association or dissociation of H^+ or OH^- on oxide surfaces in the absence of a supporting electrolyte is balanced by the dissociated H^+ or OH^- themselves. However, excess negative or positive charges can be developed on oxide surfaces by the addition of HCl or NaOH and subsequent adsorption of H^+ or OH^- . The resulting surface charge is balanced by the added Cl^- or Na^+ . These counterions will diffuse into the surrounding medium forming a diffuse double layer in the aqueous phase near the oxide surface.

Soil in the temperate region tends to be dominated by the crystalline or constant charge clay minerals of some silicate clays while the high oxide content of many extensively weathered tropical soils result in a dominance of oxides or hydrous oxides which have pH-dependent charge surfaces (7).

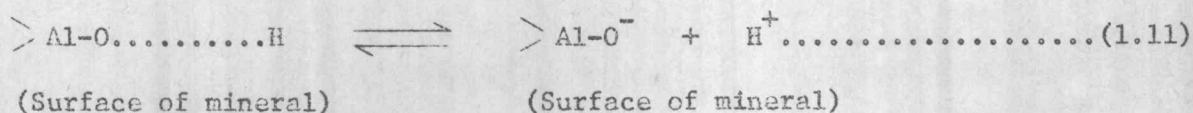
1.2.3 Sources of Positive Charges on Oxide Surface.

Nyle C. Brady (8) stated that under certain conditions colloids of the constant potential type; kaolinite, allophane, and hydrous oxides of Fe or Al, show evidence of having positive charges on their crystal surfaces. These charges are thought to have two sources : one is the protonation or adding of hydrogen ions to hydroxyl groups on the edge of these minerals, the other is the exchangeable hydroxyl groups for other anions.

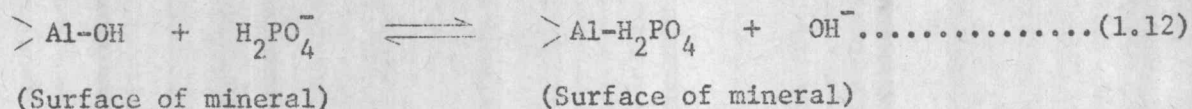
The protonation reaction can be explained by the following equation:



At low pH values, hydrogen ion tends to attach with the hydroxyl, giving rise to a net positive charge. These charges will attract anions such as H_2PO_4^- , SO_4^{2-} , NO_3^- and Cl^- . These anions are able to exchange with each other, giving rise to the term anion exchange. As the pH is higher, hydrogen ion tends to detach from oxygen, leaving a net negative charge on the surface of a colloid as shown below :



The mechanism of exchangeable hydroxyl groups for other anions, such as H_2PO_4^- can be explained by the following equation :



The reaction shown above always occurs at low pH, the negative hydroxyl ion is replaced by orthophosphate ion. By one of the two of these mechanisms; SO_4^{2-} , Cl^- and NO_3^- as well as H_2PO_4^- become adsorbed by allophane, the hydrous oxides, and kaolinitic group.

1.3 Anions Adsorption on Soils.

Anion adsorption becomes a particularly important feature in soils containing oxide minerals, and kaolinitic groups of clay mineral. It is now generally believed that anions can be adsorbed on these colloid surfaces in one of the two mechanisms as previously mentioned. They are termed non-specific and specific adsorption which are described below.

1.3.1 Non-Specific Adsorption of Anions.

Any permanent or pH-dependent charges on mineral surfaces must be balanced by an equivalent quantity of oppositely charged counterions. These counterions, held by electrostatic or coulombic forces, are located in either the Stern or Gouy-Chapman diffuse part of the electrical double layer. Adsorption of such an ion is generally termed non-specific (13,14). In a multicomponent system of equal valence ions, they are adsorbed in a simple proportion to their equilibrium activity in solution. Examples of such ions would be the anions Cl^- , NO_3^- , ClO_4^- . In this particular situation, replacement of one ion by another at constant ionic strength would not change the electrophoretic mobility of the particles. The definition of non-specific adsorption can be extended to include the effect of ion size because the size, defined as distance of closest approach to

the surface, of the ion will determine the potential distribution in the diffuse layer and hence the distribution of counterions.

1.3.2 Specific Adsorption of Anions.

In contrast to non-specific adsorption, some anions are held much more strongly by the oxide surface because these ions penetrate the coordination shell of Fe or Al atom, exchange their OH and OH₂ ligands with, and are bound by covalent bonds directly via their O and OH groups to the structural cation (14, 15, 16). This type of adsorption in the potential determining layer has been termed chemisorption or specific adsorption. Such specific adsorption of anions occurs irrespective of the sign of the net surface charge and in quantities out of proportion to their concentration or activity (17). Adsorption is relatively insensitive to the change in the ionic strength indicating that it is not directly affected by the properties of the diffuse double layer (13). It is further characterized by the ion adsorbing on neutral surfaces and surfaces with a charge of the same sign as the ion. These ions will reverse the sign of the surface charge which non-specifically adsorbed ions do not. Specific adsorption can theoretically occur for any anion capable of coordination with the surface metal anions. However, since oxygen is the ligand commonly coordinated to the metal ions in soil minerals, the oxyanions are particularly involved in such reactions with phosphate being the anion of greatest significance from an agricultural standpoint. In soils, this type of adsorption is generally limited to mineral surfaces where oxygen atoms are only partly coordinated such as the surfaces of oxides and broken edges of the layer silicates; i.e. it

does not occur on the planar surfaces of layer silicates.

Plots of the amounts of anion specifically adsorbed vs. equilibrium solution concentrations at a given pH commonly show adsorption isotherms having a shape similar to that for Langmuir isotherms as shown in Fig. 1.2 for the adsorption of pyrophosphate by goethite taken from Hingston (18). Maximum anion adsorption can be calculated from the adsorption data using the Langmuir equation.

$$m = \frac{kbc}{1+kc} \dots\dots\dots(1.13)$$

Rearrangement of equation (1.13), giving a linear form below,

$$\frac{1}{m} = \frac{1}{b} + \frac{1}{bkc} \dots\dots\dots(1.14)$$

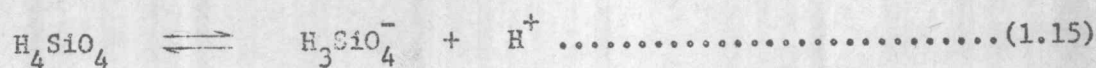
m is the amount of sorbed anion in meq/100g of soil

b is the sorption maxima

c is the anion concentration of the equilibrium solution

k is the constant

These adsorption maxima have been plotted vs. pH to obtain curves referred to as adsorption envelopes (13, 18, 19). Examples of adsorption envelopes for silicate and pyrophosphate are shown in Figs. 1.3, 1.4 (15). In the case of silicate, which behaves as a monobasic acid, the following dissociation reaction is suggested :



The adsorption maximum occurs at approximately $pH = pK_a$ where $K_a = \frac{(H_3SiO_4^-)(H^+)}{(H_4SiO_4)}$ with adsorption falling off rapidly at lower and higher pH's.

Bowden et al. (20) have proposed an explanation for the observed adsorption maximum near the point where $pH = pK_a$, based on the relative

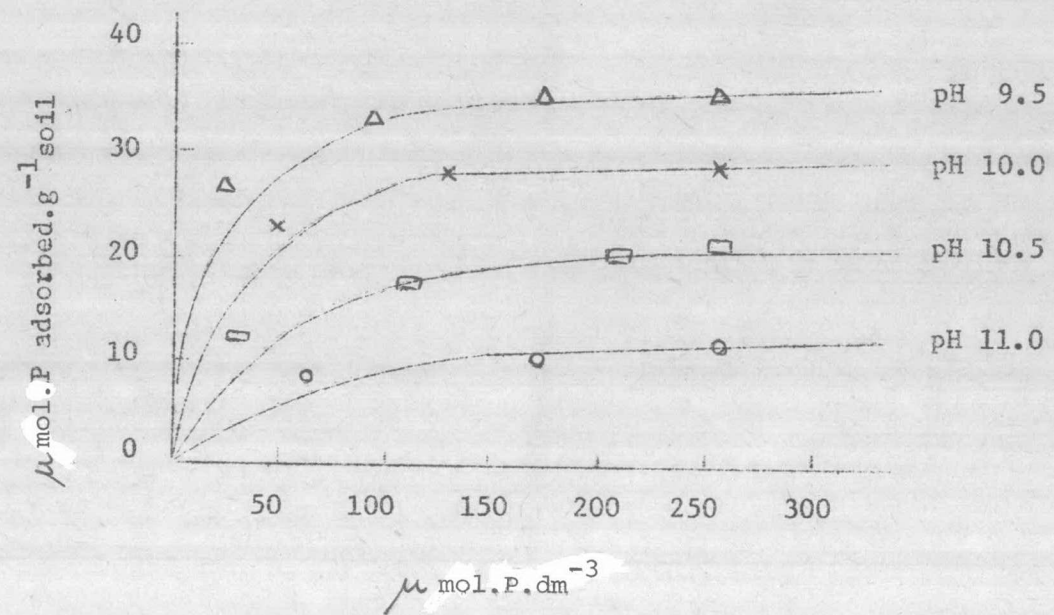


Figure 1.2 Adsorption of Pyrophosphate by Goethite

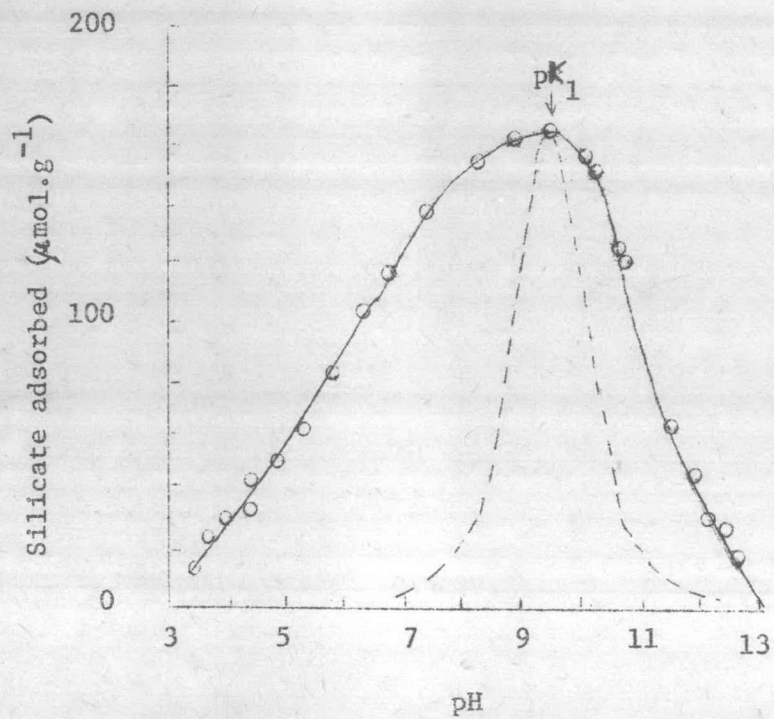


Figure 1.3 Adsorption of Silicate by Gibbsite at Different pH Values.

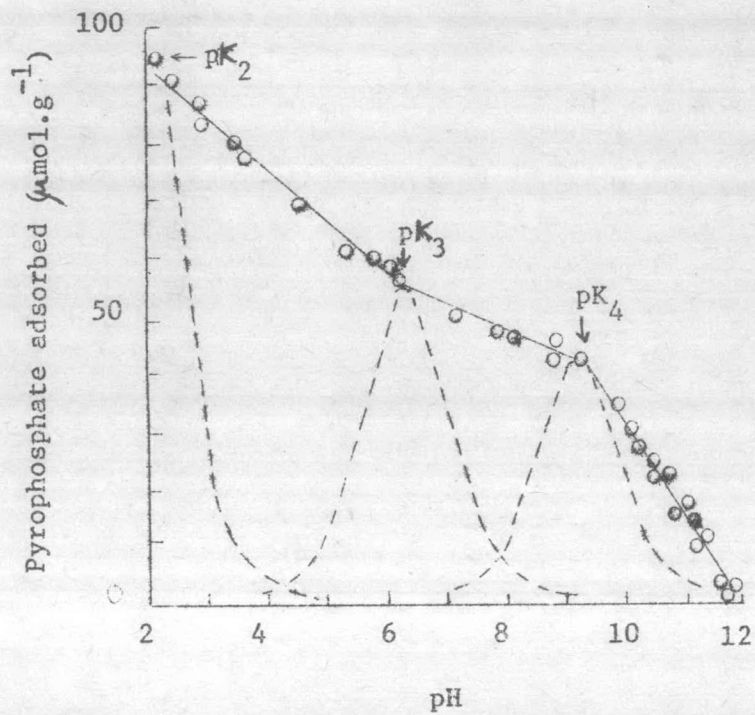


Figure 1.4 Adsorption of Pyrophosphate by Goethite at Different pH Values.

effect of pH change on the concentration of ionic species being adsorbed and the surface charge of the oxide surface. As the pH increases toward pKa, there is a more rapid increase in the number of adsorbing species than in the rate of decrease of positive charge on the surface. As a result, adsorption increases with increasing pH until the pKa is reached. Beyond this point, the surface tends to become increasingly negative at a rate greater than the rate of dissociation of uncharged molecules to form the adsorbing species. Consequently, maximum adsorption tends to occur at approximately the point where $\text{pH} = \text{pKa}$.

1.4 Factors Affecting on Anion Adsorption.

Tropical and other soils with high iron and aluminum oxides or 1:1 type clay minerals have high anion adsorption capacities (6). The amount of anion that may be adsorbed is important from the point of view of anion storage in the profile as means of avoiding losses in soils of the humid areas or during rainy season of subhumid areas and its effects on anion availability to plants. From the studies of Schofield (21), Kamprath et al. (6), and Chang and Thomas (22), adsorptions of anions apparently are limited to such soils because they have a very low negative charge and a high number of reactive sites on hydrous aluminum and/or iron oxides. There are many factors influencing the anion adsorption. These are described below :

1.4.1 The pH of the Equilibrium Solution.

The pH of the soil system has the most important effect on the amount of anions retained because the charges of these colloids are

pH-dependent. Anions retention usually increases in an approximately linear manner, as the pH of the system is decreased (6, 23, 24). At pH values above 7, essentially no anions are retained. The pH effect has been ascribed to the neutralization of hydroxyl groups replaced by added anions (23) and to the formation of anion retaining sites by proton adsorption (25).

1.4.2 Concentration of Anion in Equilibrium Solution.

At a given pH, increasing in the concentration of anions in solution has been shown to give an increase in anion retention. In many cases this relation may be described by one of the well-known adsorption isotherms; Langmuir, Freundlich, and others. The amount of anion adsorbed and maximum anion adsorption at a given pH can be calculated from the Langmuir equation as previously mentioned. Anion adsorption in concentrated solutions is difficult to measure and it is found to be considerably higher than results usually obtained with lower salt concentrations. This implies that concentration effect remains important even at a high concentration. This would be expected if there are an almost infinite number of adsorption sites compared to the number of anion adsorbed.

1.4.3 The Cation Associated with Anion.

The association of cation with the system has an appreciable effect on the adsorption of the anion. It has often been indicated that a clay system containing divalent cations adsorbs more anions than does one having monovalent cations. Verwey and Overbeek (26) found that the reflection of the effective negative charge around a colloid is extended farther when

the clay is saturated with monovalent cations than when saturated with polyvalent cations. Hence anions are screened from clay surfaces when clays are saturated with monovalent cations.

1.4.4 Effect of Time on Anion Adsorption by Soils.

Chang and Thomas (22) showed that anion retention by soils is rapidly increased at the initial stage up to a few days, followed by a slower adsorption with a linear increase up to 5 weeks.

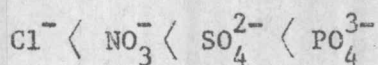
1.4.5 The Types of Various Soil Components.

Because of anion retention by soil is a surface phenomenon associated with the solid phase of soil systems. Of the solid soil constituents, hydrous Fe and Al oxides are the most dominant species. In acid range, the amount of anion adsorbed is essentially proportional to the amount of hydrous Fe or Al oxides present. The soils, which contained predominantly 1:1 type clay minerals and which are generally associated with a high content of free iron and aluminum oxides, adsorbed more anion than the soils which contained predominantly 2:1 type clay minerals (6).

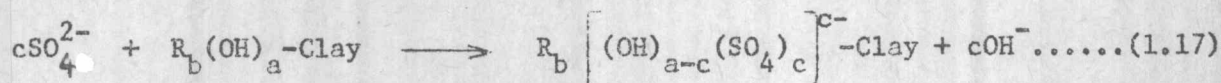
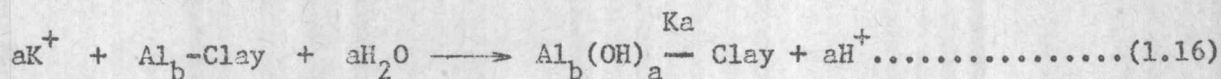
1.5 Mechanism of Anion Adsorption by Soils.

Mattson (27) showed that at low pH certain soils can retain anions such as chloride, sulphate and phosphate. He therefore concluded that soil colloids may also exhibit a weak basic character. From the studies of effect of anion retention, many workers proposed mechanisms of the reactions and explained the observations made. Overstreet and Dean (28) postulated that the mechanisms by which Cl^- , SO_4^{2-} and PO_4^{3-} are retained in an acid soil

are similar, Kunin and Meyers (29) showed that the order of increasing adsorption of mineral acids by a hydroxyl form of amberlite was



Barber and Rowell (30) stated that the increase in pH caused the increase in negative charge and decrease in positive charge. They claimed that this could be adequately explained by proton transfer on the iron oxide and kaolinite surfaces. They also found that an increase in electrolyte concentration would increase both the positive and negative charges at all pH values. Chang and Thomas (22) proposed a mechanism for sulphate adsorption and they believed that the mechanism of Cl^- and NO_3^- adsorption is very similar. A mechanism is divided into cation and anion reactions. For an easier inspection, it is presented as below: A homoionic Al-saturated clay with coatings of hydrous oxides of R(Fe or Al) is assumed.



Sites for K^+ adsorption in acid soils arise from exchange and/or hydrolysis of Al^{3+} on the clay surfaces. The product of Al^{3+} hydrolysis which is able to go into solution is H^+ . At the same time SO_4^{2-} replaces OH^- from $\text{R}(\text{OH})$ coating on the clay and substitutes for them. The replaced hydroxyl ions react with the H^+ . Whether the resulting pH of the system would be lowered or raised depends on the relative rates of the two reactions: hydrolysis and OH^- exchange. The proposed mechanism explains the observed phenomena as follow. Sulphate adsorption increases as the pH is lowered because the replaced hydroxyl ions are more effectively neutralized. An increase in cation affinity causes the replacement of more Al^{3+} and results in more hydrolysis. Similarly, the time effect

can be explained by the continuation of Al^{3+} hydrolysis, which produces H^+ , neutralizes hydroxyl ions, and carries the reaction towards completion. It has been shown that Al^{3+} in solution decreases with time when salt is added to soil. Hydrolysis, therefore, must occur while the pH of the system remains constant. It seems reasonable that the H^+ produced by hydrolysis are neutralized by replaced OH^- . Thus, the sum of cations (and anions) in solution is continually reduced as long as hydrolysis proceeds.

1.6 Applications of Adsorption Isotherm Technique.

Adsorption isotherm technique has been used to determine the soil requirements of some nutrients, especially the phosphate, in the past few years. Beckwith (31) measured sorbed phosphate at standard supernatant concentrations of P as an estimate of the phosphate need of soils. The standard value chosen from the experiments was $0.2 \text{ mg} \cdot \text{dm}^{-3}$ based on the assumption that successful growth of plants in soils would require a P concentration of approximately this magnitude in the soil solution. He recognized that the critical concentration would almost certainly vary somewhat among soils, as well as for different crops. When values for phosphate sorbed are plotted against log P remaining in the equilibrium soil solution, approximately straight line curves are obtained. The example of phosphorus sorption isotherm of selected Ultisols profiles derived from different parent materials, according to Juo and Fox (32), are shown in Fig.1.5. The slope of these curves gives an information about phosphate buffering capacity of the soils (33). The intercept at zero phosphate sorption is an estimate of phosphate in the soil solution, a value which seems to be better related to plant growth than phosphate potential

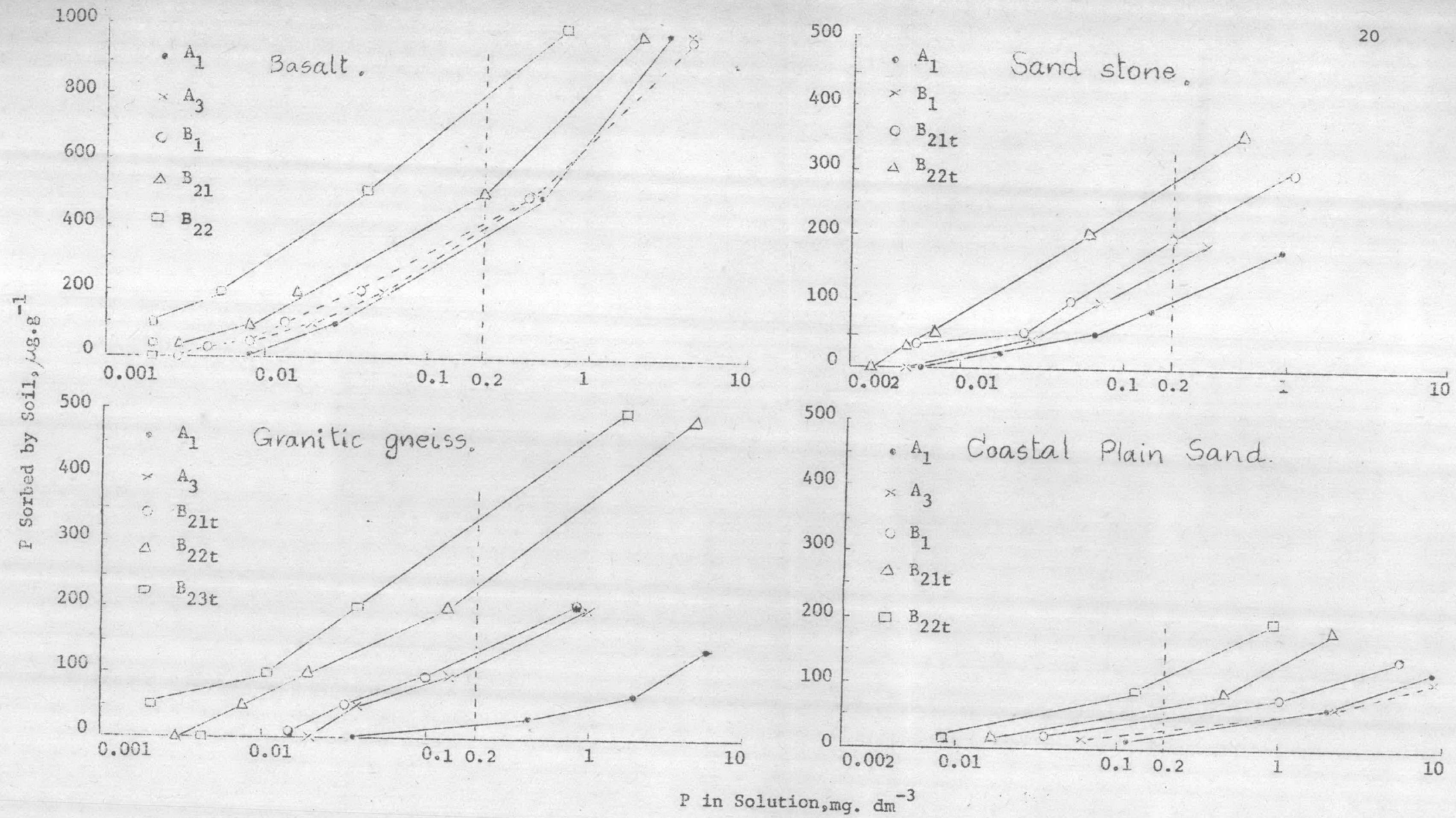


Figure 1.5 Phosphorus Sorption Isotherms of Selected Ultisol profiles derived from Different Parent Materials.

(34). Amounts of phosphate required to attain desired levels of P in the equilibrium solution can be read directly from the graph.

Ozanne and Shaw (33) indicated distinct advantages of phosphate sorption tests over the older extractant methods for soil phosphate and they have used phosphate sorption curves to estimate the amount of P required for wheat. Fox and Kamprath (35) showed that concentration of P in soil solution gives useful information about P nutrition, since concentration gradients provide the driving force for moving P to roots and, in addition, since P uptake by roots is concentration dependent. Although other variables influence the flux of P to root as well (36), but concentration of P in solution is the overriding factor since, by adjusting soil solution concentration to a standard level, P nutrition of an indicator plants is reasonably constant. Prediction of requirements for P fertilizers on soils using phosphate sorption isotherms has been successfully made by taking into account both intensity and capacity factors. They evaluated P requirements of soils for growing millet and established P levels for corn, sweet potatoes.

Fox et al. (37) and Jones and Benson (38) demonstrated the utility of phosphate sorption curves for evaluating residual effects of phosphate fertilizers and their usefulness in transferring soil management information among soils with different mineralogy. Fox and Kang (39) showed that phosphorus sorption curves, used in conjunction with external P concentration requirements, are effective tools for predicting the P fertilizer requirement of a given crop. Furthermore, if information on P sorption is collected in a systematic manner, or if the soils investigated can be fitted into a soil map, phosphorus requirement maps can be constructed as long as past management practices that

influence phosphate sorption remain reasonably uniform. Juo and Fox (32) showed that the quantity of P required to attain a standard P concentration in a solution equilibrated with the soil (or standard P requirements) as shown in Table 1.1, is a useful statistics for comparing soils of widely varying properties with parent materials. Hasan et al. (40) used sorption isotherm technique to determine sulphate requirements for Kikuya grass. In the case of chloride, none of the application of the adsorption isotherm technique is used.

Table 1.1 Classification of the Soils According to Phosphorus Sorption.

Standard P requirement $\mu\text{g P.g}^{-1}\text{soil}$	Scale	Usual mineralogy encountered
< 10	very low	quartz, organic materials
10 - 100	low	2:1 clays, quartz, and 1:1 clays
100 - 500	medium	1:1 clays with oxides
500 - 1000	high	oxides, moderately weathered ash
> 1000	very high	desilicated amorphous material