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REACTION MECHANISMS OF PHOSPHATE WITH $Al(OH)_3$ AND A SANDY SOIL

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REACTION MECHANISMS OF PHOSPHATE WITH $Al(OH)_3$ AND A SANDY SOIL

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
hoogleraar in de organische scheikunde,
in het openbaar te verdedigen
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des namiddags te vier uur in de aula
van de Landbouwhogeschool te Wageningen.

STELLINGEN

1. De interpretatie die Ryden et al. geven aan hun metingen van de fosfaat adsorptie aan een ijzer oxide gel is op essentiële punten strijdig met deze metingen.

   J.C. Ryden, J.K. Syers, and J.R. Mc. Laughlin, 1977. J. of Soil Science, 28: 62 - 71.

2. Het model voor de elektrische dubbellaag aan het grensvlak $Al(OH)_3$-elektrolyt oplossing zoals geformuleerd door Stol is niet geldig voor het plaatoppervlak van gibbsiet (γ-$Al(OH)_3$).

   R.J. Stol, 1978. Proefschrift, Rijks Universiteit Utrecht.

3. De mathematische formulering van de adsorptie van fosfaat aan oxiden zoals gegeven door Bowden, is niet in overeenstemming met het algemeen en ook door hem geaccepteerde adsorptie mechanisme voor fosfaat. Deze discrepantie is onnodig en ongewenst.

   J.W. Bowden, 1973. Proefschrift, Universiteit van West Australië.

4. Het verdient aanbeveling om naast de bestudering van de binding van individuele metalen aan humus- en/of fulvo-zuren, ook systemen te bestuderen waarbij concurrentie van verschillende metalen om dezelfde bindingsplaats optreedt. Met name de wisselwerking van Al of Fe en andere metalen met humus-/fulvo-zuren is uit het oogpunt van de bodemverontreinigings problematiek van groot belang.

5. Het regelmatig schrobben van de eigen stoep is vooral in gebieden met een hoge verkeersintensiteit, uit een oogpunt van de volksgezondheid sterk aan te bevelen.

   M.G. Keizer en W. van Vark, 1979. Verslag no. 2 Loodonderzoek Arnhem. Landbouwhogeschool, Wageningen.

6. Verondersteld moet worden dat de stelling: "Verder uitstel van de Wet op de Bodembescherming zal automatisch leiden tot afstel van deze wet", iets anders zegt dan wordt bedoeld.

   J. Beek, 1979. Proefschrift, Landbouwhogeschool, Wageningen.

7. Onderzoek dat gericht is op het verhogen van het elementredement van fosfaatbemesting is nog steeds van groot belang.

   A.C. Schuffelen, 1975. Landbouwkundig tijdschrift, pt 87-3.

8. De aanwezigheid van biodynamische veeteeltbedrijven op Terschelling biedt een goede gelegenheid om het elementrendement van fosfaatbemesting voor verschillende bedrijfssystemen te onderzoeken.

   R. ten Siethoff, 1979. Vruchtbare Aarde no. 3, Ned. Ver. tot bevordering der biologisch-dynamische landbouwmethode (p. 5 - 7).

9. Een aanzienlijk betere isolatie dan overeenkomstig de thans geldende voorschriften voor de woningbouw is technisch mogelijk en economisch aantrekkelijk.

   J.A. van de Vondervoort, 1978. Woningraad no. 5 (p 1 - 6).

10. "Small is Beautiful", geldt ook voor het composttoilet.

    E.F. Schumacher, 1973. Small is beautiful. Blond and Briggs. London.
    H.H. Leich, 1979. Compost Science - Land Utilization March/April (p 12 - 13).

Proefschrift, Willem Henri van Riemsdijk
'Reaction mechanisms of phosphate with $Al(OH)_3$ and a sandy soil'
Wageningen, 7 november 1979.

WOORD VOORAF

Het gereedkomen van dit proefschrift biedt de gelegenheid om hen die hebben bijgedragen aan de totstandkoming ervan te bedanken.

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Frans Weststrate, Cees van Rijn, Gosse Schraa, Theo Scheffers, Leo Boumans, Ton Roeloffzen, Bart Eshuis en Hubert Timmenga.

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The investigations described in this thesis have been (or will be) published with minor modifications in the form of the following papers:

Chapter 2: 'The reaction of phosphate with aluminum hydroxide in relation with phosphate bonding in soils'.
W.H. van Riemsdijk and J. Lyklema.
Colloids and Surfaces, I. (in press).

Chapter 3: 'Reaction of phosphate with gibbsite ($Al(OH)_3$) beyond the adsorption maximum'.
W.H. van Riemsdijk and J. Lyklema.
J. Colloid Interface Sci. (in press).

Chapter 4: 'Phosphates in soils, treated with sewage water; III kinetic studies on the reaction of phosphate with aluminum compounds'.
W.H. van Riemsdijk, F.A. Weststrate and J. Beek.
J. Environ. Qual. 6 (1977) 26.

Chapter 5: 'Phosphates in soils, treated with sewage water; IV Bonding of phosphate from sewage water in sand columns containing aluminum hydroxide'.
W.H. van Riemsdijk, J. Beek and F.A.M. de Haan.
J. Environ. Qual. 8 (1979) 207.

Chapter 6: 'Sorption kinetics of phosphate with an acid sandy soil, using the phosphato-stat method'.
W.H. van Riemsdijk and F.A.M. de Haan
Soil Sci. Soc. Am. Proc. (offered for publication).

CONTENTS

1. INTRODUCTION

1.1. General

Phosphate is essential for plant growth and hence it is not surprising that ca. 85% of the world production of phosphate ('ore', raw phosphate) is used to manufacture phosphate-containing fertilizers (McClellan, 1978). Another well-known use of phosphate ore is the production of tri(poly)phosphates. These phosphates are an important constituent of many presently used detergents. Roughly 5% of the world phosphate production is used for this purpose (Brinck, 1978). However, general public interest is nowadays more focused on the application of phosphates in detergents than it is on agricultural phosphate. Phosphate as such is benificial to life, but its excessive use may lead to serious problems of different kinds.

In the earlier stages of agricultural research, scientists were concerned with the problem of the low availability of soil phosphate. This problem was resolved by the application of highly soluble phosphate compounds. This was one of the factors contributing to a steady increase in the world food production. Recently, the eutrophication of surface waters has become a matter of great concern. The ensuing prodigious algal growth is mainly caused by the rise of the phosphate concentration in these waters. Extremely low phosphate concentrations, in the order of 0.3 - 2.0 $\mu mol.dm^{-3}$ may already induce a considerable algal growth (Brydges, 1978). Among the undesirable consequences that may occur, the decreasing suitability is mentioned of the water as a resource for commercial fishing, drinking water supply, recreation purposes etc.

The rise in the phosphate concentration is in general mainly caused by the discharge of sewage water into these surface waters. Phosphate can be removed from the sewage water by precipitation with aluminum, iron or calcium salts in a sewage treatment plant. The cost of this process, however, prohibits its use on a large scale sofar.

An additional problem is that the intensification of the production of live-stock, e.g. cattle, pigs and poultry, has created a situation in agriculture where in many cases far more phosphate is applied with the live-stock excreta than is necessary for efficient plant production. This excess problem is amongst others caused by the import of animal food from outside the farm and by the addition of mineral phosphate to the food. A large part of this phosphate eventually reaches the soil. Many soils have a large capacity to bind phosphate, but there are large variations and, in any case, the binding capacity is finite. Hence, prolonged (and high) application of phosphate may eventually result in leaching of phosphate, or its direct draining into surface water, leading to increased phosphate concentration in groundwater and surface waters.

A voluminous literature exists about phosphate reactions in soil. A selected fraction of this literature may be found in a review by Beek and van Riemsdijk, (1979). No generally accepted rate equations or reaction path ways of phosphate sorption have emerged up till now. Some authors divide the sorbed phosphate in different pools or compartments (Barrow and Shaw, 1975; Beek, 1979) while others do not make such a distinction (Enfield et al., 1976; Enfield, 1977).

In the 1950's it has been demonstrated that at high phosphate concentrations, c_p, several crystalline metal (Al or Fe) phosphates can be formed as a result of reaction with metal oxides or hydroxides or with soil (Haseman et al., 1950; -1951; Kittrick and Jackson, 1955; -1956). Some of these products were mixed Al-Fe-phosphates and various reaction products contained also Na or K or NH_4 as accompanying cation. Much emphasis has been laid on the equilibrium situation for these reactions (Lindsay et al., 1959). Although it was generally recognized that such equilibria would be slowly attained, little or no attention was paid to the rate of precipitation.

One of the problems involved in the study of phosphate reactions with soil, is the diversity of soils. A reaction mechanism that dominates in one soil may be absent in another. This may be caused amongst others by the fact that in soil Al or Fe can be present in different states. These states will occur in varying relative amounts for different soils and may be grouped as:

a) dissolved; this fraction is negligible, due to the low solubility of various Al (or Fe) containing minerals.

b) adsorbed to organic matter or clay minerals.

c) as a constituent of minerals, e.g. clay minerals, feldspars, hydroxides etc.

The reactivity with respect to phosphate sorption of the different forms in which Al(Fe) may be present will be different and also the sorption mechanism may be different. To illustrate this point the decrease with time of exchangeable phosphate as measured with ^{32}P in a peat soil, that contains a considerable fraction of extractable Al, is of a different order of magnitude as compared with the same in mineral soils (Larsen et al., 1965). Further it has been found that the reactivity with respect to phosphate sorption of amorphous synthetic aluminum silicates is much higher than that of amorphous $Al(OH)_3$ (Veith and Sposito, 1977). In

view of the complexity of soil systems and the importance for practice of having insight into the phosphate sorption mechanisms, it is surprising to find that only very few detailed studies on phosphate sorption exist in which well-defined pure systems were used.
Beek et al. (1976) found that aluminum is the major factor that contributes to phosphate sorption in an acid sandy soil. It is on this soil type that most of the intensive live-stock farms are found in the Netherlands. More insight into the basic reaction mechanisms may be of help to develop criteria for the amount of manure that may be safely applied to these soils. It may also be of help to indicate ways to develop more efficient phosphate fertilization procedures for soils with a high fixing capacity.

1.2 Adsorption of phosphate

Phosphate may sorb onto various (mineral) surfaces also from systems that are not supersaturated with respect to any solid phosphate mineral. In the last case the process may be identified as adsorption. However, many so-called adsorption studies were extended in the region of supersaturation, implying that in principle a precipitation mechanism may also have contributed to the total sorption.
Most authors try to describe their measurements either in terms of a Freundlich isotherm (Kuo and Lotse, 1974; Barrow and Shaw, 1975; Bache and Williams, 1971) or with a Langmuir isotherm. If one Langmuir isotherm is unsatisfactory for describing the experimental data, sets of two or three Langmuir isotherms have been proposed each with its own binding constant and adsorption maximum (Muljadi et al., 1966; Syers et al., 1973; Holford et al., 1974; Rajan and Fox, 1974). Barrow (1978) discusses using these adsorption equations for fitting soil phosphate sorption measurements. A problem arising when using the Freundlich equation may be the presence of adsorbed phosphate at the start of the experiment.
All these models are incorrect from a theoretical point of view since the surfaces onto which the phosphate adsorbs will in general carry a variable charge. This charge will vary as a function of the amount of adsorbed phosphate, pH, ionic strength etc. Recently several models have been put forward describing the charge and potential of oxides in simple electrolyte solutions (Levine and Smith, 1971; Wright and Hunter, 1973; Lyklema, 1968; Blok and de Bruyn, 1970). The models can be extended to describe adsorption of specifically adsorbed ions as well. Although these models are more in accord with reality, many uncertainties remain. For instance the capacitance of the 'Stern layer' is mostly determined by fitting experiment to model calculations, resulting in unrealistically high

values. Several explanations have been offered for these high capacitances but their real meaning remains a point of debate (Davis et al., 1978; Wright and Hunter, 1973; Bowden et al., 1977; Stol, 1978; Lyklema, 1971). A further point of discussion is the number of the equations used to describe the charging process (Stol, 1978; Wright and Hunter, 1973) and the assumed adsorption behaviour of potential determining ions in the absence of an electric double layer (Stol, 1978).

There is also much uncertainty about the occurrence and extent of adsorption of simple monovalent ions (Cl^-, K^+ etc.) in the Stern layer, that is often assumed to take place (Blok and de Bruyn, 1970; Stol, 1978; Davis et al., 1978; Yates et al., 1974).

The extension of simple models for phosphate adsorption is not straightforward. It depends on the assumed adsorption mechanism. Bowden (1973) describes the phosphate adsorption using a Stern adsorption model.

He furthermore assumes that the different phosphate species ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) have different binding constants that were determined by fitting experiments to the chosen model. However, if it is assumed that the phosphate ions are adsorbed by an exchange mechanism with singly coordinated hydroxyl or water groups as is often done (Atkinson et al., 1972; Parfitt et al., 1975; -1977) competition of OH and phosphate ions for the same surface sites has to be included in the model. Calculations with both types of phosphate adsorption models show that on a positive surface the phosphate adsorption increases with decreasing electrolyte concentration (Bowden, 1973; Van Riemsdijk, not published sofar).

A further development and testing of these models may help to increase the insight into the process of adsorption of ions from mixed electrolyte solutions onto these types of surfaces and is thus of great importance for the fields of soil fertility, soil pollution etc.

1.3 Precipitation of phosphate

Some aspects of the precipitation reaction have already been mentioned in 1.1. Recent literature suggests that the precipitation rate is constant if the pH and c_p value are kept constant (Chen et al., 1973a; Overman and Chu, 1977).Chen et al., (1973a) presume that the precipitation reaction is first order with respect to c_p, whereas Overman and Chu (1977) find that the rate is first order with respect to c_p and/or is first order with respect to the amount of adsorbed phosphate. In both cases the rate will be constant at constant c_p. Both groups of

authors report an increase in the precipitation rate with decreasing pH in the pH range 4 to 7.
In a recent publication Enfield et al. (1977) also state that the precipitation rate is first order with respect to c_p, in contrast with earlier publications by the same author.
To be able to make definite conclusions on the precipitation rate it would be appropriate to do measurements at constant c_p and pH over a considerable range of sorption in a region where the contribution of simple adsorption to the sorption rate would be negligible. The last condition can easily be met by measuring at high surpersaturation. The first condition is difficult to realize since no reliable phosphate ion selective electrode is presently available.

1.4 Outline of the investigation

This study was set up to contribute to the understanding of the reaction mechanisms of phosphate with different sorbents. Amongst others gibbsite, crystalline $Al(OH)_3$, was chosen. The structure of this mineral is well known (Schoen and Roberson, 1970), allowing a characterisation of its surface with respect to reactive surface 'sites' and surface area. This is of prime importance for the interpretation of the measurements in terms of adsorption and precipation.
A special technique was developped that has been used to study the reaction rate at constant supersaturation.

The arrangement of the presentation of experimental results, is not a reflection of the chronological order of the experiments. The experiments that use crystalline $Al(OH)_3$ as sorbent are described first. Then follows a description of experiments that were done to estimate the effect of somewhat different conditions on the phosphate sorption reaction (e.g. amorphous $Al(OH)_3$, complex ionic medium sewage water, sandy soil). These specific experimental conditions were chosen in order to be able to estimate the phosphate sorption capacity for certain field situations.

In chapter 2 phosphate sorption experiments are described with a well characterized $Al(OH)_3$ (gibbsite) in the c_p range of 10^{-7} to 10^{-2} mol/l. The experiments at high c_p were done with a so called phosphato-stat set up, that provides for both a constant c_p and pH during the sorption reaction. This method is described in detail in chapter 3, where the attention is focused on the mechanism of precipitation like reactions. In chapter 4 experiments are described with an X-ray amorphous $Al(OH)_3$ as sorbent and an inorganic synthetic sewage water medium as electrolyte solution. Chapter 5 deals with long-term column experiments. Two of the four colums used contained quartz sand while the other two consisted of a mixture of quartz sand with X-ray amorphous $Al(OH)_3$. The colums were 'treated' with raw sewage water (pH $\approx$ 8). In chapter 6 experiments are described using an acid sandy soil with a low organic matter content as sorbent. These experiments were done at constant supersaturation to be able to discriminate between different rate equations.

2. REACTION MECHANISM OF PHOSPHATE WITH GIBBSITE

The retention of phosphate in soils is to a large extent determined by insoluble metal-oxides. Model studies are described on the uptake and release of phosphate by gibbsite (γ-$Al(OH)_3$). At low phosphate concentration c_p, the uptake is a pure monolayer exchange adsorption on the edge surfaces of the gibbsite platelets. At high c_p and long reaction times t, a precipitate is formed on top of this adsorbate. Kinetic equations are given to discriminate between these processes.
Our analysis leads to arguments in favour of applying slow-release phosphate fertilizers. In addition the effect on the precipitation is analyzed of some ionic admixtures such as K^+, Na^+ and NH_4^+ that may be naturally present in or applied to the soil.

2.1 Introduction

Oxides of aluminum and iron have been recognized as important adsorbents for phosphate, even in calcareous soils (Holford and Mattingly, 1975). In addition, phosphate can adsorb on the edge faces of some clay minerals (Muljadi et al., 1966; De Haan, 1965), and on calcium carbonate. Phosphate may also bind to iron and aluminum ions that are themselves bound to organic matter or to clay platelets. At high phosphate concentrations c_p, precipitation of various aluminum, iron or calcium phosphates has been reported (Tamini et al., 1964; Taylor et al., 1965). However, some of these compounds can in principle already be formed at very low c_p. It is not feasible to locate the precise saturation limit because of uncertainties of the various solubility products involved. For wavellite ($Al_3(PO_4)_2(OH)_3.5H_2O$), which is one of the most insoluble aluminum phosphates at low c_p and pH (Nriagu, 1976), a boundary concentration as low as $c_p \gtrsim 1$ µmol.dm^{-3} can be calculated at pH 5 (Chap. 3). This implies that in most studies on phosphate adsorption on oxides the region of supersaturation with respect to at least one metal-phosphate phase may have been reached (Muljadi et al., 1966; Hingston et al., 1974; Helyar et al., 1976; Kuo and Lotse, 1974; Parfitt et al., 1977; Kyle et al., 1975; Rajan et al., 1974; Breeuwsma and Lyklema, 1973). However, experimentally it is very difficult to distinguish between adsorption and precipitation, at least for low and intermediate phosphate concentrations ($c_p \lesssim 10$ mmol.dm^{-3}).

Little agreement exists among various authors regarding the reaction time required to attain adsorption equilibrium. In the literature, values can be found varying between three hours (Rajan et al., 1974; Breeuwsma and Lyklema, 1973) and six to eight days (Kyle et al., 1975) with several authors settling for one to two days. Apparently, most authors consider the adsorption reaction to be quite slow. However, closer inspection of many observations indicates that also in these studies it is not only a simple adsorption process that has been measured. For instance, exchange experiments with radioactive phosphate showed that part of the reacted phosphate is exchanged slowly or not at all (Kyle et al., 1975; Vanderdeelen and Baert, 1971). It is also often found that the measured adsorption isotherm is not reversible with respect to c_p (Hingston et al., 1974). At pH 4 - 6, it has been observed that the phosphate sorption reaction does not reach an equilibrium state even after a few weeks reaction time (Helyar et al., 1976; Chen et al., 1973a; Van Riemsdijk et al., 1977; Van Riemsdijk and Lyklema, 1978) All of this is indicative of the occurrance of a slow precipitation process in addition to simple adsorption.

In this chapter research on the adsorption and precipitation of phosphate with gibbsite (crystalline $Al(OH)_3$) as the sorbent at pH 5.0 is reported, whereas the precipitation mechanism is discussed in more detail in chapter 3. The phosphate range studied is 10^{-7} to 2×10^{-2} mol.dm^{-3}.

The results will be shortly discussed with reference to the different problems encountered in practice as mentioned above. In particluar, attention will be paid to possibilities to discriminate between adsorption and precipitation processes and to the mechanisms by which phosphates are retained in oxide-containing soils (see also chapter 6).

2.2 Materials and methods

Most materials and methods used will be described in some detail in chapter 3. The adsorption was studied at pH 5.00 (pH-stat), under N_2-atmosphere, at 22 ^{o}C (thermostat) with various initial c_p, in a suspension of gibbsite in 0.1 mol.dm^{-3} NaCl.

2.3 General information on the reaction of phosphate with gibbsite

For the understanding of this chapter, the following information on the reaction between phosphate and gibbsite is indispensable.

The adsorption mechanism of phosphate with metal oxides is generally accepted as an exchange process with singly coordinated surface hydroxyl or water groups (Parfitt et al, 1977; Atkinson et al., 1972). Gibbsite crystals are platelike and the singly coordinated surface groups occur mainly on the edge faces of the crystals (Schoen and Roberson, 1970). A certain amount of these groups will also be present at the plate surface due to the presence of steps and other imperfections on this surface. The fraction of the total surface area exhibiting singly coordinated groups was estimated from shadowed electronmicrographs and amounted to 0.14 ± 0.03. With this figure, the maximum adsorption density of phosphate, Γ_m, can be calculated per total area. Using the cross-section of one phosphate molecule (0.235 nm^2) (Vissers, 1968) it amounts to 1.0 ± 0.2 $\mu mol.m^{-2}$. The amount of singly coordinated groups can be calculated from crystal parameters and it turns out that this 'site density' is about twice as high as the adsorption maximum for phosphate. Adsorption may thus be a mono and/or bidentate ligand exchange (Parfitt et al., 1977; Atkinson et al., 1972). The amount of phosphate reacted (sorbed) will be expressed per total (B.E.T.) surface area.

2.4 Results

2.4.1 Adsorption and monolayer kinetics

Sorption isotherms constructed for four different reaction times are shown in Fig. 2.1. With sufficient c_p and reaction time, the edge adsorption capacity is exceeded. This is not surprising since at these concentrations the suspensions are supersaturated with respect to for instance variscite ($AlPO_4.2H_2O$) and wavellite ($Al_3(PO_4)_2(OH)_3.5H_2O$) (Chap. 3). However, at low c_p and short reaction time t, the precipitated amount will be negligible, since the precipitation rate increases strongly with c_p (see eq. 2.2 below). Fig. 2.1 further shows that the adsorption after five minutes (first measurement) is independent of c_p and is equal to 0.46 ± 0.03 $\mu mol.m^{-2}$. Analysis of the experimental data (of Fig. 2.2) shows that the reaction rate for two experiments with low c_p is independent of c_p for the first few hours of the reaction, although c_p differs by as much as a factor of two during this time. Apparently, this first step may be identified as an adsorption. On the other hand, at longer reaction times the rate increases with c_p. This is logical because then precipitation starts to contribute significantly, the more so the higher c_p (see also following section 2.4.2). Thus, the analysis shows that:

a) Γ (initial) is independent of c_p;

b) the adsorption rate is only dependent on the surface coverage $\theta = \Gamma_a/\Gamma_m$,

where Γ_a is the phosphate adsorption density.
These results apply to systems in which Γ_m can be reached, given sufficiently long reaction time.

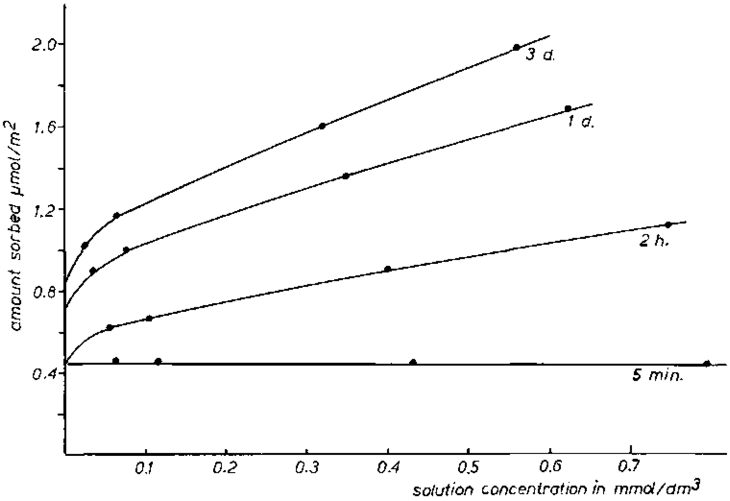


Fig. 2.1. Sorption of phosphate on gibbsite.
pH = 5.00; T = 22 °C. The reaction time is given.

Apparently, rearrangements of the adsorbate are the rate-determining step. For such a type of adsorption kinetics, Langmuir (1940) proposed the following equation:

$$(\Gamma_m - \Gamma_a)^{-2} = a + bt \qquad (2.1)$$

Here, a and b are constants, and Γ_a, Γ_m and t have been defined before. Linear regression analysis of our sorption data (choosing t < 5 hours for the experiment with the lower c_p and t < 1.5 hours for the other experiment) according to eq. (2.1) resulted in an excellent fit ($r^2 = 0.99$) for various trial values of Γ_m within a certain margin around the calculated maximum adsorption capacity. The concentration calculated to remain in solution was plotted for three values of Γ_m and one suspension concentration as a function of $\sqrt{t}$ and compared with the experimental data (Fig. 2.2). The time axis was chosen as shown, because in 0.1 M KCl the amount precipitated is found to be proportional to $\sqrt{t}$ (eq(2.2)). Moreover, in this way data for short and long reaction times can be plotted accurately in one diagram.

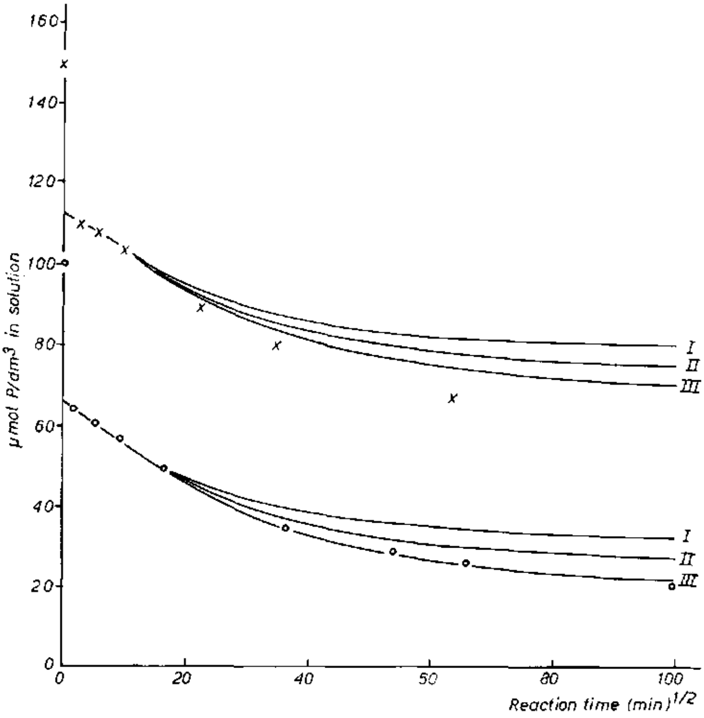


Fig. 2.2. The phosphate concentration in bulk for an initial concentration of 150 μmol.dm^{-3} (x) and for 100 μmol.dm^{-3} (o) with a suspension concentration of 1.8 g. dm^{-3}. The curves are calculated according to formula (1) with:
I. Γ_m = 1.0 μmol.m^{-2}; a = 3.88 x 10^{12}, b = 2.30 x 10^{10};
II. Γ_m = 1.1 μmol.m^{-2}; a = 2.91 x 10^{12}, b = 1.44 x 10^{10};
III. Γ_m = 1.2 μmol.m^{-2}; a = 2.16 x 10^{12}, b = 7.86 x 10^{9}.

Table 2.1 shows the calculated adsorbed fractions θ for various reaction times for the three different values of Γ_m considered. The table shows that for $\theta > 0.45$ the adsorption is very slow indeed. The computations leading to the curves of Fig. 2.2 are based on the presumption that Γ_m is determined by adsorption on singly coordinated OH(H) groups only. The excellent agreement between the Langmuir theory and the experiments strongly supports this mechanism.

The initial part of the adsorption isotherm was determined for a reaction time of one day (Fig. 2.3). A contribution of precipitation reactions to these sorption data may be excluded since precipitation is either impossible for these low c_p values or negligible due to slow rate at very low supersaturations (see also eq. (2.2)).

Table 2.1. The fractional saturation $\Theta = \Gamma_a/\Gamma_m$ at various times for the three different cases considered (see Fig. 3.2).

Time	Θ (I)	Θ (II)	Θ (III)
0	0.49	0.47	0.43
2 h.	0.62	0.58	0.53
1 d.	0.85	0.81	0.77
3 d.	0.91	0.89	0.86
6 d.	0.93	0.93	0.90
30 d.	0.97	0.96	0.95

These data are also in full agreement with the proposed adsorption mechanism. The fractional coverage of about 0.45 is already reached at $c_p \simeq 0.5\ \mu\text{mol.dm}^{-3}$. Beyond this coverage the slow process obeying eq. (2.1) starts.

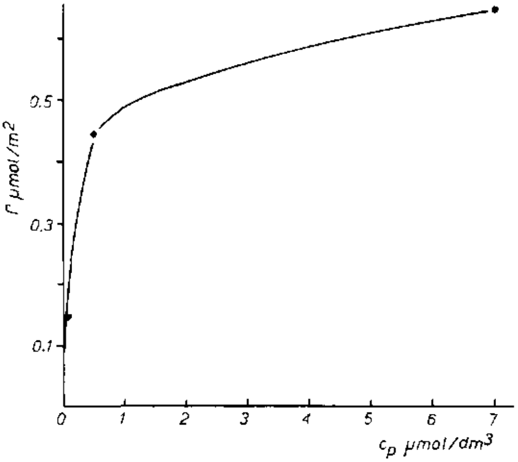


Fig. 2.3. Adsorption of phosphate on gibbsite in the low concentration range; pH = 5.00; T = 22 °C; Reaction time: 1 day.

2.4.2 Sorption beyond monolayer coverage

2.4.2.1 General experience

Several studies have been made on the interaction of metal oxides with phosphate under conditions conducive to precipitation, that is at high c_p (0.3 - 3 mol.dm^{-3}) (Tamini et al., 1964; Haseman et al., 1950; Kittrick et al., 1956). Such high c_p values may occur in practice near dissolving fertilizer granules. The main reason for undertaking these studies was the relatively low efficiency of the phosphate fertilizer. For instance, in pot experiments three successive croppings may use only 20 - 40% of the phosphate added as fertilizer (Taylor et al., 1963). In most of these studies, the emphasis has been on the identification of the crystalline phosphates formed. Several reaction products have been identified. Although in the systems studied the supersaturation with respect to several metal phosphates is tremendous and although some crystalline metal phosphates were identified, it is noteworthy that only a small fraction of the original oxide is transformed into the metal phosphate, even after prolonged reaction times (Tamini et al., 1964; Haseman et al., 1950). Literature experience shows also that the coarser the oxides the lower their reactivities. This suggests that some surface process is rate-determining in the precipitation. Unfortunately, the oxides used were in general not very well characterized, so that it is not possible to arrive at definite conclusions.

2.4.2.2 Experiments with $Al(OH)_3$

In chapter 4 it is shown that upon sorption beyond the exchange adsorption the surface of the gibbsite particles is transformed into an aluminum phosphate phase. The (integrated) rate equation that was found to describe this precipitation reaction in the presence of 0.1 mol.dm^{-3} KCl as the supporting electrolyte is:

$$\Gamma_p = 1.6 \times 10^{-5} \, c_p \sqrt{t} \qquad (2.2)$$

where Γ_p is the amount of phosphate precipitated (mol.m^{-2}) and where c_p and t are expressed in mol.dm^{-3} and minutes, respectively.

It is now possible to calculate the relative contributions of adsorption and precipitation if both processes take place concurrently (eqs. (2.1) and 2.2)). These contributions will be a function of t and c_p. The relative contribution of the precipitation reaction as a function of t for different c_p values is plotted in Fig. 2.4. This figure shows that, even at moderate phosphate concentrations, the precipitation reaction is already the dominant process from the very beginning. It is also evident that the precipitation process may contribute significantly for longer reaction times at low c_p.

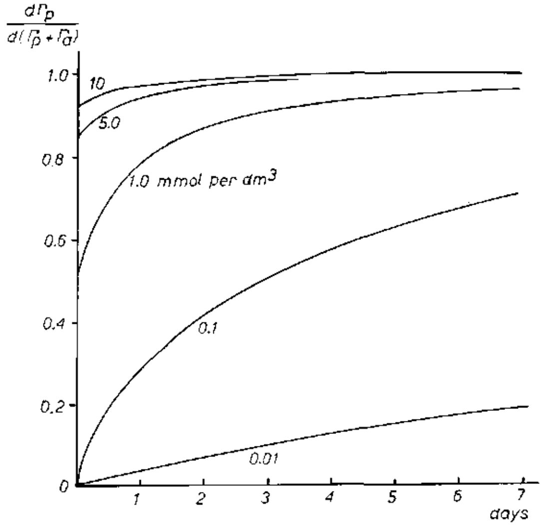


Fig. 2.4. Fractional contribution of precipitation to the total phosphate uptake by gibbsite for the values of c_p given (mmol.dm^{-3}); pH = 5.00; T = 22 °C.

It was shown (Van Riemsdijk and Lyklema, 1978) that the precipitation reaction exhibits a constant ratio of the amount of phosphate sorbed over the amount of hydroxyl produced during the reaction. This allowed the construction of the so-called 'phosphato-stat'. This set-up consists of an automatic titrator that keeps both the pH and the c_p constant during the reaction. This is a great advantage since the kinetics of the sorption reaction can now be studied at constant supersaturation; in other words: the influence of alterations of c_p on the rate of the precipitation can be eliminated in this way. It was furthermore shown that potassium ions are incorporated into the new surface phase and that the reaction rate is also a function of the potassium concentration.

Fig. 2.5 shows the difference between systems containing sodium, potassium, ammonium and rubidium ions measured as the phosphate sorption 'rate'. These measurements were obtained with the phophato-stat set-up. It turns out that the system with potassium and rubidium behave similarly. The ammonium system has initially the same rate as the potassium containing one, but it starts to lag behind at higher sorption values. The sodium containing system shows a very pronounced decrease of the reaction rate with increasing phosphate sorption.

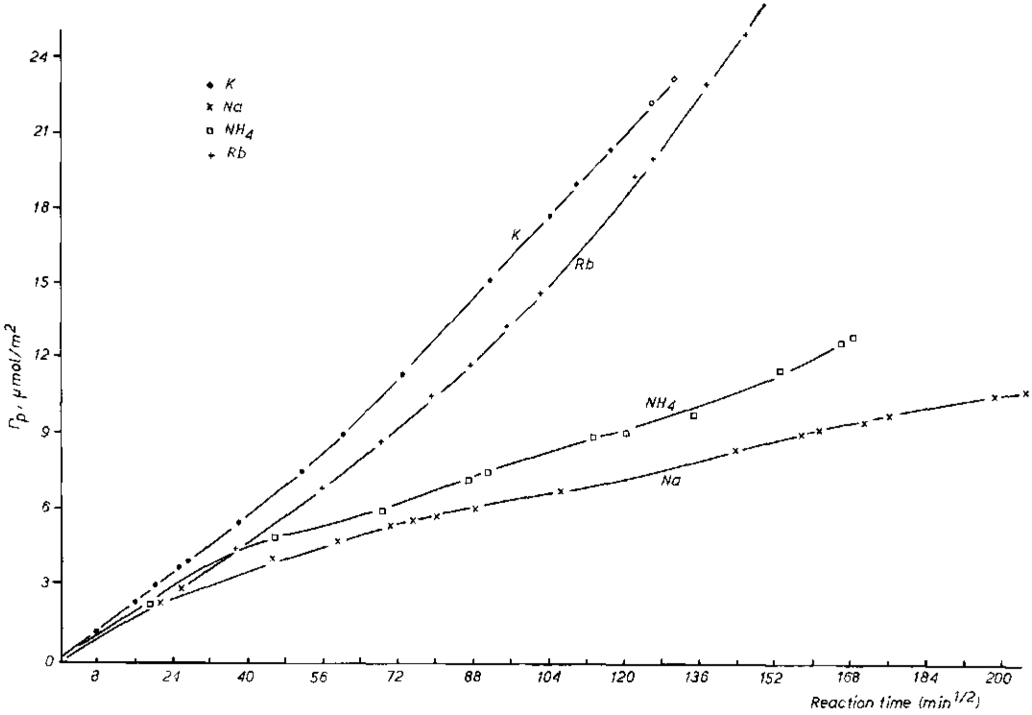


Fig. 2.5. Sorption of phosphate on gibbsite as a function of $\sqrt{t}$ in different electrolyte solutions; 100 mmol.dm^{-3} of the chloride salt of the cation indicated; the cation was common to the chloride and the phosphate except in the case of RbCl where NaH_2PO_4 was used; c_p constant at ≈ 9 mmol.dm^{-3} (phosphato-stat); pH = 5.00; T = 22°C.

The decrease of the reaction rate at constant supersaturation is caused by the formation of a protective surface layer of increasing thickness, through which diffusion has to occur to enable the reaction to proceed (Chap. 3). The physico-chemical nature of the new surface phase, e.g. its porosity and its electric surface potential, will thus to a large extent determine the kinetics of the reaction.

The mechanism of this type of reaction is in many respects analogous to the same for the oxidation of metals. A well-known example is the oxidation of aluminum. The oxidation rate is strongly reduced by the build-up of a thin coating. The oxide coating effectively protects the underlying metal from further oxidation.

2.4.3 Exchangeable phosphate at high Γ_p

The concentration of phosphate at the surface of the particles can be determined by subjecting the system to exchange with labeled phosphate, provided the system is in equilibrium and diffusion in the solid is negligible (Kolthoff, 1936; McAuliffe et al., 1947; Kukura et al., 1972). According to (2.2), the sorption process is never completed if it is due to precipitation. However, the sorption rate will become practically zero for long reaction time at a certain c_p (eq. (2.2)).

For the exchange experiments, samples were used that had per gram gibbsite 1.9 mmol phosphate, sorbed at pH 5.0 in 0.1 M KCl and $c_p = 14$ mmol.dm^{-3}, using the phosphato-stat technique. The samples had been stored under these conditions for a sufficiently long time to be practically in equilibrium. The exchange experiments were performed at several c_p obtained by diluting the original sample with 0.1 M KCl. Part of the exchange reaction was slow, but the exchange was complete after three days reaction time. The results are shown in Fig. 2.6. This figure corroborates the findings (Chap. 3) that the surface area increases as a result of the precipitation process, since the surface concentration should be less than ca. 7 μmol.m^{-2} (monolayer capacity). The surface concentration of phosphate per total surface area (measured after reaction with phosphate) is ca. 6 μmol.m^{-2} for the highest c_p value (Fig. 2.6). This value is close to the value for maximum surface coverage, implying that the entire surface present in the system contains exchangeable phosphate. This is in contrast to adsorption at low c_p, where phosphate resides mainly on the edge faces of the gibbsite crystals. The surface phase present at high sorption values consists of a K-Al-phosphate (Chap. 4).

The charge, the electric potential and the compsition of its surface will be determined by the concentrations of the 'potential determining ions', i.e. ions reacting with the particle and contributing to the surface charge density, such as K^+, HPO_4^{2-}, Al^{3+}, H^+ etc. This may help to explain the dependence of the exchangeable phosphate on c_p (Fig. 2.6). The average thickness of the potassium-aluminum phosphate layer can be estimated assuming this layer to be taranakite $\{H_6K_3Al_5(PO_4)_8 \cdot 18H_2O\}$. It amounts to ca. 2 nm (equivalent to a thickness of '5 layers'). The percentage of the total phosphate that is exchangable can also be calculated from these data; it amounts to 16 - 25%.

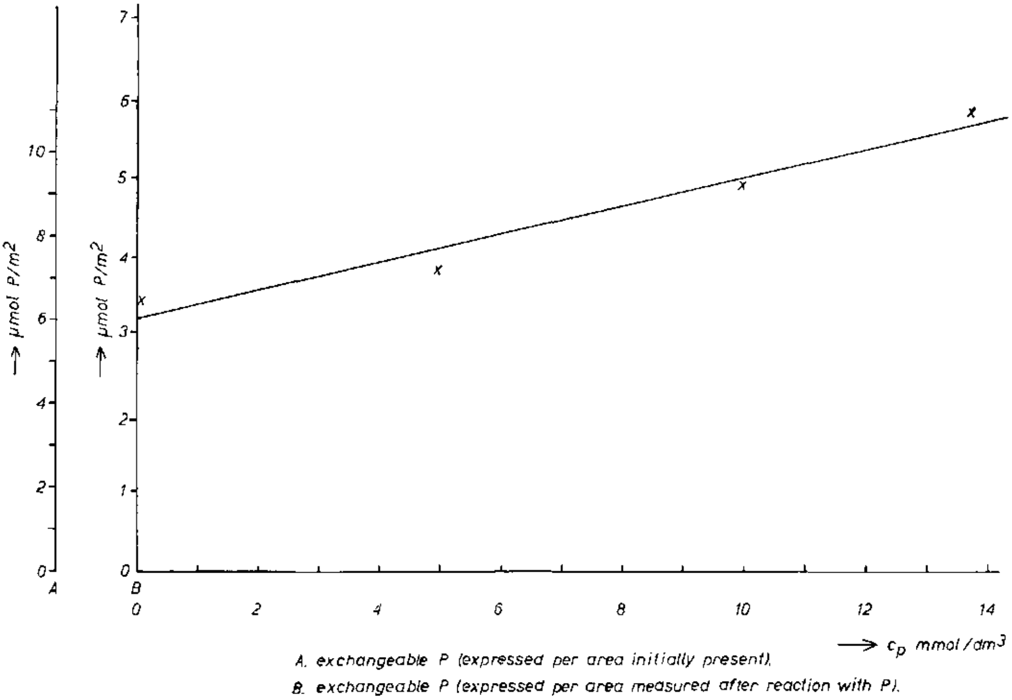


Fig. 2.6. The surface concentration of phosphate (μmol.m^{-2}) as determined with labeled phosphate for different c_p-values, for a sample that contained 1.9 mmol P per gram. The specific surface area of this sample was 81 m^2.g^{-1}

2.5 Discussion

The mechanism and the rate of the reaction of phosphate with oxides is of great importance. To be able to roughly compare some of the experimental conditions with practical situations table 2.2 is given. This table presents the average concentrations of several relevant elements in different materials, that are regularly applied to soil in high amounts.

Precipitation of phosphate ultimately results in the formation of very insoluble phosphate compounds. The rate, the extent and the reversibility of the different sorption reactions will determine the efficiency (recovery) of applied phosphate fertilizer. The present study shows that the precipitation rate is greatly enhanced by increasing the phosphate concentration. Concentrated admixtures of potassium and ammonium (also used in fertilizers and often inadvertedly present, (see table 2.2) enhance the precipitation rate even further. This precipitation will decrease the availability of the phosphate for agricultural or biological cycles, suggesting that slow release phosphate fertilizers might have a higher efficiency than the presently used highly soluble fertilizers.

Table 2.2. Average concentrations of various elements ($mmol.dm^{-3}$) in different slurries and sewage water calculated from literature. DM = dry matter content. About 20 - 50% of the phosphate will be organic phosphate, the remainder being orthophosphate.

	(ref)	NH_4	P	K	Na	Ca	DM%
cattle slurry	(a,b)	180	26	103	35	27	9
pigs slurry	(a,b)	340	52	69	48	40	7
poultry slurry	(c)	?	170	150	?	?	24
sewage water	(d)	1	0.3	1	6	2	?

(a) Kofoed, (1977). (b) Tunney, (1977); (c) Tunney, (1975); (d) Beek et al., (1977).

The results presented here show also that the precipitation rate decreases with increasing sorption. 'Fixation' problems are thus expected to become prominent for soils which contain a considerable fraction of reactive metal oxides and which have not received much phosphate fertilizer in the past, as is the case with many tropical soils.

2.6 Conclusions

a) In systems that are not supersaturated with respect to any aluminum phosphate the adsorption of phosphate with gibbsite is in agreement with an exchange adsorption with singly-coordinated OH(H) groups.

b) In the occupancy range $0.45 < \theta < 1$, adsorption is a slow process, independent of c_p. The kinetics of this reaction can be studied under very restricted conditions of c_p and t only, and appear to satisfy a rate equation proposed by Langmuir.

c) There is a transitional range of c_p and t where both adsorption and precipitation determine the reaction rate.

d) For $c_p > 5\ mmol.dm^{-3}$ precipitation is the rate-controlling process. It is diffusion-controlled and leads to the formation of a potassium containing aluminum phosphate that covers the gibbsite particles. The rate of this reaction follows a law distinct from that mentioned under b; it increases with increasing supersaturation and decreases with increasing amount reacted.

e) The precipitation rate depends on the nature and the concentration of the cations present in the system.

3. REACTION OF PHOSPHATE WITH GIBBSITE ($Al(OH)_3$) BEYOND THE ADSORPTION MAXIMUM

A study has been made of the interaction of dissolved phosphate with gibbsite ($Al(OH)_3$). The reaction was studied at a constant supersaturation with the help of a pH- and phosphato-stat. The phosphato-stat technique is described. The maximum exchange-adsorption capacity for phosphate is established. Measured sorptions exceed this adsorption capacity if the system is supersaturated with respect to an aluminum phosphate phase. The rate of this sorption increases with increasing supersaturation and is inversely proportional to the amount of phosphate that has been sorbed. This process is interpreted as a chemical precipitation reaction. The reaction product forms a coating on the original gibbsite particles. Due to this precipitation, the total surface area increases. Potassium, if present in the system, is part of the reaction product. The surface coating prevents the system to reach a thermodynamic equilibrium within several weeks. The activation energy of the reaction is determined.

3.1 Introduction

The interaction of orthophosphate (P) with dispersed, insoluble metal oxides is amongst others of interest in the field of soil fertility, geochemistry, medicine and environmental sciences. For instance, a detailed knowledge of the adsorption and other reactions at intermediate and low phosphate concentrations is a prerequisite for the development of reliable P-transport models describing the movement and retention of P through soils (Beek, 1979; Mansell et al., 1977). One of the main problems is that under many conditions the interaction of P with oxides involves at least two steps: adsorption and precipitation. These steps can occur consecutively and/or simultaneously and, hence, are not always easily distinguishable. An additional difficulty is that the chemical compositions of any products formed depend strongly on the chemical composition of the solution, the pH and temperature. The nature of the oxide plays also a role. Hence, it is not surprising that no generally accepted picture has emerged yet. In several instances also the experiments are conflicting.

The majority of the many studies on the interaction between phosphate and metal oxides (Muljadi et al., 1966; Hingston et al., 1974; Kyle et al., 1975; Helyar et al., 1976; Kuo and Lotse, 1974) are concerned with adsorption only. In other papers there are also indications of precipitation (van Riemsdijk et al., 1977; Chen et al., 1973a; Haseman et al., 1950; Kittrick and Jackson, 1955; Kittrick and Jackson, 1956). It may be characteristic that, as a rule, no simple adsorption isotherms are found but curves without a definite platform, that is usually time dependent (Muljadi et al., 1966; Helyar et al., 1976; Rajan et al., 1974; McLaughlin et al., 1977). It seems well-established that at least on goethite and gibbsite, P adsorption occurs only with singly-coordinated surface hydroxyl-or water groups; this process is viewed as a ligand exchange (Parfitt et al., 1975; Parfitt et al. 1977). The results as presented in Chap. 2 support this. Precipitation of a metal phosphate, as a result of the reaction of phosphate with metal oxides, has been clearly demonstrated to occur at high P concentration (> 0.1 mol dm^{-3}) (Haseman et al., 1950; Kittrick and Jackson, 1955; Kittrick and Jackson, 1956). For intermediate phosphate concentrations (10^{-5}-10^{-2} mol dm^{-3}) data on metal phosphate precipitation from oxide suspensions are scarce (van Riemsdijk, et al., 1977; Chen et al., 1973a). The mechanism of the precipitation reaction under these conditions is at present largely unknown, for one thing because many experiments have been done with insufficiently defined oxides.

As a contribution to unravel the two (or more) sorption steps, a study is presented on phosphate sorption exceeding the exchange-adsorption capacity with gibbsite (crystalline $Al(OH)_3$) as the sorbent. Gibbsite was chosen because:

a. it is known that $Al(OH)_3$ is quite reactive regarding P sorption (van Riemsdijk et al., 1977);
b. its surface structure is well known (Hsu, 1977);
c. it is a rather common soil mineral, especially in some tropical soils.

The formation of an aluminum-phosphate precipitate as a result of the reaction of phosphate with gibbsite is thermodynamically possible already at very low phosphate concentration (10^{-6}-10^{-5} mol dm^{-3}) for pH ≈ 5 (Chen et al., 1973b). Because of the low solubility of gibbsite, this precipitation only proceeds to a substantial extent if the gibbsite particles decompose in concurrence with the formation of the new solid phase.

3.2 Experimental

3.2.1 Materials

Gibbsite was made by dialyzing for 3-4 weeks an amorphous $Al(OH)_3$ precipitate against distilled water at 70 ^{o}C (Gastuche and Herbillon, 1962). Several samples have been used in the present study with B.E.T. areas (A) in the range of 26-39 $m^2\ g^{-1}$. The specific surface area of the edge faces, $A_e (m^2\ g^{-1})$, was determined by measuring the edge area and the volume of many particles from shadowed electronmicrogramphs employing the following formula;

$$A_e = (\Sigma \text{ edge area})\ (\Sigma \text{ volume } x\ \rho)^{-1} \qquad (3.1)$$

where ρ is the density of gibbsite. The edge area was approximately 14% of the total B.E.T. area. The error in A_e is 10-20%.

3.2.2 Edge area, maximum exchange-adsorption capacity

Gibbsite particles are more or less hexagonal platelets. The plate side, if perfect, consists of a close-packed hydroxyl layer in which each hydroxyl ion is coordinated to two aluminum atoms (Hsu, 1977). On perfect crystals, singly coordinated OH(H) groups, which determine the exchange-adsorption capacity of phosphate are present on the edge faces only.

On real crystals, a certain amount of these groups will also be present at the plate surface due to steps, kinks and other imperfections. The surface area exhibiting singly coordinated groups was estimated as a fraction of the total area from shadowed electronmicrographs and amounted to 0.14 ± 0.03. From this, using the area of one phosphate molecule (0.235 nm^2 or 7.1 $\mu mol/m^2$) (Vissers, 1968) the maximum exchange-adsorption density of P is calculated as $(0.14 \pm 0.03) \times 7.1 = 1.0 \pm 0.2$ µmol per total surface area (m^2).

In this chapter all amounts sorbed will always be expressed per total (B.E.T.) surface area.

3.2.3 Phosphate sorption experiments

All experiments were performed at constant ionic strength of 0.10 mol dm^{-3} using KCl unless stated otherwise. The temperature was either controlled by a thermostat or the experiments were performed in a constant temperature room. The temperature was 22 °C unless stated otherwise. Moist Co_2-free nitrogen was led over the suspensions. The CO_2 was removed with the help of a soda-lime column and the nitrogen gas was moistened by washing with distilled water. Except for the preliminary experiments the pH was kept constant by means of an automatic titrator set up (pH-stat) using an HCl solution as the titrant. In preliminary experiments the mixture was brought in a plastic container after one day of reaction and from then on the pH was regularly adjusted. A glass electrode and an Ag/AgCl electrode were used. The latter electrode consisted of a platinum wire coated with Ag/AgCl mounted in a glass tube containing the same electrolyte solution as the suspension (0.1 mol dm^{-3}KCl) and contacting the suspension through a narrow hole. Prior to mixing, the phosphate solution and the gibbsite suspension were placed for several hours in a vacuum desiccator containing a concentrated NaOH + $BaCl_2$ solution to remove any carbonate. Suspensions were made by pipetting the desired amount of the stock suspension in the reaction vessel and adding water and background electrolyte. Both the suspension and the phosphate solution were brought to the desired pH. Then the phosphate solution was added to the suspension in the reaction vessel. The initial total volume was always 300 or 400 cm^3. After filtration through a 0.01 μm membrane filter the phosphate concentration in solution were measured, by the molybdenum blue method (Murphy and Riley, 1962). The phosphate and potassium content of the solid reaction product were analyzed after dissolution of the reaction product by boiling in a solution of concentrated acid. The potassium was determined with a flame photometer.

3.3 Results

3.3.1 Preliminary experiments at pH 5

A series of preliminary sorption experiments was carried out to investigate the kinetics and the extent of the sorption reaction over a wide range of phosphate concentrations (c_p = 10^{-2}-10^{-5}mol dm^{-3}) for a reaction time of ca. 40 days at pH 5.0. At the end of these experiments the amount of phosphate reacted varied between 1.4 and 23 μmol m^{-2}, showing that the calculated exchange-adsorption maximum (1 μmol m^{-2}) is definitely exceeded. At high c_p the sorbed amount is even several times higher than the amount that can be accomodated on the entire gibbsite surface (7.1 μmol m^{-2}).

It has been stated in literature (Helyar et al., 1976; van Riemsdijk et al., 1977; Chen et al., 1973a) that the long-term sorption reactions, connected with precipitation conform to a first order rate equation. First order plots (log c_p-t), of these experiments approached linearity after some time, in accordance with the cited literature. However the measured first order rate constants differed for different experiments. This indicates that simple first order kinetics does not apply for these systems.

3.3.2 Sorption of phosphate, OH/P ratio

Sorption experiments were performed at pH 5, 7 and 9 at a constant pH, obtained by the pH-stat technique. At pH 7 or 9 all sorbed amounts are lower than the maximum exchange-adsorption capacity, because the solubility of aluminum phosphate in equilibrium with $Al(OH)_3$ increases strongly with pH (Chen et al., 1973b). This is in accord with the idea that any sorption, in excess of the exchange-adsorption maximum, is caused by precipitation.

The adsorption reaction is described in more detail in chapter 2. Below, the precipitation step is mainly considered. The sorption data at pH 5 are given in Fig. 3.1.

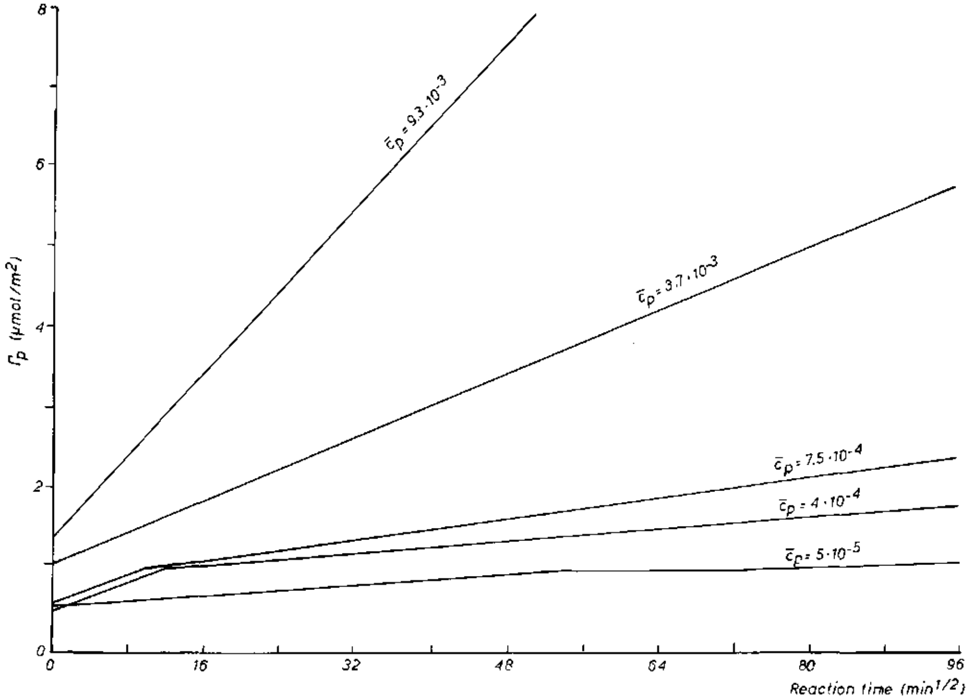


Fig. 3.1 The sorption of phosphate on gibbsite at pH 5.0 as a function of time at different phosphate concentrations, c_p. The average value of c_p during the sorption in the range exceeding 1 µmol m^{-2} is indicated by $\bar{c}_p$ (mol dm^{-3}). Lineair regression lines are drawn ($r^2 > 0.95$ for $\Gamma_p > 1$ µmol m^{-2}).

The time-axis was chosen as such considering that diffusion might play a role in the sorption-reaction. Fig. 3.1 shows a break in the curves around the calculated adsorption maximum of 1 μmol m^{-2}, suggesting that adsorption kinetics are dominant below this value (Chap. 2) whereas above it precipitation kinetics determine the reaction rate. Both processes appear to be diffusion controlled. The slopes of the straight lines after ca. 1 μmol m^{-2} was sorbed (excess sorption) are proportional to the concentration in solution. Hence, the data for the uptake in excess of adsorption can be represented with:

$$\Gamma_p^e = \Gamma_p(\text{total}) - \Gamma_p(\text{ads. max.}) = kc_p\sqrt{t} \qquad (3.2)$$

where Γ_p^e is the excess sorption expressed in moles phosphate sorbed per m^2 gibbsite, c_p the phosphate concentration in solution in mol dm^{-3}, t the reaction time in minutes and k a proportionality constant in m $min^{-\frac{1}{2}}$, including a factor of 10^3 for the conversion of dm^{-3} into m^{-3}.

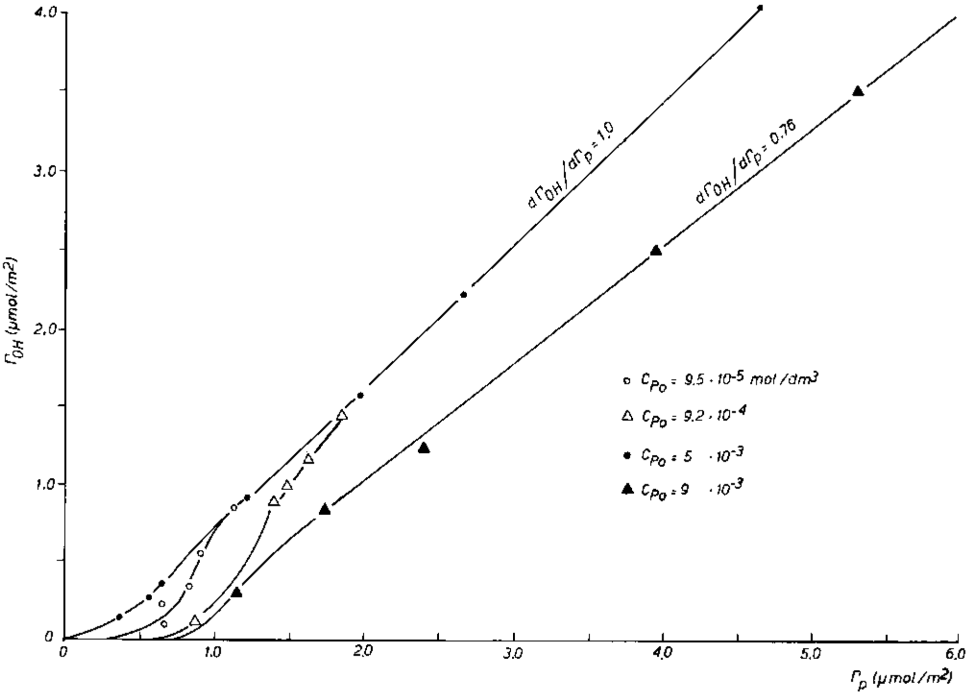


Fig. 3.2 The amount of hydroxyl ions liberated upon the sorption of phosphate by gibbsite at pH 5.0. c_{po} indicates the initial c_p at the beginning of the experiment.

In these experiments the concentration of solid was chosen in such a way as to achieve a compromise between accuracy of measurement and maximum constancy of the

phosphate concentration. $\bar{c}_p$ is the average concentration in solution during the sorption in the range exceeding 1 μmol m^{-2}. The variation of $\bar{c}_p$ is on the average ca. 12%. The straight lines will bend towards the time axis if c_p would decrease considerably during the reaction. The proportionality constant in eq. (3.2), determined from the experiments of Fig. 3.1 is equal to:
$k = (1.6 \pm 0.2) \times 10^{-5} m\ min^{-\frac{1}{2}}$.
Another way to follow the reaction is to measure the ratio R of the amount of hydroxyl ions produced to the amount of phosphate sorbed (Breeuwsma and Lyklema, 1973). In Fig. 3.2 the hydroxyl production is plotted as a function of the amount of P sorbed for different phosphate concentrations. The R-value is the slope of these curves. It changes rapidly with Γ_p, if Γ_p is low. However, for higher Γ_p, R becomes independent of it. For an initial P-concentration, c_{po}, of 5×10^{-3} mol dm^{-3} R approaches 0.7 for larger Γ_p than represented here, a value which is also attained at $c_{po} = 9 \times 10^{-3}$ mol/l.
Constancy of R for high Γ_p may indicate that the nature of the phosphate-oxide interaction (and hence the composition of the product formed) is independent of the extent of reaction.

3.3.3 Phosphato-stat experiments

It follows from a combination of data such as in Figs. 3.1 and 3.2 that R becomes constant after a very short reaction time for c_p around 9×10^{-3} mol dm^{-3}. This provides the opportunity to let the pH-stat function as a 'phosphato-stat' as well, meaning that both pH and c_p can be controlled simultaneously. This is realized by bringing a phosphate solution of specified pH in the burette of the pH-stat. The excess (with respect to the reaction mixture), of protons of the titration fluid divided by the excess phosphate should be equal to R of the reaction studied. In formula this is:

$$\frac{\{3c_p^*\alpha_0' + 2c_p^*\alpha_1' + c_p^*\alpha_2' + c_H^*\} \quad - \quad \{3c_p^*\alpha_0 + 2c_p^*\alpha_1 + c_p^*\alpha_2 + c_H\}}{c_p^* - c_p} = R \qquad (3.3)$$

with c_p^* = total P-concentration titrant
c_p = total P-concentration reaction mixture
α_i' (α values at pH titrant)
α_i (α values at pH reaction mixture)

and $\alpha_0 c_p = c_{H_3PO_4}$ (3.3a)

$\alpha_1 c_p = c_{H_2PO_4}$ (3.3b)

$\alpha_2 c_p = c_{HPO_4}$ (3.3c)

The respective α values are a function of the pH and the ionic strength and can be calculated from the dissociation constants of phosphoric acid, taking for c_p the sum of the concentration of all the phosphate species (Stumm,and Morgan, 1970). The kinetics of the sorption reaction can now be studied at constant c_p and constant pH, i.e. at a constant supersaturation. Sampling was incidentally done for control measurements.

The reaction of phosphate with gibbsite was studied with the phosphato-stat at the following temperatures 2, 12, 22 and 46 °C.

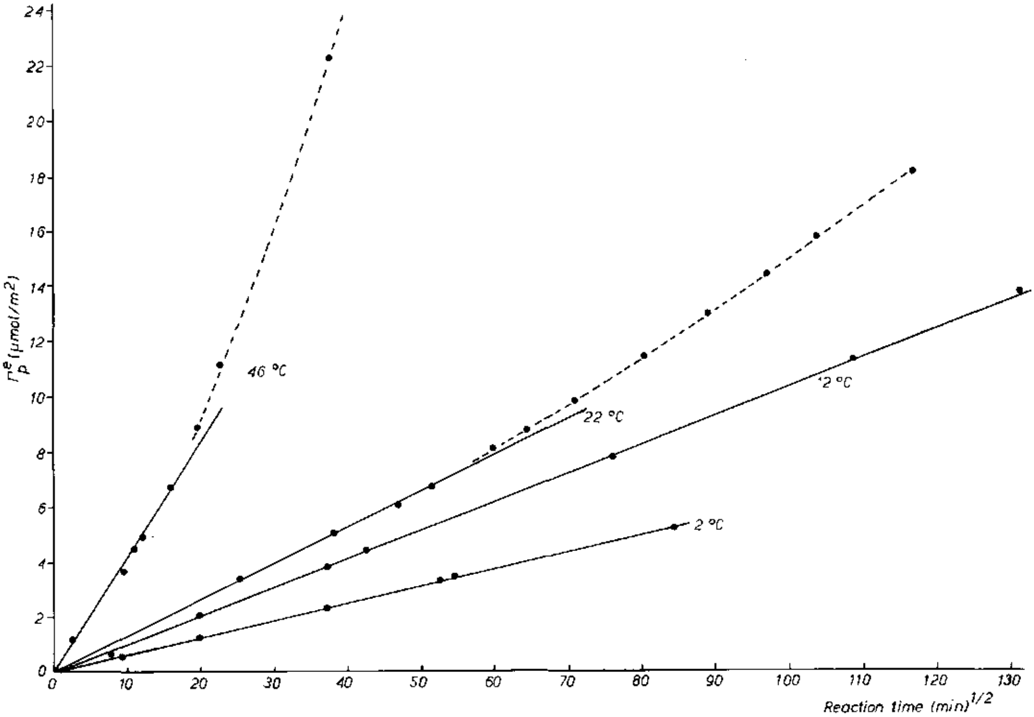


Fig. 3.3 Temperature dependency of the phosphate sorption on gibbsite at pH 5.0. Phosphato-stat experiments at $c_p = 9 \times 10^{-3}$ mol dm^{-3}.

The results (Fig. 3.3) confirm, first of all, beyond doubt that the sorption reaction cannot be represented by simple first order kinetics. Again the linear

$t^{\frac{1}{2}}$ relationship fits most data perfectly. The measurements at 22 and 46 ^{o}C start to deviate from this linearity at higher sorption values. This might be caused by an increase in surface area during the experiments. Such increases were found for experiments with high sorptions (e.g. from 29 to 81 $m^2\ g^{-1}$ for sorptions of 0 to 20 mmol P g^{-1}). This increase in surface area during sorption will lead to an upward bending of the straight $\Gamma_p^e\ (t^{\frac{1}{2}})$ plots if the increase of the surface area is not accounted for. The constant k of eq. (3.2), calculated for the straight line section of the phosphato-stat experiment at 22 ^{o}C equals 1.6×10^{-5} m $min^{-\frac{1}{2}}$.

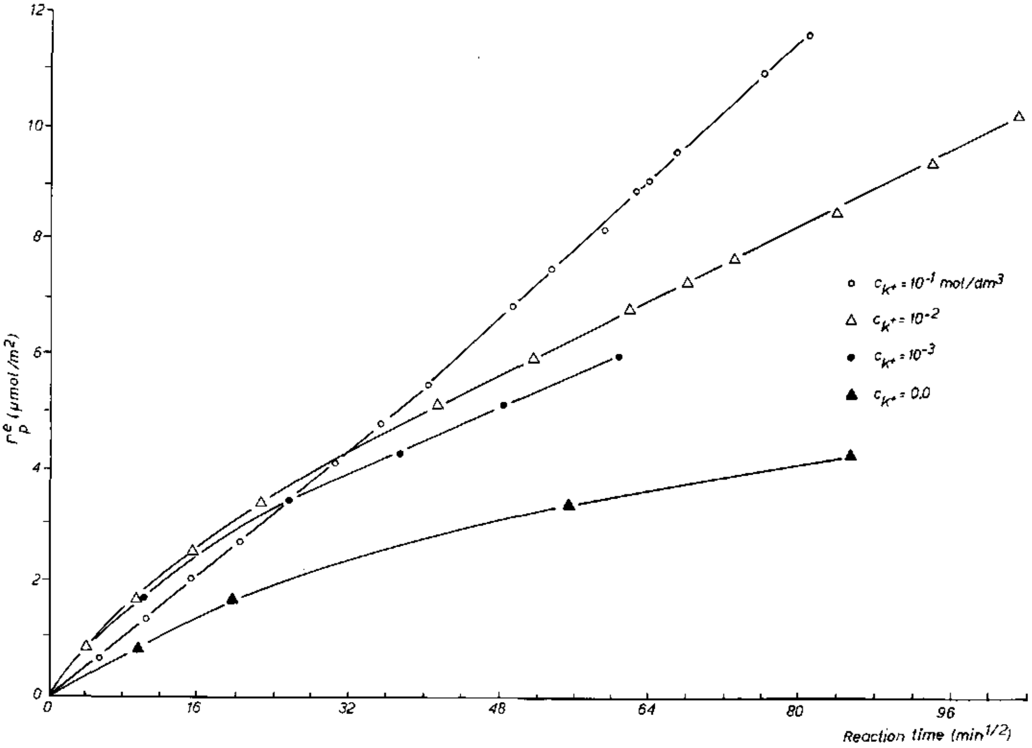


Fig. 3.4 The sorption of phosphate on gibbsite at pH 5.0 at different c_{K^+} (indicated). Phosphato-stat experiments at $c_p = 9 \times 10^{-3}$ mol dm^{-3}. The total ionic strength was kept constant (at 0.1 mol/l) for all experiments, by adding NaCl.

This value compares very well with the constant determined in the previous section. The activation energy of the reaction can be calcualted from the temperature dependenc according to Arrhynius.The activation energy, thus calculated is 63 ± 4 kJ mol^{-1}, confirming that the precipitation is a chemical, rather than a physical process. The effects of the potassium concentration and the pH on the sorption kinetics were studied with the phosphato-stat as well. The performance of the phosphato-stat in keeping c_p constant was found to function satisfactorily. The results are shown in Figs. 3.4 and 3.5. Fig. 3.4 clearly shows the specific effect of potassium ions on the reaction rate again indication that it is likely that these ions are incorptorated in the solid phase.

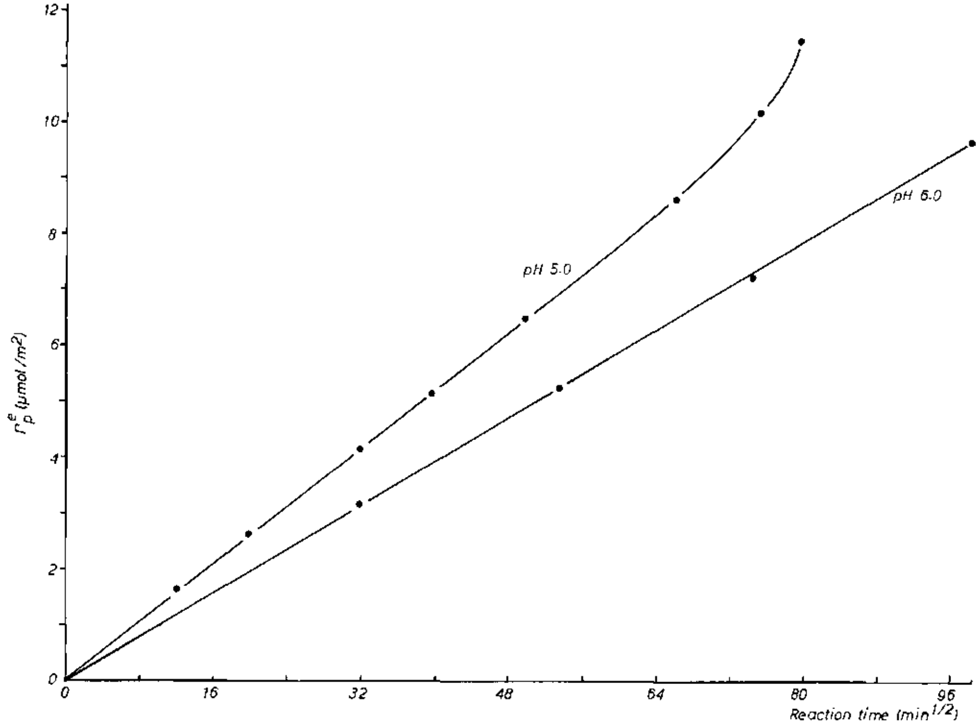


Fig. 3.5 The amount of phosphate sorbed at two different pH values as measured with the phosphato-stat ($c_p = 9 \times 10^{-3}$ mol dm^{-3}).

3.3.4 Dissolution of the precipitated phosphate product

Any aluminum phosphate that could have been formed at pH 5.0 due to phosphate-gibbsite interaction is highly unstable (soluble) at pH 9, where gibbsite is still relatively insoluble. The dissolution of precipitated phosphates was studied at pH 9 with samples containing high amounts of sorbed phosphates: 20-60 μmol m^{-2}, that is several factors more than the maximum adsorption capacity. Dissolution was very rapid if at the start of the dissolution the phosphate concentration was low. Dissolution, corrected for residual adsorption, was in that case complete within an hour. At high c_p dissolution was much slower. Additional experiments were performed to investigate the possibility that traces of amorphous $Al(OH)_3$, if present at the surface of the gibbsite would first absorb phosphate at pH 5 and then dissolve at pH 9, as opposed to the formation and dissolution of a surface potassium-aluminum-phosphate phase. First gibbsite was dialyzed at pH 9 against distilled water for two days to remove any $Al(OH)_3$ which readily dissolves at this pH. On a gibbsite sample, pretreated in this way a large amount of phosphate was sorbed at pH 5 with the phosphato-stat technique. Subsequently, a diluted sample was brought to pH 9 for the desorption experiment. Again a rapid and complete dissolution (residual adsorption negligible compared to total sorption) was found. From this it is concluded that the reaction product, due to the interaction between phosphate and gibbsite, is formed on the surface of the gibbsite particles and/or is present as separate particles.

3.4 Discussion

3.4.1 General

The above results show that Γ_p can easily exceed the exchange-adsorption capacity of 1 μmol m^{-2} on gibbsite at pH 5. The sorbed amounts may even exceed several times the calculated monolayer capacity for the whole surface (7 μmol m^{-2}). The exchange-adsorption capacity is only exceeded when the reaction system is supersaturated with respect to the formation of a (potassium) aluminum phosphate (Chap. 2). Moreover, the reaction at 12 °C (Fig. 3.3) obeys the same rate equation from $\Gamma_p^e = 0$ to $\Gamma_p^e \simeq 13$ μmol/m^2. These findings indicate that uptake in excess of the exchange-adsorption maximum is virtually attributable to some precipitation process.
This sorption can be described with

$$\Gamma_p^e = k_1 \sqrt{t} = k_1' \, c_p \sqrt{t} \qquad (3.4)$$

or

$$\frac{d\Gamma_p^e}{dt} = 0.5 \, k_1^2 \, (\Gamma_p^e)^{-1} \qquad (3.5)$$

where Γ_p^e has been defined before.
It is also clear from the reported data that k_1 is a function of pH, c_{K^+} and c_p.

The constancy of R at 0.76 (at pH 5, $c_p = 9 \times 10^{-3}$ mol dm^{-3} and $c_{K^+} = 0.1$ mol dm^{-3}) for high sorptions (Fig. 3.3) suggests again coprecipitation of some cationic species, especially K^+. This conclusion was corroborated by dissolution and anlysis of the solid phase for high amounts reacted. The relationship $\Gamma_p^e = kc_p\sqrt{t}$, which was derived from Fig. 3.1 is in accord with the 'adsorption isotherms' for phosphate on gibbsite as published by Muljadi et al. (1966). They find a linear isotherm for $c_p \simeq 10^{-3}$ -10^{-1} mol dm^{-3} and a reaction time of 48 hours. Their measurements were obtained at an almost constant c_p and pH, realized by working with a high solution-solid ratio. To explain these results, they assume a penetration of phosphate and K^+ in amorphous surface layers of the gibbsite particles. Furhtermore, they conclude that equilibrium has been reached in their experiments. This last conclusion is in conflict with the data as presented here. However, in a more recent study on phosphate-gibbsite interaction Kyle et al. (1975) report that it takes 6-8 days to reach a well-defined equilibrium. Rajan (1974) reports that adsorption of phosphate on amorphous $Al(OH)_3$ above c_p = 6×10^{-3} mol dm^{-3} in solution at pH 5 and 6 involves a breaking of hydroxyl bridges linking aluminum atoms (Al-OH-Al), thus, creating new phosphate adsorption sites. The data presented here show that the phenomena penetration and disruption occur only when the system is supersaturated with respect to at least one aluminum-phosphate, and that they are not equilibrium adsorption phenomena.

3.4.2 Thermodynamic considerations on the relative stability of various Al-P minerals

The most stable aluminum phosphate for the conditions of the phosphato-stat experiments can be found from a stability diagram of different aluminum phosphate and potassium-aluminum-phosphate minerals. Such a diagram can be constructed if the standard free energies of formation of these minerals are known. A wide variety of potassium-aluminum-phosphates has been found in precipitation studies at high P-concentration (Haseman et al., 1950; Haseman et al., 1951). However, only of one of these minerals, namely taranakite, has the solubility product been determined (Egan et al., 1961; Taylor and Gurney, 1961). This solubility product has been determined from a solubility study (Taylor and Gurney, 1961) and from a calorimetric study (Egan et al., 1961). Both values are used to construct stability diagrams (Fig. 3.6) including in addition to taranakite also variscite and wavellite. Variscite was chosen because its solubility product has been measured (Lindsay et al., 1959) and wavellite because it is considered to be the most stable aluminum phosphate al low c_p and low pH (Nriagu, 1976). The solubility

product of wavellite was taken from Nriagu (1976).
It should be noted that solubility products of aluminum phosphates as determined from solubility studies are apparent constants. This is amongst others caused by the absence of reliable stability constants for aluminum phosphate complexes.

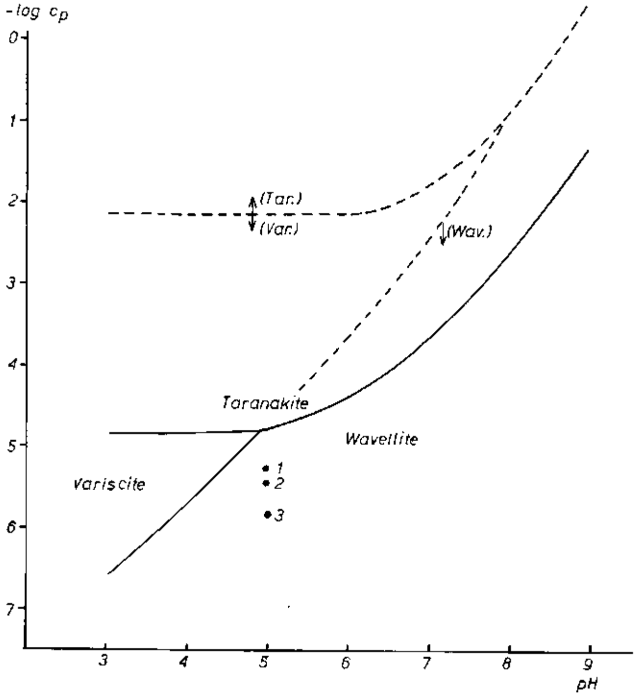


Fig. 3.6 Stability diagram for $H_6K_3Al_5(PO_4)_8.18H_2O$ (taranakite), $AlPO_4.2H_2O$ (variscite), and $Al_3(PO_4)_2(OH)_3.5H_2O$ (wavellite), with $c_{K^+} = 0.1$ mol dm^{-3}. The drawn curves represent the boundaries of the stability regions of the different minerals, calculated with the help of the solubility product of taranakite obtained calorimetrically. The dashed curves represent the corresponding diagram calculated with the taranakite solubility from solubilities. Points 1, 2 and 3 indicate the equilibrium solubilities of the respective pure minerals at pH 5.

So Fig. 3.6 gives only a rough estimate of the relative stabilities.
The constructed diagrams show that taranakite is the stable phosphate mineral for the phosphato-stat experiment with $c_{K^+} = 0.1$ mol dm^{-3}.
X-ray diffraction of samples containing high amounts of sorbed phosphate showed, however, only the gibbsite lines. This does not preclude the formation of a crystalline (potassium)-aluminum-phosphate since gibbsite is still the dominant phase for the samples analyzed. Only 10-15% of the gibbsite would be transformed for the highest sorptions measured, a fraction which may be too low for detection in X-ray diffraction analysis.

The reaction equation for the formation of taranakite from gibbsite and phosphate may be represented as:

$$5Al(OH)_3\ (s) + 3K^+ + 8H_2PO_4^- + 5H + 3H_2O \rightleftarrows H_6K_3Al_5(PO_4)_8 \cdot 18H_2O(s) \qquad (3.6)$$

The affinity A, of reaction (3.6) can be calculated at 25 °C as (Stumm and Morgan, 1970; Singh, 1976; Egan et al., 1961);

$$A = -\Delta G_r = RT\ln K/Q = RT\ln(Kc^8_{H_2PO_4^-}\, c^3_{K^+}\, c^5_{H^+}) \qquad (3.7)$$

Where Q is the reaction quotient of eq. (3.6), K the equilibrium constant of the same equation and ΔG_r the free energy change of the reaction. At equilibrium Q = K and $\Delta G_r = 0$. Taranakite can only be formed if A is positive; the larger A, the greater is the supersaturation of the reaction system with respect to taranakite formation.

The phosphato-stat experiments are performed at constant supersaturation, implying that complete conversion of gibbsite into taranakite is in principle possible, provided the reaction time is sufficiently long.

Figures 3.1, 3.4 and 3.5 show that the reaction rate constant (eqs. (3.4) and (3.5)) is still a function of c_p, c_{K^+} and pH. These data are in accord with the presumption that a K-Al-phosphate is formed, with a rate of formation that increases with increasing supersaturation. More data are required to find a more precise expression for the dependence of the rate on c_p, c_{K^+} and pH. Moreover, the reaction rate is expected to depend on the surface charge (or -potential) of the newly formed surface. However, data for these quantities are not yet available. At the present stage it is concluded only that the precipitation rate increases with increasing supersaturation and that it is inversely proportional to the amount that has reacted for the potassium containing systems.

Although the reaction rate for the system with pure NaCl as the supporting electrolyte is much slower than for the systems which contain KCl it is still clear that the general characteristics are retained namely:

a) sorption occurs in excess of edge adsorption,
b) there is a decrease in reaction rate at constant supersaturation with continuing sorption,
c) the reaction rate is dependent on the supersaturation (Chap. 2).

The R-value calculated from (3.6) is 0.63 and may be compared with the limiting value 0.76 at high c_p. The difference may be caused by the formation of a K-Al-phosphate with a slightly different composition than taranakite. For variscite or wavellite formation R would have to be 1.0. This is clearly at variance with our data.

3.4.3 Mechanism and rate equations

The mechanism of the reaction of potassium phosphate with gibbsite is reminiscent of the oxidation mechanism of metals (Evans, 1955; Roberts, 1962). Oxidation of most metals is possible already at low oxygen pressures. The first step in these reactions is chemisorption of oxygen at the surface of the metal. After this, oxide formation starts and a metal oxide layer of increasing thickness is formed. The following rate law is often found to apply after a certain thickness has been reached:

$$\frac{dl}{dt} = k_2 l^{-1} \qquad (3.8)$$

(Evans, 1955; Roberts, 1962), where l is the thickness of the oxide layer which is sometimes directly measured. The similarity with (3.5) is striking. However, the precise relationship between the sorption and the thickness of a possible surface K-Al-phosphate is almost impossible to establish for these experiments mainly because of difficulties in assessing the surface area that is needed in the calculation:

a) the formation of the new surface phase probably starts mainly at the edges where the initial adsorption takes place, but most probably spreads over the plate sides at higher sorptions (Fig. 3.7a, b) and,

b) an increase in total (B.E.T.) area was found during the experiments (e.g. from 29 to 81 $m^2\ g^{-1}$ for sorptions of 0 to 20 mmol P g^{-1}).

This increase in surface area might be the result of a roughening of the surface of the original particles and/or the result of the formation of new particles. New particles can be formed by a chipping off of the newly formed surface phase. It is likely that the increase of the surface area will be larger the higher the temperature and the greater the sorption. This increase would lead to an upward bending of the straight lines in the $r_p^e - \sqrt{t}$ plots if the increase of the surface area is not accounted for. Such a bending is indeed observed in Fig. 3.3 where the effect is the strongest for the highest temperature. Shadowed electron micrographs of a sample with a high amount of sorbed phosphate show a considerable surface roughening and also more small particles as compared to the pure gibbsite

(Fig. 3.7a, b).
The Γ_p^e- $\sqrt{t}$ relationship can be theoretically derived for diffusion into a semi-indinite medium. It leads to (Cranck, 1956):

$$\Gamma = 2c\ (Dt/\pi)^{\frac{1}{2}} \tag{3.9}$$

where c is the concentration of the diffusing species at the liquid-solid interface if diffusion in the solid is the rate controlling step.

a

b

Fig. 3.7 Shadowed electron micrographs of gibbsite (a) and of gibbsite with sorbed phosphate (ca. 2 mmol/g) (b). Magnification 86.000 x.

The magnitude of the diffusion coefficient, calculated from our data according to eq. (3.9), $D = 3 \times 10^{-14}$ cm^2 s^{-1}, corroborates this. However, in practice it is found that eq. (3.9) will only hold for low sorptions and small diffusing ions (Ward, 1931; Gallagher and Philips, 1968; Bérubé et al., 1967). As an alternative, diffusion through a surface layer which increases in thickness as a result of the reaction (tarnishing reactions), would lead to the following formula, (assuming a linear concentration gradient in the interfacial layer and a negligible concentration of the diffusion species at the crystal/surface layer boundary) (Booth, 1948):

$$\Gamma = k\sqrt{c}\sqrt{t} \qquad (3.10)$$

The physical model from which (3.10) is derived seems to be in accord with most of the results discussed so far. However, the concentration dependence of eqs. (3.10) and (3.2) is not the same. The concentration in eq. (3.10) represents the concentration at the surface (amount adsorbed) while for the application of eq. (3.2) the concentration in solution is used. More precise elaboration of diffusion models in general is hindered for the same reasons as discussed in connection with the application of eq. (3.9) (Chap. 2).
Exchange experiments with radioactive phosphorus (Chap. 2) show that a considerable fraction of the new surface contains exchangeable phosphate. This implies that the adsorption isotherm of the 'phosphated gibbsite' will differ considerably from the isotherm as determined at low c_p for the pure gibbsite.

3.5 Conclusions

1. On gibbsite, phosphate can sorb in excess of the maximum monolayer exchange capacity determined by the number of singly coordinated hydroxyl groups.
2. This excess sorption occurs only when there is the possibility of the formation of a (potassium)-aluminum-phosphate.
3. The rate of the excess sorption increases with increasing supersaturation and it decreases with the amount that has already been sorbed.
4. The rate is furthermore dependent on the nature of the cation present in the system.
5. Potassium, if present, is part of the reaction product.
6. The reaction product forms a surface coating on the gibbsite particles.
7. The total surface area increases during the reaction.
8. The collected evidence shows that phosphate uptake in excess of monolayer exchange capacity has some characteristics of a simple adsorption but in fact it is a precipitation process.

4. REACTION OF PHOSPHATE WITH ALUMINUM COMPOUNDS IN A SYNTHETIC SEWAGE WATER MEDIUM

The reaction of phosphate with aluminumhydroxide and αAl_2O_3 *was studied at an initial phosphate concentration level of 0.35 mmol/l and a temperature of* 20^oC*. Solutions of* KH_2PO_4 *and synthetic inorganic sewage water were used as phosphate sources. In all experiments involved, a marked change of the reaction rate was found after about 1 day in the case of* $Al(OH)_3$ *and about 4 days in the case of* αAl_2O_3*. This can be explained by the assumption that at these points the formation of a solid aluminum-phospate is initiated. This new phase was later identified as Sterrettite by means of electronmicroscopy, electron diffraction and X-ray diffraction.*

4.1 Introduction

Long term disposal of raw sewage water on a sandy soil resulted in the accumulation of phosphates in the soil profile. With respect to the mechanism of the phosphate retention by the soil system it was suggested by Beek and de Haan (1973) that precipitation reactions may play an important role in addition to adsorptive bonding on soil constituents.

Careful fractionation studies (Beek et al., 1977) indicated that the accumulated phosphates are most likely associated with aluminum. In view of these findings the reaction of phosphate with X-ray amorphous $Al(OH)_3$ and αAl_2O_3 was studied. The main objective of this study was to investigate the possible formation of a new solid phosphate phase under the experimental conditions and to identify such a new phase. The kinetics of such precipitation reactions constitute a prerequisite for the development of mathematical models for the description of phosphate behavior in soils intermittently treated with large amounts of sewage water. The system under study here, thus, is a model system, which may give insight in the reaction mechanisms involved.

In the experiments use was made of synthetic sewage water as a phosphate source. For comparison, similar experiments were performed using a pure KH_2PO_4 solution as the phosphate source. Results of these latter experiments have been published in part elsewhere (van Riemsdijk et al., 1975).

4.2 Materials and Methods

Using a ball mill, αAl_2O_3 (Merck, Germany) was ground. Following separation by wet sieving, the fraction < 50 μ was used in the experiments. Preparation of $Al(OH)_3$ was performed according to Hsu and Rennie (1962). The amorphous state of the reaction product was confirmed by X-ray diffraction. Both adsorbents were subjected to specific surface area measurements with a Perkin-Elmer Model 212-c Sorptometer, using nitrogen gas. In the calculation of the specific surface area use was made of the B.E.T. equation. Values for specific surface area were found as 3.8 m^2/g for αAl_2O_3 and 226 m^2/g for $Al(OH)_3$. The adsorbents were suspended in solutions which contained all main inorganic ions of the sewage water at the same average concentration levels as present in the wastewater used on the sewage farm. This is with the exception that HCO_3^- was substituted by Cl^- and that silicate was excluded. Replacement of HCO_3^- by Cl^- was done because it is impossible to obtain the same pH in the synthetic sewage water as in the raw sewage water if both contain the same amount of HCO_3^-. This is caused, amongst others, by the fact that the sewage water is oversaturated with CO_2 with respect to equilibrium with the atmosphere. Solution compositions are presented in Table 4.1. In addition, solutions of 0.35 mmol/l KH_2PO_4 (pH 5) were used.

Table 4.1. Composition of the inorganic synthetic sewage water medium (SSW medium).

	pH 5 (SSW 5)	pH 6 (SSW 6)
	mmol/l	
$CaSO_4 2H_2O$	0.84	0.84
$CaCl_2 2H_2O$	0.94	0.93
NH_4Cl	1.86	1.87
$MgCl_2$	0.34	0.35
KNO_3	0.19	0.19
NaF	0.01	0.01
KCl	0.34	0.17
KOH	-	0.16
NaCl	6.25	6.29
KH_2PO_4	0.35	0.35

The concentration levels of Table 1 represent initial values at the start of the adsorption experiments. Preparation of the solutions was performed at twice these initial reaction concentrations, as the solutions were mixed 1:1 with suspensions of both adsorbents involved. The pH was adjusted within 0.1 pH unit by using NaOH and HCl, and was constant after approximately one week.

After addition of the various solutions the suspensions were continuously mixed by means of an end-over-end shaker at a temperature of 20.5 ± 0.1 °C. The final suspension concentration was 2.5 g/l when αAl_2O_3 was used as sorbent and 0.1 g/l with $Al(OH)_3$ as sorbent. The pH of the suspensions was measured with a combined calomel reference-glass electrode in unstrirred suspensions; these pH measurements were performed after a sedimentation period of 20 minutes. During the experiments the pH was kept constant by addition of HCl. Phosphate concentrations were measured according to the method of Murphy and Riley (1962) following filtration through a 0.1 μm membrane filter.

Samples used for X-ray diffraction were filtered after a reaction time period of 62 days. Following washing with distilled water and vacuum drying, these samples were analyzed with a Philips diffractometer using Co-Kα radiation. A Philips model EM 301 electron microscope was employed in the electrondiffraction measurements.

4.3 Results

The Experimental results are presented graphically in Fig. 4.1 and 4.2. Fig. 4.1 shows the course of the phosphate solution concentration as afunction of reaction time. Fig. 4.1.a refers to the $Al(OH)_3$ system, indicating that for the time period from about 1 day until about 40 days after the start of the experiment the rate of the reaction can be described by first order kinetics according to:

$$\ln \frac{c_o'}{c_t} = k\,t \qquad (4.1)$$

Where c_t is the phosphate concentration at time t, c_o'. is the phosphate concentration at about 1 day reaction time, k is the rate constant (in day^{-1}), and t is the reaction time (in day). The rate constant (k) depends, amongst others, on the magnitude of the surface area available for adsorption and on the pH of the system.

Results for the αAl_2O_3 system are given in Fig. 4.1.b. In that case, the first order reaction starts after a reaction time of about 4 days. Chen et al. (1973a) have reported similar observations for the reaction of phosphate with αAl_2O_3 and with kaolinite.

When these same experimental data are expressed in terms of amount of phosphate removed from the solution per gram of adsorbent and plotted on a double log scale as a function of time, two straight intersecting lines are found for each reaction system as indicated by Fig. 4.2. The rate of phosphate removal increases considerably at about 1 day and 4 days reaction time for Al$(OH)_3$ and αAl_2O_3, respectively, relative to the fast adsorption which slows down very rapidly after several hours.

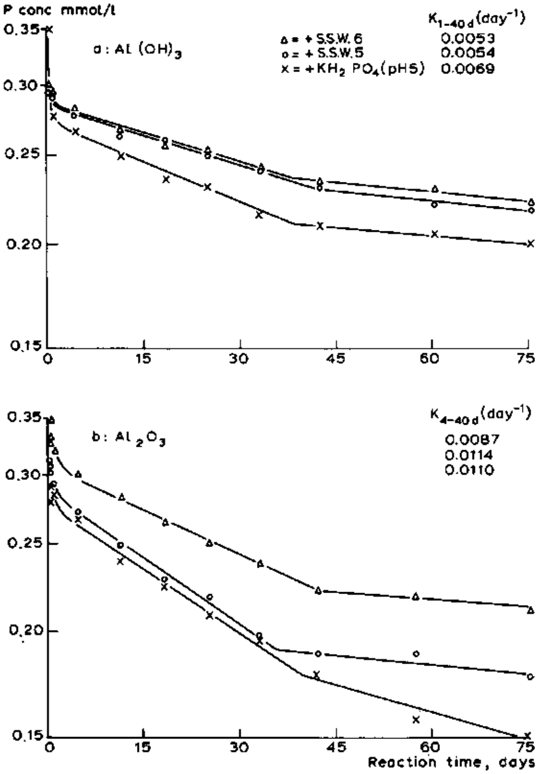


Fig. 4.1. A semilog plot of the measured phosphate concentration as a function of reaction time.

The straight line in the initial phase of each reaction represents the fast phosphate adsorption at the surface of the aluminum compound. Kuo and Lotse (1973) obtained simular results for short term reactions of phosphate with gibbsite and hematite.

Surface adsorption may also be expressed in terms of surface coverage. Surface coverage can be calculated from the specific surface area of the adsorbent and the surface area of a PO_4 ion. Using for the latter the value of 23.5 $\AA^2$

as given by Vissers (1968), PO_4 monolayer adsorption would correspond to an adsorbed amount of phosphate of 7.1 μmol/m^2. Monolayer coverage in practice usually corresponds to less than this theoretical value of 7.1 μmol/m^2, depending on the structure of the adsorbing surface and on the stoichiometry of the adsorption.

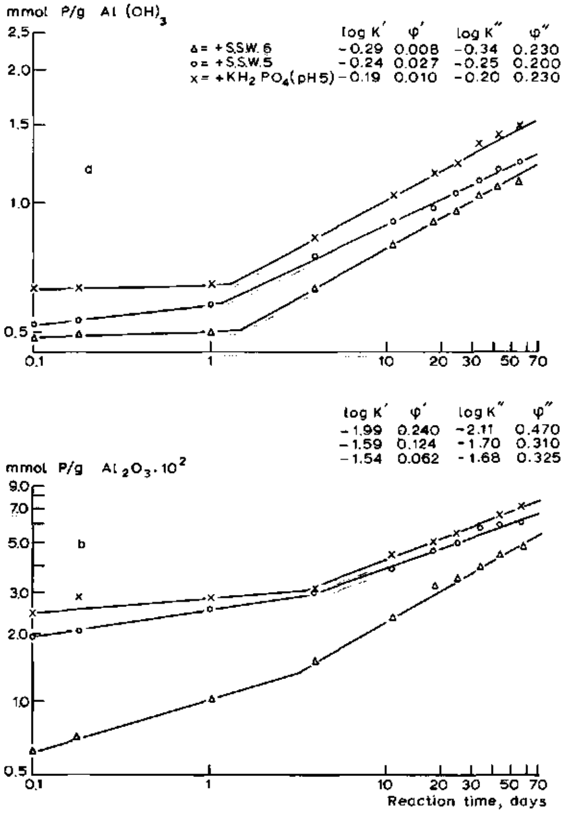


Fig. 4.2. A double log plot of the amount of phosphate removed as a function of reaction time. Expressing the lines shown as $\log X = \log K + \phi \log t$, with X = phosphate removed (mmol g^{-1}). K' and ϕ' are the constants for the initial straight line and K" and ϕ" dito for the second part of the reaction.

Vissers (1968) studied phosphate monolayer adsorption on zirconium, ceric- and thoriumoxide, resulting in values ranging from 25.1 to 44.0 Å^2 per PO_4 ion, corresponding with 6.6 to 3.8 μmol phosphate/m^2, respectively. Phosphate adsorption values in μmol corresponding to the phosphate adsorption at the intersection points of Fig. 4.2 are presented in Table 4.2. Comparison with the above data indicates that attainment of monolayer coverage at this stage of the experiment may be concluded for at least two cases.

Table 4.2. Phosphate 'adsorbed' ($\mu mol/m^2$) at the intersection points of Fig. 4.2.

solutions	intersection point in days	$\mu mol/m^2$ P adsorbed
	$Al(OH)_3$	
SSW 5	1.1	3
SSW 6	1.4	2
KH_2PO_4 5	1.3	3
	αAl_2O_3	
SSW 5	3.8	8
SSW 6	3.2	3
KH_2PO_4 5	3.4	8

It is, thus, not unlikely that from this point on the continued and increased removal of phosphate from solution is caused by the growth of a crystalline aluminum phosphate. In order to confirm the presence of such a new aluminum phosphate electronmicroscopy (E.M.), electron diffraction (E.D.) and X-ray diffraction techniques have been applied. As a result of the grain size distribution caused by ballmilling the adsorbent such as in the case of αAl_2O_3 prior to use in the experiments, newly formed crystals could not be distinguished in the αAl_2O_3 systems. In the $Al(OH)_3$ samples, the presence of newly formed platy crystals with a diameter of 0.5 to 4 µm can be seen (Fig. 4.3).

Crystals which were further examined all showed the same diffraction pattern. The d-spacings of these patterns were measured with a gold pattern as reference. Table 4.3 presents these d-values along with those obtained by X-ray diffraction. Comparison with d-values of different aluminumphosphates and aluminumhydroxides indicates that this new phase is most probably constituted of Sterrettite. This compound, formed from solutions containing aluminum and phosphate at pH 5.5, has been identified by Cole and Jackson (1950). The latest American Society for Testing and Materials (ASTM) card, however, lists Sterrettite as a Scandiumphosphate.

Fig. 4.3. An Aluminum phosphate crystal with a diameter of 1.5 μm grown in the SSW 5 medium + $Al(OH)_3$.

Table 4.3. Al-phosphate d-spacings investigated as found by Xray diffraction (X), electron diffraction (E), compared with the tabulated values of Sterrettite (S) (ASTM 2.0177), Metavariscite (M) (ASTM 15311) and Variscite (V) (ASTM 15281). (Numbers in parentheses refer to intensities).

X	S	E	M		V	
			0.1 nm(=1Å)			
	6.94		6.37 (4)	2.16	5.365 (1)	1.952
	5.25	5.26	4.77	2.11	4.82	1.903
4.90 (1)	4.88 (1)		4.575 (3)	2.07	4.257 (1)	1.852
4.51 (2)	4.51 (2)	4.55	4.43	2.01	3.887	1.809
3.75	3.79 (4)		4.25 (2)	1.961	3.625	1.779
	2.90 (3)		4.04	1.933	3.366	1.752
	2.76 (5)		3.52	1.865	3.204	1.715
2.62	2.66	2.63	3.37	1.824	3.039 (1)	1.656
	2.44		3.25	1.793	2.957	1.640
	2.33		3.12	1.771	2.853	1.604
	2.24	2.25	3.02	1.743	2.63	1.588
	2.07 (6)		2.90	1.721	2.568	1.574
	1.87		2.79	1.670	2.48	1.557
	1.77		2.71 (1)	1.646	2.39	1.519
	1.71 (7)	1.72	2.65	1.630	2.33	1.496
	1.61		2.59	1.612	2.278	1.438
	1.54	1.52	2.50	1.591	2.136	
	1.49		2.41	1.560	2.081	
	1.37		2.30	1.539	2.047	
	1.35		2.21		2.014	
	1.31	1.31		plus 15 lines to 1.258		

4.4 Discussion and conclusions

The amount of phosphate removed from solution reaches the highest value when using KH_2PO_4 solutions in the experiments. This might be attributed to the absence of competition of other anions for adsorption. Moreover the ionic strength of the KH_2PO_4 system is much lower and, consequently, the phosphate activities of especially HPO_4^{2-} and PO_4^{3-} are much higher as compared to the synthetic sewage water systems. The kinetics of the reaction might be expected to be influenced by the surface structure of the adsorbent. The mechanism, however, appears to be similar with both types of adsorbent involved. The aluminum phosphate formed is the same for the $KH_2 PO_4$ systems and the synthetic sewage water systems.

The phosphate removal reactions are characterized by a two step mechanism; the first part refers to a fast adsorption of phosphate on the surface of the adsorbent; the second step is most probably constituted of the formation of a solid aluminum phosphate phase. Under similar experimental conditions with αAl_2O_3 Chen et al. (1973a) found a very small (± 0.25 μm diameter) newly formed crystal after five days of reaction time which supports the proposed two-step mechanism as indicated in Fig. 4.2. That crystal, however, was too small to allow identification. Little attention has been given in the past to this slow but continued process of phosphate removal at experimental conditions of practical interest. The amount of phosphate which can be removed during a time period of, e.g., 1 month (i.e., the time between two successive floodings at the sewage farm) is considerable.

After about 40 days the reaction rate does not fit the first order equation as presented any longer. Whether this in fact represents a third step in the reaction mechanism or the approach of an equilibrium remains speculative so far because the experiments have not been extended over longer time periods.

4.5 Discussion with reference to the results of chap. 2 and 3

The results of the experiments, as presented in this chapter so far, were published before the research as described in chap. 2 and 3 was started. The general concept of a dominance of adsorption in the early stage of the reaction followed by a dominance of precipitation when the reaction proceeds (in supersaturated solutions) remains unchanged. The values of the initial adsorption furthermore, support preliminary model calculations (chap. 1), with respect to the effect of pH and ionic strength on the adsorption.

The effect on the reaction rate of the amount of phosphate precipitated, at constant supersaturation was not recognized as such in the early publication (Van Riemsdijk et al. 1975). Fig. 4.4 shows the results of the $Al(OH)_3$ experiment expressed according to the concepts of chap. 2 and 3. The results for the αAl_2O_3 experiments give a similar picture.

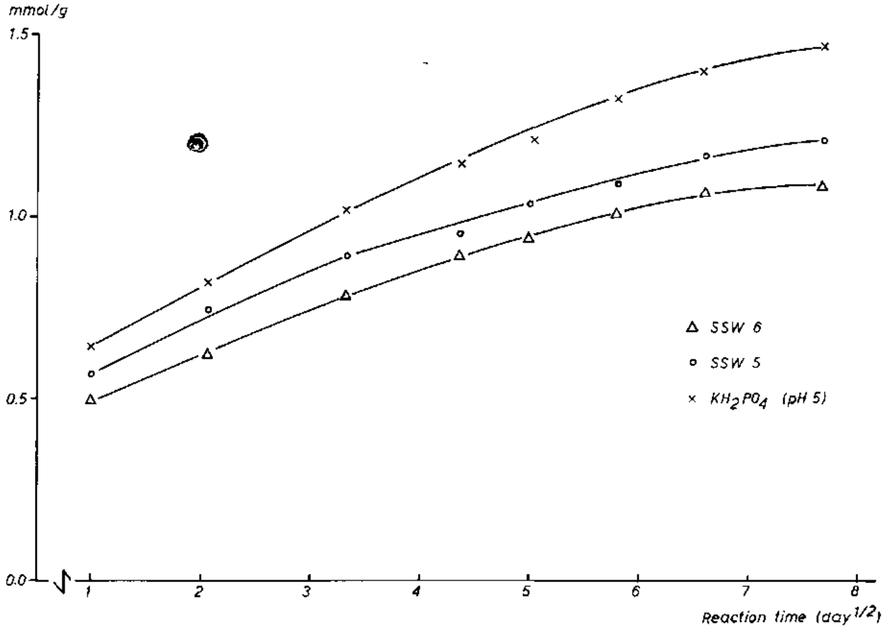


Fig. 4.4. Sorption of phosphate on $Al(OH)_3$ as a function of $\sqrt{t}$ in different electrolyte solutions as indicated.

The slight deviation from linearity may be explained by the decrease of the phosphate concentration during the course of these experiments. This figure, thus, suggests that the precipitation kinetics of phosphate with amorphous $Al(OH)_3$ decreases with increasing amounts precipitated as in the case of gibbsite as sorbent. This could be caused by the formation of a surface precipitate in addition to the same for the pure crystals that were identified as Sterretite. It should be expected that potassium is a part of these crystals considering the results of the experiments with gibbsite. The experiments of Haseman et al. (1950) show that Sterretite is indeed a potassium aluminum phosphate.

It can thus be shown that the results of these experiments support the concepts as developed from the more elaborate experiments with gibbsite.

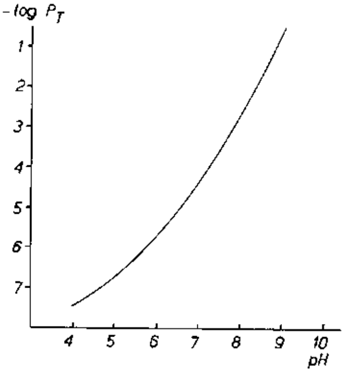
5. BONDING OF PHOSPHATE FROM SEWAGE WATER IN Al(OH)3 CONTAINING SAND COLUMNS

The reaction of phosphate (P) with $Al(OH)_3$ *can be distinguished by adsorption and a process designated here as 'long-term reaction'. The long-term reaction may remove several times the amount of P removed initially. No long-term reaction of P (0.5 mmol/l) and X-ray amorphous* $Al(OH)_3$ *was detected at pH 8. To columns of quartz sand mixed with* $Al(OH)_3$ *domestic sewage water (pH≈8) was added during 10 months once every two weeks. The phosphate retention in these columns was much higher than could be expected from the pure* $Al(OH)_3$ *system experiments, indicating the occurrence of a long-term reaction. Column segments were analyzed for organic-, (Al + Fe)-, and Ca-P. Negligible Ca-P was formed. SEMEDXRA showed quartz particles, Al containing particles with no detectable P, and particles containing Al, P, and Ca. Formation of the Al-P-Ca particles contributes to the capacity of soils to store or retain P.*

5.1 Introduction

It has been widely reported that the reaction of phosphate (P) with $Al(OH)_3$ is comprised of a 'fast' reaction followed by a much slower one, which are usually distinguished somewhat arbitrarily (Chen et al., 1973b; Helyar et al., 1976). The fast reaction may last from one hour to several days and, hence, what most authors have called the adsorption or fast reaction is not fast at all. Chemisorption may be slow if the monolayer coverage region is being approached or completed, but the amount of P taken up in the slow adsorption may amount to 30 to 40% of the initial rapid adsorption (Langmuir, 1940). The monolayer adsorption capacity is dependent upon the surface area and the fraction of the surface that is active, which has been well established for iron oxides via IR, (Russel et al., 1974; Parfitt et al., 1975; Parfitt et al., 1977).

Mechanistic studies with amorphous oxides-hydroxides are difficult because they cannot be as well characterized as for crystalline materials, but they have the definite advantage of faster reaction rates. The 'long-term' reaction (not to be confused with slow adsorption) of P with $Al(OH)_3$ may be associated with the formation of a discrete aluminumphosphate phase, (Chen et al., 1973a; Van Riemsdijk et al., 1975; Van Riemsdijk et al., 1977), but it can also be evisaged as the formation of a surface phase of a several molecular layer thickness (Van Riemsdijk and Lyklema, 1978; Chap. 2 and 3 of this publication). Regardless of reaction mechanisms, the long-term reaction rate increases as pH decreases. This is in accord with the solubility-diagram of the system $Al(OH)_3$ (s)-$AlPO_4.2H_2O$(s) - H_2O (Fig. 5.1), assuming that the rate increases with increasing supersaturation.



The solubility of $Al(PO_4).2H_2O$ (s) in equilibrium with $Al(OH)_3$.
(P_T = total phosphate in Kmol/m^3 = mol/l)

Fig. 5.1. The solubility (expressed in mol/l total phosphate P_T) of the system $Al(OH)_3$ (s)-$AlPO_4.2H_2O$ (s)-H_2O at equilibrium as a function of the pH, using a pK value of 31.31 for the equilibrium $Al(OH)_3 + PO_4^{3-} + 3H^+ \rightleftarrows AlPO_4.2H_2O$. The activity coefficients were calculated with the Davies formula for an ionic strength of 0.02.

The amount of phosphate removed from solution at low pH in the long-term reaction may reach several times the amount initially removed (Chen et al., 1973a; Van Riemsdijk et al., 1977), distinguishing it from the slow monolayer adsorption type mentioned previously. In addition, the long-term reaction can not be considered as a pure bulk diffusion of phosphate into the $Al(OH)_3$, because this process would only depend on the structure of the solid phase and on the surface concentration of phosphate, and not so dramatically on the pH. At higher pH values the reaction might thus be confined to adsorption, at least for moderate phosphate concentrations.

The reaction at a high pH, however, is of practical interest because alumina is an important factor in phosphate adsorption even in calcareous soils (Holford and Mattingly, 1975); moreover liquid manure and sewage water, which are sometimes applied in excessive amounts on non calcareous sandy soils, often have a pH of around 8.

Specific constituents of manure and of sewage water may increase or decrease the amount of phosphate removed. An increase may be caused by for instance Ca, Mg, NH_4, Fe, Al (Chen et al., 1973b; Helyar et al., 1976) and a decrease by some organic anions, bicarbonate, arsenate, etc. (Nagarajah et al., 1968; 1970). The cations present in liquid manure or sewage water can even cause direct precipitation of phosphate from solution on standing (Fordham and Schwertmann, 1977a; 1977b). When these P-sources are brought into contact with soil or other P-adsorbents, however, adsorption is initially the most important process which hinders the direct precipitation (Fordham and Schwertmann 1977a). Further long-term reactions are then surface reactions, which may result in the ultimate formation of stable phosphate compounds.

The experiments described here investigate the long-term reaction of P with X-ray amorphous $Al(OH)_3$ at pH 8, (i) in a batch experiment at 10 mmol/l $NaNO_3$ and with an initial orthophosphate concentration of 0.5 mmol/l constantly kept at pH 8, and (ii) by applying raw sewage water once every 2 weeks for 10 months to columns of quartz sand and to columns of quartz sand mixed with X-ray amorphous $Al(OH)_3$.

5.2 Materials and methods

5.2.1 Batch experiments

X-ray amorphous $Al(OH)_3$ was used as sorbent (Hsu and Rennie, 1962). A suspension of 0.5 g/l $Al(OH)_3$ was made which contained 10 mmol/l $NaNO_3$. The initial potassium phosphate concentration was 0.5 mmol/l and the solution concentration was measured during the reaction by filtrating aliquots through a 0.1 µm membrane filter. The pH was kept constant by means of an automatic titrator. In one experiment moist air was led over the suspension and in the other moist N_2, the latter in order to determine the sorption capacity without interfering ions.

5.2.2 Column experiments

Four perspex cylinders, 0.70 m long and 0.10 m diameter, each contained 6.25 kg quartz sand with an average particle diameter of 0.2-0.4 mm. Two cylinders contained 20 g $Al(OH)_3$ in addition to the quartz sand. These were filled by first adding 10 cm (1.25 kg) pure quartz sand; then 10 portions of 0.50 kg

quartz sand, each mixed with 2 g X-ray amorphous $Al(OH)_3$, were added. Thin thoroughly washed grass sods with a known P-content were placed on top of the columns. The columns were shielded from daylight to prevent algal growth. The amount of water that remained in the columns after water application was 1 liter. Once every 2 weeks 1.5 liter of raw domestic sewage water (from the village Bennekom) was put on each column. The raw sewage water and the collected effluents were analyzed for total phosphate, total dissolved phosphate, dissolved orthophosphate and pH. A 0.45 µm filter was used to separate the so-called dissolved P from P-total. Digestion of the sewage water and of the effluent with $HClO_4$ and H_2O_2 gave the most consistent results for the total phosphate determination and was used throughout the experiment. The phosphate determinations were performed according to Murphy and Riley (1962).
At the end of the leaching experiments column segments were analyzed for organic-, (Al + Fe)-, and Ca-phosphates (Kurmies, 1972), and for total aluminum (Hill, 1966). The total aluminum was determined after dissolution by boiling in a concentrated H_2SO_4/HNO_3 solution. Fractions of the segments richest in P were analyzed with the scanning electron microscope (SEM) and with an energy dispersive X-ray analyzer (EDXRA).

5.3 Results

The results of the batch experiments are shown in Fig. 5.2. The increase of the amount of P sorbed per kg $Al(OH)_3$ between 2 and 16 days reaction time amounts to < 10% of the final sorption, regardless atmospheric or N_2 conditions. The amount of P removed from solution under N_2, however, is considerably larger than that removed under atmospheric conditions. This effect is ascribed to the competition of bicarbonate.
The average composition of the sewage water is given in Table 5.1.

Table 5.1. Average composition of the sewage water used in the column experiments.

Parameter	composition	
	mg/l	mmol/l
P-total	18.3	0.59
P-total-dissolved	15.5	0.50
P-ortho-dissolved	12.8	0.41
Ca	30	0.75
pH	8.0	

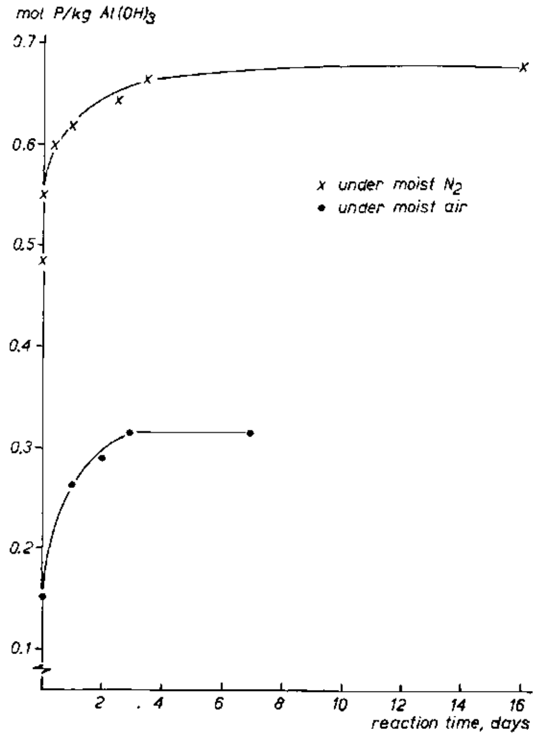


Fig. 5.2. The amount of phosphate removed from solution per kg adsorbent as a function of reaction time for the batch experiments.

The total amount of phosphate retained (calculated as the difference between the amount applied and the amount wich leaves the column with the effluent) relative to the amount applied at the end of the experiment is given in Table 5.2.

Table 5.2. Efficiency of P removal by the different columns.

Column	Total P added, mg P	Added P retained, %
1. quartz sand	466.5	14.7*
2. quartz sand	466.5	13.0*
3. quartz + $Al(OH)_3$	466.5	99.7
4. quartz . $Al(OH)_3$	466.5	97.6

* corresponding with the suspended P fraction of the sewage water.

The proportion of the applied P retained in the quartz sand columns (14.7 and 13.0% for comuns 1 and 2, respectively, Table 5.2) is similar to the proportion of total P present as sediment bound P in sewage water (15.0% Table 5.1), indicating that P retention may be restricted in these columns to the P combined with the solid fraction of the sewage water, the removal thus being limited here to a physical sieving action only.

The pH of the effluents was 7.9 ± 0.2 for all columns after the second sewage water addition.

The columns with $Al(OH)_3$ added to the quartz sand (columns 3 and 4) show a very high efficiency in retaining added P. Fig. 5.3, indicating the P concentration in the effluent of these columns, shows a complete removal of P in the first number of leachates.

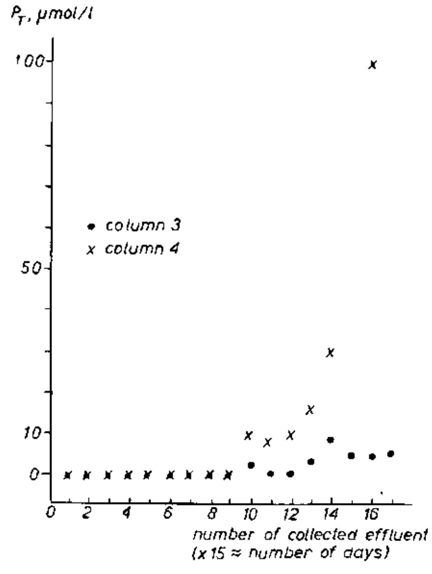


Fig. 5.3. The phosphate concentration in the effluent, collected after each addition of sewage water.

Then the effluent concentration of one of the two columns is rapidly rising, (however, still 80% is removed) while the other (a duplicate) is not. The results of the analysis of the column segments at the end of the experiment are shown in Fig. 5.4. This figure indicates that for both columns a real break-through is not yet reached. The difference between the amount of P removed, as calculated from influent and effluent data, and the amount determined in the column segments, is +4% for one and -4% for the other Al-containing column.

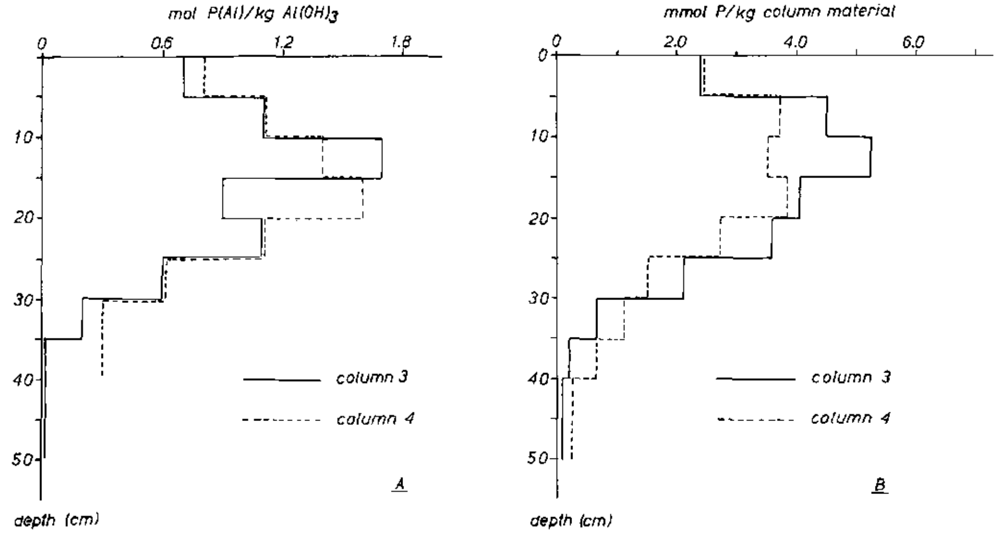


Fig. 5.4. Phosphate distribution as a function of depth in the columsn; (A) aluminum bound phosphate; (B) total phosphate.

The analysis of total aluminum shows that 25-35% of the aluminum in the columns has been washed out. This may have been caused by the fact that the mixing of $Al(OH)_3$ with the quartz sand did not directly result in a mixture of sufficient physical stability against the displacing forces of the applied sewage water. The loss of Al was more or less equally distributed over the whole column. The loss in Al is not accompanied by a loss in phosphate, which implies that the Al was probably lost before appreciable phosphate adsorption had taken place on this Al, and thus most likely at the beginning of the leaching experiment.

The amount of phosphate retained by the remaining $Al(OH)_3$ in the leaching experiment is considerably larger than would be expected from the pure system experiments (cf Fig. 5.2 and 5.4). A possible explanation of this phenomenon could be the formation of a solid calcium phosphate phase after an initial adsorption on $Al(OH)_3$, which would result in a permanent adsorption capacity on the surface of the $Al(OH)_3$. In order to check this possibility column segments were fractionated according to the method of Kurmies (1972) to discern between (Al + Fe)-, Ca-, and organic-phosphates. On the average 86% of total phosphate was correlated with Al, 2% with Ca and 12% was organic phosphorus. This shows that the formation of Ca phosphate is not important in this system. The (Al + Fe)₋ P fraction related to the measured amount of Al in each segment at the end of the experiment is shown in Fig. 5.4.A.

5.4 Discussion and the results of measurements with the scanning electron microscope (S.E.M.)

The results suggest that an aluminum phosphate has been formed in columns 3 and 4. The formation of variscite ($AlPO_4 \cdot 2H_2O$) under the experimental conditions is impossible (e.g. see Fig. 5.1). The solubiltity of other aluminumphosphates like evansite ($Al_3(PO_4)(OH)_6 \cdot 6H_2O(s)$), augelite ($Al_2(PO_4)(OH)_3(s)$), and wavelite in equilibrium with $Al(OH)_3$ can be calculated with the respective relevant stability constants as they are given by Nriagu (1976). The result is strongly dependent on the choice of the ΔG_f^o for $Al(OH)_3$ (s), e.g. the calculated solubility of these aluminumphosphates at pH 8 in equilibrium with crystalline $Al(OH)_3$ (s) is in the range 10^{-1} - 10^{-2} mol/l P, whereas this range shifts to 10^{-5} - 10^{-7} mol/l P when 'amorphous' $Al(OH)_3$ is considered. As in the present study amorphous $Al(OH)_3$ was used, the solubility will probably be near the lower range, although the real values cannot be calculated because of the unknown value for the solubility of the $Al(OH)_3$ involved.

The pure system showed no significant long-term reaction, indicating that adsorption was the only major process involved. The phosphate retaining capacity of the columns, in the segments rich in phosphate, is two to four times as large as in the pure systems. The components of the sewage water, or the different experimental conditions must have caused this effect. The most likely explanation is that a combination of Al, P and a cation of the sewage water is involved, which forms a stable combination. The effect is probably too large to ascribe it to co-adsorption of phosphate with such a specifically sorbed cation only (Chen et al. 1973b, Helyar et al. 1976). In order to find out which cation is involved, sieved fractions (< 0.05 mm) of the segment richest in P were analyzed with the S.E.M. and with E.D.X.R.A. (energy dispersive X-ray analyzer) for element analysis of the different particles.

The analysis clearly showed quartz particles which contained no phosphate, particles in which only aluminum could be detected (P conc. probably below the detection limit of the analyzer), and particles which contained Al, P and Ca.

This indicates that a Ca-Al-phosphate has been formed in the columsn. Grandallite ($CaAl_3(PO_4)_2\ (OH)_5 \cdot H_2O$ (s)) is according to the equilibrium constants as given by Nriagu (1976) the most stable Ca-Al-phosphate for conditions pertaining to columns 3 and 4. The phosphate concentration in equilibrium with 'amorphous' $Al(OH)_3$ is calculated as 0.1 μmol/l. While X-ray diffraction showed no lines, crystals that showed electrondiffraction were found with the electromicroscope. However, the collected information did not allow identification of these crystals.

6. REACTION OF PHOSPHATE WITH A SANDY SOIL AT CONSTANT SUPERSATURATION

Phosphate sorption experiments are described with an acid sandy soil at constant supersaturation with respect to metal phosphates. This constant supersaturation was obtained in two different ways viz. 1) the phosphato-stat (c_p-stat) technique, which enables accurate measurement of the reaction rate at constant supersaturation and 2) by taking a large ratio of solution to soil. The reaction rate is found to decrease with the amount sorbed, S, *according to* $dS/dt = k_1 \exp(-k_2 S)$. *This is ascribed to the formation of coatings of metal phosphates on top of the metal oxides present in the soil. The reaction rate is also dependent on the accompanying cation (Na, K). The above mentioned rate equation is also applicable to systems that already contain phosphate at the start of the measurements, implying that it can be used for the prediction of the long term sorption capacity of similar agricultural soils.*

6.1 General introduction

In chaps. 2 to 5 the reaction of phosphate with synthetic $Al(OH)_3$ has been described. In this chapter results will be presented of experiments with an acid sandy soil. The pH of the soil is 4.6. According to Fig. 5.1 this pH value implies that supersaturation with respect to the formation of aluminum (and iron) phosphates will already exist at very low phosphate concentration, c_p. All experiments reported here deal with supersaturated systems.
The results will be discussed with reference to the foregoing chapters and with reference to the litterature. The soil used, contains a very low fraction of organic matter, no calciumcarbonate and a reasonable amount of extractable iron and aluminum, with a presumably negligible clay fraction. The reaction of phosphate with this soil will thus be restricted to sorption on aluminum and iron oxides-hydroxydes, that may be present as individual particles or as coatings on quartz particles. The oxides will most probably contain some organic matter that will influence their structure and thus the sorption characteristics (Ng Kee Kwong and Huang, 1978);
The research described here was undertaken to test wether the phenomena, observed in the $Al(OH)_3$-phosphate system, would also occur in a soil containing

metal oxides-hydroxides.

6.1.1 Kinetics and reaction mechanisms

The kinetics of the phosphate sorption reaction with soil are of importance if one wants to predict the amount of phosphate that can be applied to the soil without risk to the environment (Beek, 1979). Insight into the reaction mechanism might also be of help to improve the efficiency of phosphate applied as fertilizer.

It is generally accepted that phosphate sorption may consist of adsorption and/or precipitation. It has been suggested in the literature that the precipitation reaction is a first order reaction with respect to the amount of phosphate adsorbed (Overman and Chu, 1977), assuming a reversible and time independent adsorption isotherm. This rate equation implies that the precipitation rate will be constant if the phosphate concentration is kept constant. This is in sharp contrast with the precipitation kinetics as observed with gibbsite (Chap. 2 and 3).

The main features of the sorption kinetics in the case of gibbsite were found as:

a) initially adsorption is the dominant reaction mechanism, with an adsorption maximum that is determined by the amount of singly coordinated OH(H) groups present on the hydroxide surface.

b) at high degree of supersaturation precipitation is the dominant reaction mechanism, almost from the start of the experiment (minutes, cf. Fig. 2.4).

c) the rate of precipitation increases with increasing supersaturation and decreases with the amount reacted.

d) the cation in the system (K^+, Na^+ etc.) influences the kinetics.

In order to clearly discriminate between the kinetics as proposed by a.o. Overman and Chu (1977) and kinetics where the amount sorbed decreases the reaction rate, all experiments with soil were performed at a constant c_p and pH over a considerable range of total sorption, S (mmol/kg). It may be noted that the equilibrium situation for the experiments reported here would be a complete conversion of the aluminum and iron oxides to corresponding metal phosphates. This then corresponds with the theoretical sorption maximum. Rate equations that predict equilibrium sorptions (dS/dt = 0) that are a function of c_p are thus not in agreement with the fundamentals of the precipitation process. This, however does not necessarily mean that such a type of equation can not mathematically describe the sorption data over a restricted range of

S and t.

A decrease in precipitation rate during the course of an experiment at constant supersaturation may for instance be caused by:

a) the presence of different sorbents with different reactivities;

b) a decrease of reactive surface area during sorption;

c) the formation of a surface layer of increasing thickness through which diffusion has to take place to let the reaction proceed.

6.2 Materials and methods

6.2.1 Soil samples

The soil used was a sandy soil, according to the Dutch Soil Classification a 'Kanteerd' Soil (De Bakker en Schelling, 1966), and has not been in use for agricultural purposes. Samples were taken at a depth of 70 - 110 cm. Sample B is a 1:1 mixture of the indicated layers (table 6.1). The extractable iron and aluminum of the soil samples was determined by three succesive extractions with citrate-dithionite-bicarbonate (CDB) (Mehra and Jackson, 1960) and with acid ammonium oxalate (OX) (Tamm, 1932; Schwertmann, 1964). Table 6.1 presents some data of the samples used in the experiments.

Table 6.1 Some data of the soil samples used in the experiments.

Sample	depth	Al	Fe	Al	Fe	Org. C
	cm	mmol/kg		mmol/kg		%
		(CDB)		(OX)		
A	70 - 80	71	33	65	8	0.23
B	90 - 100	23	33	-	-	0.15
	100 - 110	39	29	110	16	-

6.2.2 Phosphato-stat experiments

The experimental procedures for the phosphato-stat experiments are similar to those described in chaps. 2 and 3. The conditions of the experiments were: 300 ml 20 mmol/l NaCl or KCl; 90 gram soil; pH = 4.62 (= equilibrium pH of the soil in this solution); different c_p values in the range of 0.1 mmol/l to 10 mmol/l (NaH_2PO_4 or KH_2PO_4).

The soil was brought in the reaction vessel together with the background electrolyte, stirred for 1 to 1.5 hrs. and kept at pH 4.62 with HCl and/or

NaOH. After this time the drift in pH was negligible. Then phosphate was added to the system and the pH was kept constant with the phosphato-stat set up. At time intervals samples were taken and analyzed for phosphate after filtration.

The stirring of the reaction system may cause some decomposition of the soil particles (Beek, 1979), thus possibly increasing the surface area of the soil during the experiment. This effect will probably be the largest in the pre-equilibration period (before the phosphate is added). If it still occurs during the phosphate sorption its effect will be an increase of the reaction rate with time. As will be shown this effect is not strong enough to obscure the precipitation mechanism. The experiments lasted 3 to 5 days. To be able to estimate the effect of the experimental conditions on the reaction rate and to obtain sorption data for much longer reaction times, also so called batch experiments were performed.

6.2.3 Batch experiments

All batch experiments were done in duplicate and had 20 mmol/l NaCl as background electrolyte with varying c_p values ($NaH_2 PO_4$). The c_p value was maintained at a constant level by using a wide solution to soil ratio, 360, a method used before by Muljadi et al. (1966). 5 gram soil was brought in plastic containers of 2 liters and pre-equilibrated in the presence of the electrolyte solution until the pH drift was negligible. The containers were mechanically shaken (horizontilly) for the first day of reaction. After this period, the content of containers was gently mixed from time to time by end over end shaking by hand. The pH was adjusted if necessary.

At the end of the reaction period (9 - 81 days) the soil particles were separated from the liquid by filtration, dried, ground with a ball mill and treated with Fleischmann acid (H_2SO_4: HNO_3 = 1:1) prior to phosphate determination. The destruction was done in duplicate. The c_p value as measured in the destruate allows calculation of S. The S values were corrected for the phosphate initially present in the soil samples (blank 3.5 mmol/kg).

6.3 Results and discussion

6.3.1 Phosphato-stat experiments

Preliminary experiments indicated that the ratio between the hydroxyl production and phosphate sorption, R, was constant after some time. This constant ratio allows the construction of the so called phosphato-stat (Chaps. 2 and 3). The ratio varied somewhat for the different experiments (Fig. 6.1). It seems that the ratio decreases slightly with increasing c_p value. According to the reasoning as presented in Chaps. 2 and 3, this may indicate that the co-sorption of cations is somewhat dependent on c_p.

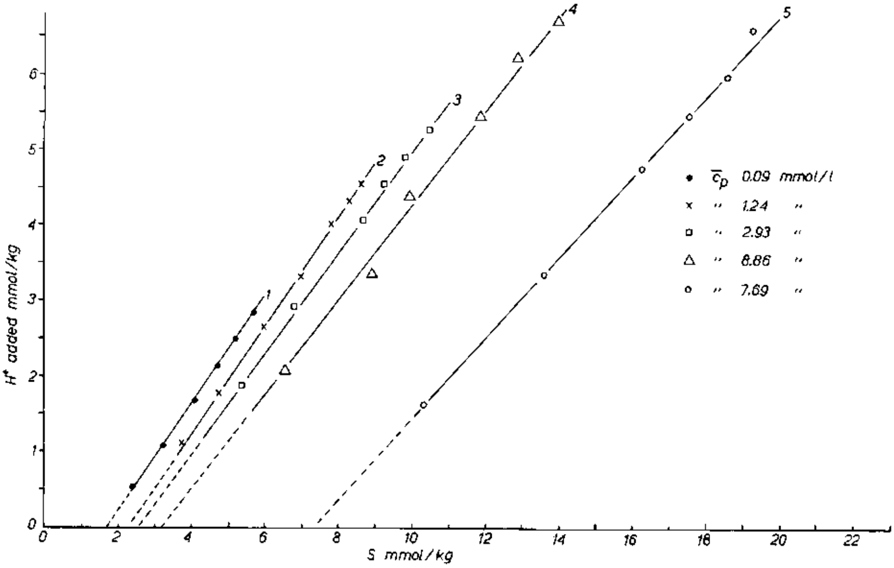


Fig. 6.1. The amount of acid required to keep the pH constant as a function of phosphate sorption for 5 phosphato-stat experiments: sample B, pH 4.62, 20 °C. Experiment 1 to 4 had 20 mmol/l NaCl as supporting electrolyte using NaH_2PO_4 as source of phosphate; experiment 5 had 20 mmol/l KCl as supporting electrolyte and KH_2PO_4 was used. Data of linear regression analysis are given below, S_o^* indicating the intercept with the horizontal axis.

Exp.	r^2	R	S_o^* (mmol/kg)
1	0.999	0.707	1.67
2	1.000	0.708	2.93
3	0.998	0.661	8.86
4	0.993	0.628	7.69
5	0.999	0.529	6.67

The c_p value decreased slightly during the experiments due to a difference in the pre-estimated R-value and the measured R-value. The deviation from the average concentration, $\bar{c}_p$, was less than 6% except for experiment 1 where it was 19%. All the reported sorptions are calculated from the amount of phosphate added during the experiment and from the measured change in c_p. The sorptions of the different experiments as a function of $\sqrt{t}$ (t = time) are shown in Fig. 6.2.

It is to be expected (Chap. 2) that precipitation phenomena dominate the reaction kinetics already shortly (minutes - a few hours) after the start of the experiments due to the high supersaturations involved.

This is supported by the constancy of the R-value after a short reaction time. Broken lines, calculated from linear regression analysis for $t > 1$ hr, are drawn also in Fig. 6.2. The shape of the measured curves suggests that the precipition is not adequately described by this type of equation ($S = k_1 \sqrt{t} + k_2$) in spite of the close agreement between calculated and measured values. Experiments over longer reaction times support this (See 6.3.2). Extrapolation of the regression equation would thus lead to an overestimation of the sorption.

It can be inferred from Fig. 6.2 that the reaction rate of all experiments decreases strongly with increasing sorption. Assuming that metal phosphates are formed that belong to one of the minerals as identified by Haseman et al. (1950, 1951) with a phosphate to metal ratio ranging from 2 to 1, it follows from the measured sorptions as shown in Fig. 6.2 in combination with the Al + Fe contents of the samples as given in table 6.1, that only a fraction of the metal oxides is needed to form these (presumed) metal phosphates. It is thus not unlikely that the decrease of the reaction rate is caused by the formation of a coating of metalphosphates on the metal oxides.

At this stage it is already clear that this type of soil does not follow the precipitation kinetics as proposed by Overman and Chu (1977). The results furthermore show that potassium has a positive effect on the reaction rate as compared with sodium. These findings are in accord with the results as found from the experiments with gibbsite (Chaps. 2 and 3).

The presumed precipitation mechanism has much in common with the oxidation mechanism of metals (Evans, 1955; Roberts, 1961; Fehlner and Mott, 1970). Several theoretical rate equations are used to describe the oxidation kinetics of metals. Often it is difficult to discriminate between the different equations on the basis of experimental data. The equations that are most commonly used to describe oxidation measurements are of the following types (constant supersaturation),

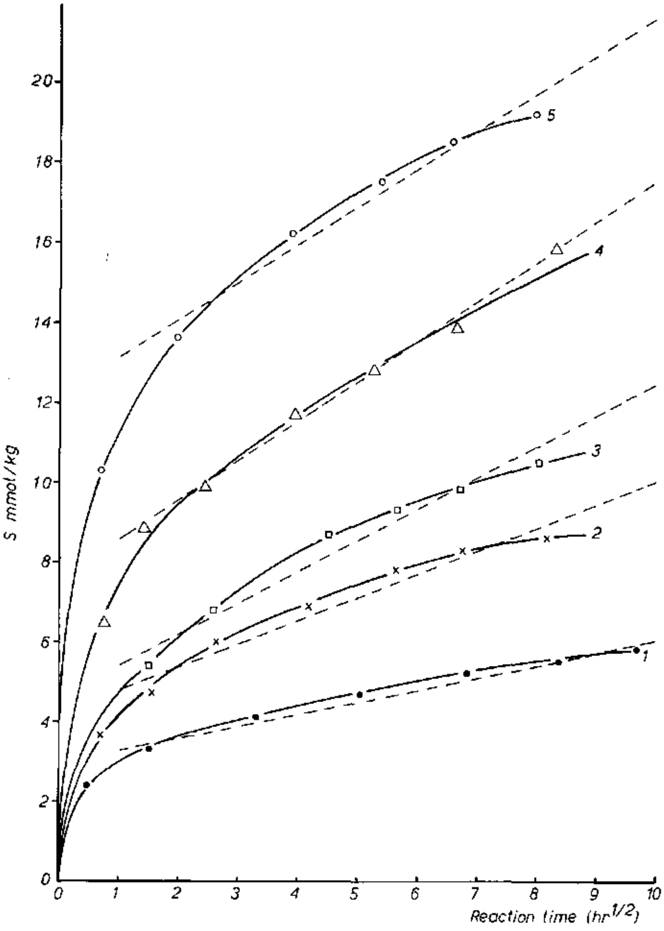


Fig. 6.2. Sorption of phosphate on sandy soil (B) at constant c_p and pH (phosphato-stat) as a function of $\sqrt{t}$. The experimental conditions are given in Fig. 6.1. Data of linear regression analysis (broken lines) for t > 1 hr according to $S = k_1 \sqrt{t} + k_2$ are given below.

Exp.	r^2	k_1	k_2
1	0.964	0.291	3.04
2	0.958	0.580	4.24
3	0.961	0.768	4.69
4	0.995	0.995	7.56
5	0.969	0.937	12.2

$$\frac{dl}{dt} = k_1(l)^{-1} \qquad (6.1)$$

$$\frac{dl}{dt} = k_1(k_2 l + k_3)^{-1} \qquad (6.2)$$

$$\frac{dl}{dt} = k_1 e^{-k_2 l} \qquad (6.3)$$

$$\frac{dl}{dt} = k_1 e^{k_2/l} \qquad (6.4)$$

with l the thickness of the surface coating formed. l is proportional to the amount reacted S, for the condition of constant surface area. k_i (i = 1, 2 or 3) is rate 'constant', dl/dt is reaction rate.

Since the thickness of the presumed coatings cannot be measured all results will be interpreted here as a function of S instead of l.

Some other types of equations that have been used to describe phosphate sorption (Enfield et al., 1976) are;

$$\frac{dS}{dt} = k_1(k_2 - S) \qquad (6.5)$$

$$\frac{dS}{dt} = k_1 S^{k_2} \qquad (6.6)$$

Some k_i parameters will be a function of the supersaturation.
The applicability of the different rate equations to the experiments can be tested in the differential form and/or after integration of the respective equations. In fact equation 6.1 was tested in its integrated form already (Fig. 6.2). In general the adsorption kinetics will dominate the initial stage of the reaction and thus the first stage of the reaction period should not be included if one wishes to study the applicability of the different rate equations to the precipitation kinetics. The precipitated amount will be equal to,
$S_p = S + S_o - S_a$, where S_a represents the contribution of the amount adsorbed to the measured sorption, S, and S_o the precipitated amount at the start of the experiment. The uncertainty about the values of S_o and S_a has no effect on the test of the validity of equations 6.2, 6.3 and 6.5. Using S instead of S_p influences 'only' the value of one of the 'constants' of the respective equations. However, this will cause problems if one wants to know the dependence of the

different k_i's on the supersaturation. Equation (6.1) may only be tested safely by using its integrated form, because then the above mentioned uncertainty has no influence on its applicability. Equations 6.4 and 6.6 may only be tested for the condition that $S_o - S_a$ is negligible compared to S, implying that these equations preferably should be tested for higher S values and thus starting at longer reaction times.

The reaction rate can be calculated from the measured points of Fig. 6.2 or from recorder curves. In fact a recorder was connected with the burette of the c_p-stat and registered the volume of acid required to keep the pH of the system constant as a function of time. With the help of Fig. 6.1 in combination with the known concentrations in the burette, and the soil solution ratio, the recorder curve can be converted to the amount of phosphate reacted per amount of soil as a function of time. On the average 10 different reaction rates were calculated per experiment with this method. Calculation of reaction rates from the data points (Fig. 6.2) would lead to much less data per experiment.

Equations (6.1) to (6.6) were tested with the data from the 5 experiments for $t > 1$ hr. Equations 6.1 and 6.2 were tested in the integrated form.

The results could best be described by (6.3) with coefficients of determination (r^2) ranging from 0.98 to 1.00 for the individual experiments, and second best with (6.1) (for r^2 values cf. Fig. 6.2). The worst fit was obtained with (6.5) with r^2 ranging from 0.77 to 0.89.

The calculated k_2 values of (6.5) are for exp. 1 - 5: 5.3, 8.9, 9.7, 13.7 and 18.7 mmol/kg, respectively. These are thus the maximum S values as predicted by this equation and are clearly a function of c_p, whereas the k_1 value of (6.5) is almost independent of c_p (0.11 ± 0.02). This type of equation is often used (Hornsby and Davidson, 1975; Enfield et al., 1976) to describe the results of sorption experiments but should not be expected to hold if precipitation occurs (see section 6.1.1). Using this equation here may lead to a considerable underestimation of S for longer extrapolated reaction times (see also Fig. 6.3 and section 6.3.2).

According to above discussed reasons equation 6.3 is selected as the best and most convenient rate equation to describe the sorption experiments. This equation is sometimes referred to as the Roginsky-Zeldovich equation (Roginsky and Zeldovich, 1934) or in the integrated form as 'the direct logarithmic equation' (Evans, 1955). It is often found applicable for activated sorption processes (Roberts, 1961). The calculated rate coefficients are shown in table 6.2. It can be seen that both k_1 and k_2 are a function of c_p. It is seen that the value of k_2 decreases with increasing c_p and also decreases if sodium is replaced by potassium

Table 6.2 Calculated values of k_1 and k_2 of (6.3) by curve fitting the calculated reaction rates (recorder curves) of exp. 1 to 5. k_1^* was obtained by substracting S_o^* of Fig. 6.1 from the different S values.

Exp.	k_1	k_1^*	k_2	r^2
	-mmol/kg hr-		-kg/mmol-	
1	13.8	1.55	1.31	0.988
2	14.0	2.53	0.772	0.979
3	21.1	4.1	0.661	0.996
4	91.1	14.9	0.564	0.992
5	165.6	7.06	0.434	0.991

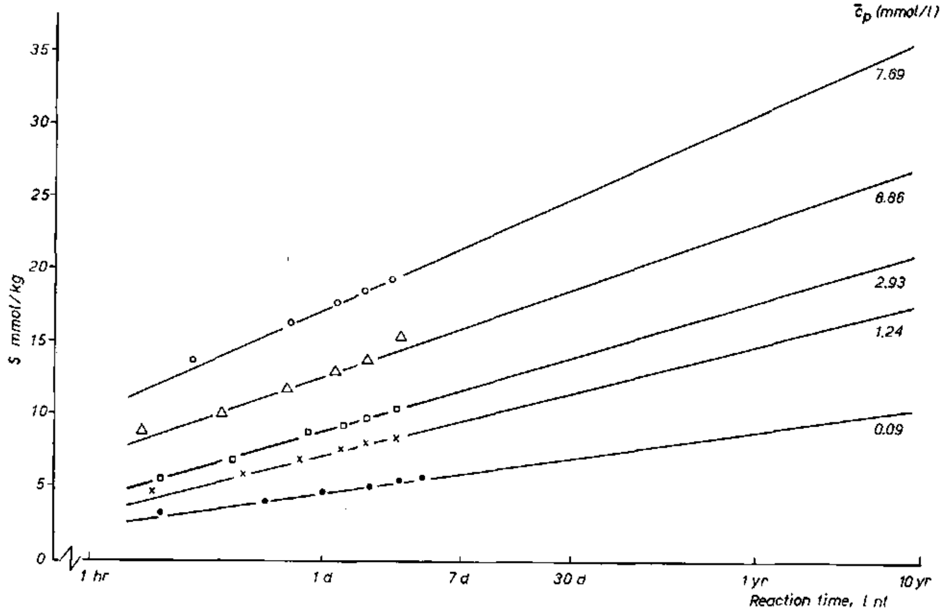


Fig. 6.3 Sorption of phosphate on sandy soil (B) at constant c_p and pH (phosphato-stat as a function of lnt. The experimental conditions are given in Fig. 6.1. The solid lines are calculated with (6.7), with k_1 and k_2 values as calculated from the recorder curves of the c_p- stat (see text for explanation).

(Exp. 4 and 5). This may be explained by different physical chemical properties of the surface layer formed (e.g. its porosity, surface potential, change in surface area with S etc.). It may be noted that Barry and Stone (1960) also find a decrease of k_2 with increasing oxygen pressure (comparable with c_p here) for oxidation experiments with zinc.

k_1 increases with increasing supersaturation but the dependency of k_1 on c_p is greatly influenced whether or not a correction is applied to S, to obtain an estimate of S_p.

In table 6.2 k_1 is calcultated using the total sorption as measured, and by using S_o^* (Fig. 6.1) as correction term yielding k_1^*. k_1 is more or less proportional to c_p ($k_1 = a\ c_p^b \rightarrow r^2 = 0.94$, $a = 9.8$, $b = 0.97$) whereas k_1^* is more or less proportional to $\sqrt{c_p}$ ($k_1^* = a\ c_p^b \rightarrow r^2 = 0.80$, $a = 3.5$, $b = 0.45$). More measurements at short reaction times are necessary to evaluate the correction that should be made on S in order to get the real precipitation rate parameter and its dependence on c_p. In fact also a soil that contains even less initial phosphate should be used for this purpose. The integrated form of (6.3) for the condition, that $S = 0$ at $t = 0$ is,

$$S = k_2^{-1}\ \ln(t + (k_1k_2)^{-1}) + k_2^{-1}\ \ln k_1k_2 \qquad (6.7)$$

Figure 6.3 shows the sorption as a function of lnt calculated with the help of (6.7) and the data of table 6.2 for the different experiments (lines) together with the individual measurements (points). Referring to the foregoing discussion on the amount of metal phosphates that can be formed in the soil used, it can be seen that the predicted S values are well below the maximum amount of phosphate that can be precipitated even after ten years reaction time.

6.3.2 Batch experiments

The batch experiments were done to test the effect of the experimental conditions, with respect to prolonged reaction time and stirring on the reaction. Since they were extended for relatively long reaction times (81 days), they also offer the opportunity to test extrapolations made on the basis of (6.7) with the constants as obtained from the c_p-stat experiments.

The results of the batch experiments are shown in Fig. 6.4. It can be seen that these experiments can also be described by (6.7) ($1/k_1k_2 \ll 1d$). However, the data are much less accurate than those of the c_p-stat experiments leading to some scatter of points and less reliable values of k_1 and k_2. The irregular dependence of the slopes of the regression lines on c_p is probably due to experimental error.

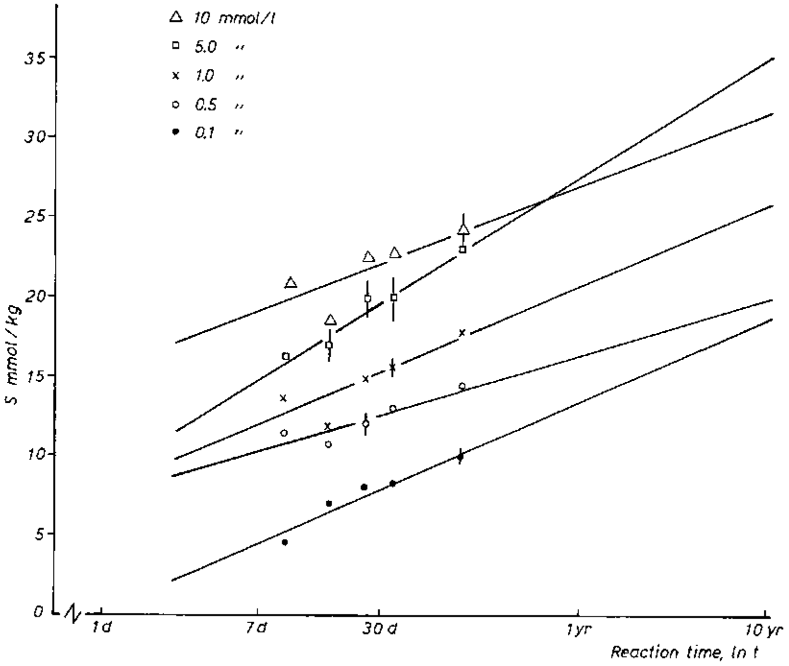


Fig. 6.4 Sorption of phosphate on a sandy soil (A) at constant c_p and pH as a function of lnt. (pH = 4.62, 20 mmol/l NaCl, 20° C) as measured with batch experiments.

Since a different soil layer was used for the batch experiments, as compared with the experiments as reported in 6.3.1, some additional c_p-stat experiments were done to be able to compare the results of both techniques for the same layer. The results are shown in Figs. 6.5, 6.6 and 6.7, together with the results of comparable batch experiments. Comparing these c_p-stat experiments with corresponding ones of Fig. 6.3 shows that sample A is somewhat more reactive than sample B. This may be caused by the higher organic matter content (Ng Kee Kwong and Huang, 1978) and/or a higher specific surface area of A compared with B.

The differences, between the sorptions predicted for longer reaction times from the c_p-stat experiments and the values as measured in the batch experiments, are

on an average quite small for the experiments of Figs. 6.5 and 6.6. The slightly higher predicted values in Fig. 6.5 may be caused by the higher c_p value in the c_p-stat experiment as compared with the batch experiment. For the experiment with c_p is 10 mmol/l a larger difference is observed in the order of 30%.
It is thus seen that extrapolation of (6.7), using constants as obtained from short term c_p-stat experiments, leads to a reasonable estimate of the sorption for longer reaction times.

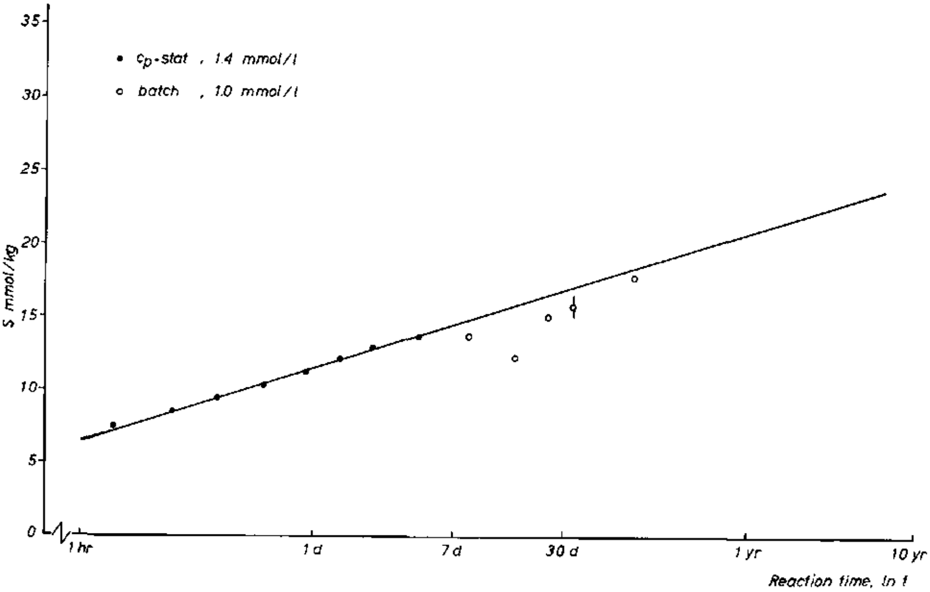


Fig. 6.5. Sorption of phosphate on sandy soil (A) as a function of lnt as measured with phosphato-stat and with batch experiment. Calculated k_1 = and k_2 values (equation (6.7)) for the phosphato-stat experiment are: k_1 = 105 mmol/kg hr and k_2 = 0.64 kg/mmol. The line is calculated with (6.7) and the given constants.

This is in strong contrast with projections made on the basis of a $S - \sqrt{t}$ fit. These overestimate the sorptions as measured with the batch experiments considerably (more than 1.5 times) and predict a complete conversion of all available metal ions within 1 - 10 yr.
As discussed in 6.2.2 it may be expected that the surface area of the soil increases somewhat due to the stirring of the soil-electrolyte system.
This effect is minimized in the batch experiment but may be considerable in the c_p-stat experiments. The effect of the surface area on the rate 'constants' will

now be derived starting with (6.3).

$$\frac{dl}{dt} = k_1 e^{-k_2 l} \qquad (6.3)$$

The relationship between the measured S value and l will be:

$$Al\rho/M = S \qquad (6.8)$$

Where A is the specific surface area of the soil (area/mass), ρ the density of the formed surface coating, M the molecular mass of this coating per unit phosphate, l and S have been defined before.

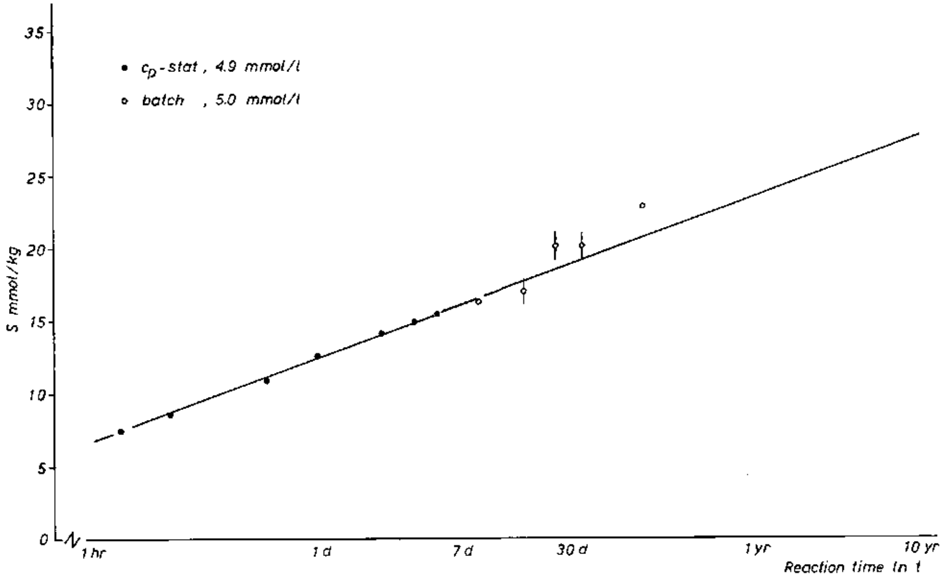


Fig. 6.6 Sorption of phosphate on sandy soil (A) as a function of lnt as measured with phosphato-stat and with batch experiment. Calculated k_1 and k_2 values (6.7) for the phosphato-stat experiment are: k_1 = 71 mmol/kg hr, and k_2 = 0.52 kg/ mmol.

(6.3) can now be converted into units of S with the help of (6.8) leading to,

$$\frac{dS}{dt} = k_1 A \frac{\rho}{M} \exp \left(-k_2 \frac{1}{A} \frac{M}{\rho} S\right) = k_1 A \lambda \exp \left(-k_2 \frac{S}{A\lambda}\right) \qquad (6.9)$$

with $\rho/M = \lambda$.

For conditions of constant surface area and constant composition of the surface layer Aλ can be incorporated in the rate 'constants' k_1 and k_2 as was done so far.

These 'combined' constants can be determined from experiment. A difference in surface area of comparable batch and c_p-stat experiments could thus be determined from the respective experimental k_2 values.

The difference in k_1 should not be used because of uncertainties in its interpretation (see for instance table 6.2). The experimental k_2 value of the batch experiments can be determined from the slopes of the lines of Fig. 6.4 (see (6.7)).

However, as has been discussed before, these k_2 values will be quite inaccurate. The effect of an increase in surface area would be a proportional increase in the slope of these lines.

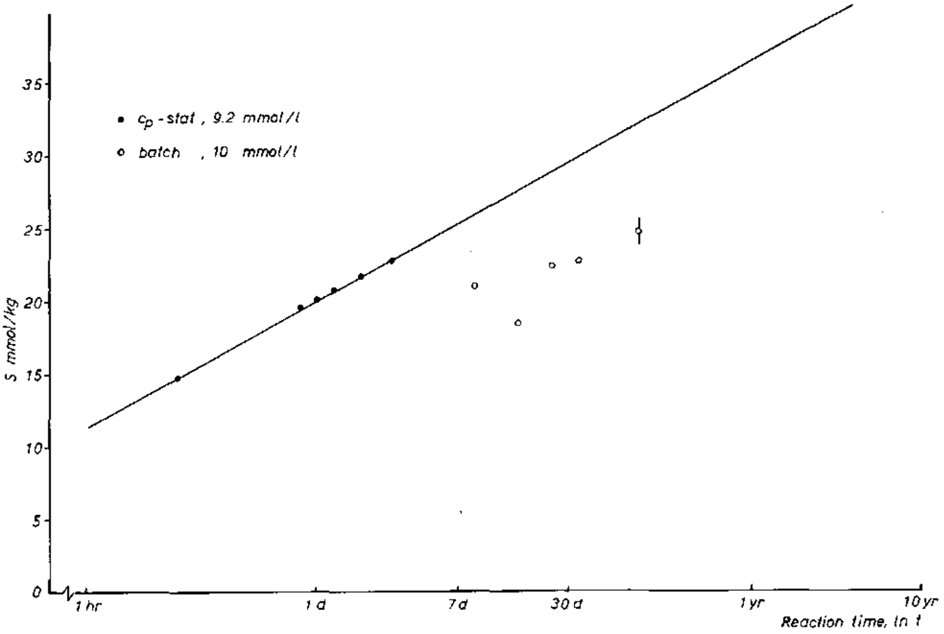


Fig. 6.7 Sorption of phosphate on sandy soil (A) as a function of lnt as measured with c_p-stat and with batch experiment. Calculated k_1 and k_2 values for the c_p-stat experiment are: k_1 = 161 mmol/kg hr, and k_2 = 0.37 kg/mmol.

Comparison of the data of Fig. 6.6 shows that the best linear line that can be drawn through the points of the batch experiment has a larger slope than the line as drawn through the points of the c_p-stat experiment. This is opposite to what is expected. However, Fig. 6.4 suggests that the determined slope of this batch experiments may be too high, comparing this experiment with the other batch experiments.

The slopes of the lines of Fig. 6.7 are about the same. In conclusion it may be stated that a difference of surface area of the soil in both techniques created during the pre-equilibration period can in principle be determined from the different k_2 values of comparable experiments, but that the data of the batch experiments are not accurate enough to draw any conclusion in this respect.

6.3.3 *Exchange experiments with* ^{32}P

The results of the experiments described in 6.3.1 and 6.3.2 show that the sorption that is found after a certain reaction time is a function of c_p. The larger c_p, the larger sorption is measured. The assumed reaction mechanism is the formation of coatings of metal phosphates on the soil metal oxides through which diffusion has to take place. If this is the case, it is to be expected that the fraction of sorbed phosphate exposed to the solid-solution interface is lower the higher c_p during the sorption, corresponding with thicker coatings. This effect was estimated by performing exchange experiments with ^{32}P. For this purpose the samples of the experiments described in 6.3.1 were used. These samples had been stored for a long time (months) and exhibited a negligible sorption rate at the moment the exchange experiments were done.

The results are shown in table 6.3.

Table 6.3 The percentage of total phosphate of experiment 1 to 4 (see Fig. 6.1 for experimental conditions) found exchangeable with ^{32}P after various exchange times.

time (days)	Number of Experiment			
	1	2	3	4
1	50	32	13	10
3	56	41	21	17
7	69	59	32	26

It can be seen that the fraction that is exchangeable decreases with an increasing c_p during the experiment as expected according to the suggested mechanism, irrespective of the duration of the exchange experiment. These results support the comments on fertilization practice, that were made in Chap. 2.

6.4 Application of the c_p-stat method for inventory purposes

The estimation of the long-term phosphate sorption capacity of soils to which large amounts of phosphate are being added annualy, is a prerequisite if one wants to estimate the potential environmental pollution of intensive life stock production (see chap. 1 and Beek, 1979) with respect to phosphate. The above mentioned farming method is in the Netherlands mainly practiced on slightly acid sandy soils. The c_p-stat method may thus be of use in making an inventory of the (estimated) phosphate sorption capacities (rates) of these agricultural soils. The data obtained can be used in combination with a transport model, to predict the leaching of phosphate for a certain management system (Mansell et al., 1977; Enfield, 1977; Beek, 1979).
Some automation would be helpfull in collecting the required rate data for many different soil samples. The c_p-stat method can be partially automated by connecting the burette to a (micro) computer. The computer can be programmed to calculate the reaction rate provided additional information is also made available. Such additional information is for instance the soil-solution ratio, the measured c_p-values at various reaction times etc. Furthermore, the computer can be used to test different rate equations and to predict the sorption capacity for reaction times on the basis of a selected rate equation.

6.5 Conclusions

It has been shown that the measured R value of the different experiments becomes constant after a short reaction time. This enabled accurate experiments at constant c_p and pH with the c_p-stat. The reaction rate decreased with increasing S at constant c_p during each experiment. The reaction rate of all experiments could best be described with one type of rate equation, already after a very short reaction time. These facts are in accord with the presumed reaction mechanism, as the formation of a coating of metal phosphates. Such coatings are supposedly formed by conversion of the outer layers of the metal oxides into metal phosphates. The R-value suggests that sodium and potassium will be part of the reaction product because its value is < 1 (chap. 3). These sort of reaction products have been identified in other studies. (Haseman et al., 1950; 1951).
The reaction rate increases when sodium is subsitituted for by potassium. All these aspects were also found for the experiments with gibbsite (Chaps. 2 and 3) although the rate law was a different one.

The batch experiments showed that extrapolations of the c_p-stat experiments with respect ot time on the basis of the selected rate equation gives satisfactory results. An important practical advantage of the selected rate equation is that it can also be applied to soils that contain an unknown amount of phosphate at the start of the experiment. It may thus be used for the estimation of the long-term sorption capacity of agricultural soils that are found to obey this rate equation.

SUMMARY

$Al(OH)_3$ is a very effective sorbent for orthophosphate especially at low pH. At low phosphate concentration c_p, phosphate is adsorbed by an exchange mechanism with singly coordinated OH(H) groups residing on the surface of the $Al(OH)_3$. In chapters 2 and 3 experiments are described using a well defined gibbsite (crystalline $Al(OH)_3$) as sorbent. A rate equation is selected that describes the adsorption reaction for a fractional coverage (amount adsorbed/ maximum adsorption capacity) between 0.5 and 1.0. At intermediate and high c_p values the sorption can easily exceed the maximum exchange-adsorption capacity. The maximum adsorption capacity of the gibbsite used was estimated with the help of shadowed electron micrographs. The sorption beyond the exchange-adsorption maximum is identified as a precipitation process, i.e. it only occurs in supersaturated systems. The rate of this precipitation reaction is shown to increase with increasing supersaturation and to decrease with increasing amounts sorbed. Evidence is presented that indicates that the decrease of the reaction rate with increasing sorption is caused by the formation of coatings of a (K)-Al-phosphate on the gibbsite particles. The activation energy of this reaction is determined. The ratio of the OH that is produced during this sorption reaction and the phosphate sorption is found to be independent of the extent of the reaction, for certain reaction conditions. A so called phosphato-stat (c_p-stat) has been constructed that provides for both a constant pH and c_p during the sorption reaction. The amount precipitated is found proportional with the square root of reaction time for the condition of constant supersaturation.

The relative contribution of precitation and adsorption has been calculated as a function of c_p and reaction time. It is furthermore shown that the nature and concentration of the accompanying cation has an effect on the precipitation rate (constant total electrolyte concentration).

In chapter 4 experiments are described using X-ray amorphous $Al(OH)_3$ and α Al_2O_3 as sorbent. A pure phosphate solution and a so called inorganic synthetic sewage water medium are used as electrolyte solution. There is some effect of the electrolyte medium on the sorption rate as expected. The general characteristics of the sorption reaction described in this chapter are

similar to the results as found with gibbsite; in the initial stage of the reaction adsorption is the dominant reaction mechanism, whereas precipitation dominates the kinetics for longer reaction times.

In chapter 5 experiments are described that make use of columns either filled with quartz sand or quartz sand mixed with X-ray amorphous $Al(OH)_3$. Raw domestic sewage water (pH $\approx$ 8) was added to the columns once every two weeks during 10 months. It is shown that the sorption of phosphate from sewage water in the Al-containing column is higher than would be expected from pure inorganic system experiments. Evidence is presented that indicates that a Ca-Al-phospate has been formed in the Al-containing sand column (Ca was absent in the pure system experiments to prevent the complication of the formation of calciumphosphates). The quartz sand columns acted as a sieve for solid compnents of the sewage water only.

Experiments using an acid sandy soil with a low organic matter content as sorbent for phosphate are described in chapter 6. The main characteristics of the sorption reaction as determined from the experiments using $Al(OH)_3$ were also found in the sorption experiments using this soil. Use has been made of the phosphato-stat to provide conditions of constant supersaturation during the reaction. It is shown beyond doubt that the reaction rate continuously decreases at constant supersaturation as the reaction proceeds. The components of the soil that are active in the phosphate sorption process are most probably the (amorphous) aluminum-iron-oxides-hydroxides of the soil. The amount of extractable iron and aluminum was determined.

The mechanism of the phosphate sorption reaction using metal oxides as sorbent is compared with the oxidation mechanism of metals.

The phosphato-stat method may be used in combination with a (micro) computer, facilitating the collection of phosphate sorption rate data on a somewhat larger scale for practical applications.

SAMENVATTING

Reeds bij zeer lage concentraties wordt fosfaat in belangrijke mate gebonden aan $Al(OH)_3$, vooral wanneer de pH van de suspensie laag is. Bij lage fosfaatconcentratie, c_p, is het bindingsmechanisme een uitwisselings-adsorptie met enkelvoudig gecoordineerde OH(H) groepen welke aanwezig zijn op het $Al(OH)_3$ oppervlak. In de hoofdstukken 2 en 3 worden fosfaat sorptie experimenten beschreven waarbij gebruik gemaakt is van goed gedefinieerd gibbsiet (kristallijn $Al(OH)_3$). Een adsorptie snelheidsvergelijking wordt beschreven die geldig is voor een relatieve bedekking (hoeveelheid geadsorbeerd/maximum adsorptie capaciteit) van 0.5 tot 1.0. De sorptie kan de maximum uitwissel-adsorptie capaciteit reeds overschrijden bij relatief lage fosfaatconcentraties. De maximum adsorptie capaciteit van het gebruikte gibbsiet werd bepaald met behulp van foto's gemaakt van geschaduwde preparaten na vergroting d.m.v. de electronenmicroscoop. De sorptie welke uitgaat boven het gedefinieerde adsorptie maximum wordt gekenmerkt als een precipitatie reactie; dit verschijnsel treedt nl. uitsluitend op wanneer het reactie systeem oververzadigd is t.o.v. aluminium fosfaat vorming. De snelheid van deze precipitatie reactie blijkt groter te worden wanneer de oververzadiging toeneemt en af te nemen met toenemende hoeveelheden gereageerd fosfaat. Verschillende experimenten leiden tot de conclusie dat deze afname van de reactie snelheid met toenemende sorptie waarschijnlijk wordt veroorzaakt door de vorming van een huidje van een (K)-Al-fosfaat om het gibbsiet. De activeringsenergie van deze reactie is bepaald.

De verhouding tussen de (netto) hoeveelheid OH die vrij komt tijdens de sorptie reactie en de fosfaat sorptie blijkt voor bepaalde reactie omstandigheden onafhankelijk te zijn van de hoeveelheid fosfaat die heeft gereageerd. Dit geeft de mogelijkheid tot constructie van een zogenaamde phosphato-stat (c_p-stat). Deze opstelling zorgt voor zowel een constante pH als fosfaatconcentratie gedurende de sorptie reactie. Bij een constante oververzadiging blijkt de hoeveelheid geprecipiteerd fosfaat evenredig te zijn met de wortel uit de reactie tijd.

De bijdrage van de adsorptie en de precipitatie werd berekend als een functie van c_p en reactie tijd. Soort en de concentratie van het kation dat in het reactie systeem aanwezig is naast H^+ (Na, K etc.) blijken van invloed op de precipitatie snelheid van het fosfaat.

In hoofdstuk 4 worden experimenten beschreven, waarbij X-ray amorf $Al(OH)_3$ en

α Al_2O_3 worden gebruikt als sorbent. Als electroliet oplossing worden een zuivere (ortho) fosfaat oplossing en een zogenaamd synthetisch anorganisch riool water oplossing gebruikt. De aard van het medium heeft, zoals te verwachten is enig effect op de sorptie snelheid. Het mechanisme van de in dit hoofdstuk beschreven proeven komt in grote lijnen overeen met hetgeen bij de gibbsiet proeven gevonden werd: adsorptie is het belangrijkste mechanisme bij de aanvang van de reactie, terwijl precipitatie processen de kinetiek bepalen na langere reactie tijden.
In hoofdstuk 5 worden experimenten beschreven welke gebruik maken van kolommen die gevuld zijn met kwartszand of met een mengsel van kwartszand en X-ray amorf $Al(OH)_3$. Ruw huishoudelijk afvalwater (pH ≃ 8) werd gedurende 10 maanden eenmaal per 2 weken aan de kolommen toegediend. Aangetoond wordt dat de opslag van fosfaat in de Al-houdende kolom groter is dan te verwachten was op grond van experimenten gedaan met een vergelijkbaar zuiver anorganisch reactie systeem. Er zijn aanwijzingen dat er een Ca-Al-fosfaat gevormd is in de Al-houdende kolom (Ca was afwezig in de vergelijkbare puur anorganische sorptie proeven om de vorming van zuivere calciumfosfaten te voorkomen). De kolommen gevuld met kwartszand fungeerden louter als een zeef voor vaste bestanddelen van het afvalwater.
In hoofdstuk 6 worden proeven beschreven waarbij een zure zandgrond (laag organisch stof gehalte) wordt gebruikt als sorbent voor fosfaat. De hoofdkenmerken van de sorptie reactie van fosfaat met deze grond en met $Al(OH)_3$ zijn dezelfde. Een konstante oververzadiging tijdens de reactie kon ook hier bereikt worden m.b.v. de fosfato-stat. Aangetoond wordt dat de reactie snelheid ook bij constante oververzadiging voortdurend afneemt bij een voortschrijdende reactie. De componenten van de grond die de fosfaat sorptie veroorzaken zijn zeer waarschijnlijk de (amorfe) aluminium-ijzer-oxiden-hydroxiden van de grond. De hoeveelheid extraheerbaar aluminium en ijzer werd bepaald.
Het mechanisme van de fosfaat sorptie reactie aan metaal oxiden wordt vergeleken met het oxidatie mechanisme van metalen.
De phosphato-stat methode, kan gebruikt worden in combinatie met een (micro) computer. Deze combinatie kan van groot nut zijn wanneer gegevens betreffende de fosfaat sorptie kinetiek van veel verschillende gronden moet worden bepaald.

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