

DESORPTION OF PHOSPHATE FROM GOETHITE

L. MADRID* and A. M. POSNER

(Department of Soil Science and Plant Nutrition, University of Western Australia, Nedlands, W.A. 6009, Australia.)

Summary

The reversibility of the adsorption of phosphate on goethite was measured by diluting suspensions of goethite on which phosphate was adsorbed with large volumes of phosphate-free solution at the same ionic strength. The effect on the reversibility of various adsorption and desorption conditions was studied, particularly pH, temperature, ionic strength and time of reaction.

The apparent irreversibility of the adsorption reaction seems to be due to a slow adsorption reaction of part of the phosphate after a very rapid initial adsorption, with a similar behaviour when the phosphate is desorbed. When the total adsorption plus desorption time is long enough, both adsorption and desorption points tend to lie on a single curve which corresponds to the isotherm calculated according to the Stern double-layer theory.

Introduction

DESPITE the considerable volume of work done by many authors on adsorption of phosphate by mineral surfaces, comparatively little progress has been made in studies of desorption. There is evidence that when solids on which phosphate is adsorbed are washed at a constant electrolyte concentration and pH, the desorption points are located above the adsorption isotherms (Muljadi *et al.*, 1966; Kafkafi *et al.*, 1967; Hingston *et al.*, 1974) demonstrating the presence of hysteresis, the origins of which are not clear. Atkinson *et al.* (1972) found that most of the phosphate adsorbed on goethite was isotopically exchangeable, which means that it should be in equilibrium with the solution, and Neoh (1975) found a high proportion of the phosphate remaining on goethite after desorption to be isotopically exchangeable. These facts suggest that the hysteresis is due to the very slow desorption of the so-called 'non-desorbable' phosphate.

Hingston *et al.* (1974) believed that the lack of reversibility of the isotherms could be related to the kinetics of adsorption and desorption. Later, other authors, *e.g.* Barrow and Shaw (1975), Munns and Fox (1976), Ryden and Syers (1977) and White and Taylor (1977), have also suggested that the apparent irreversibility of adsorption isotherms can be due to slow equilibration during adsorption. They found that there is even an apparent re-adsorption during the desorption step, attributed to a very slow adsorption reaction for part of the phosphate. Ryden and Syers (1977) believe that the initially desorbable phosphate (which they call 'region III' or 'more-physically sorbed') undergoes a shift to 'chemisorbed' forms ('regions I and II' of their isotherms), which can only be desorbed with an increase in the pH

*Permanent Address: Centro de Edafología y Biología Aplicada del Cuarto, C.S.I.C. Apartado 1052, Sevilla, Spain.

of the desorbing solution. A similar idea had been previously suggested by Muljadi *et al.* (1966).

In the experiments described here, the aim was to investigate the reversibility of the adsorption of phosphate on goethite as influenced by the conditions of adsorption and desorption.

Experimental

The preparation of the goethite has been described elsewhere (Hingston *et al.*, 1972). Its specific surface area was $84 \text{ m}^2 \text{ g}^{-1}$ and its pzc was at pH 8.

Adsorption experiments

Six ml of a well-stirred suspension of goethite in water (19.5 mg ml^{-1}) was added to polythene bottles containing 50 ml of NaCl solutions of varying ionic strengths, pH and temperatures, with known concentrations of ^{31}P + ^{32}P . After allowing a given time of adsorption, samples of these suspensions were filtered through $0.2 \mu\text{m}$ Millipore filters, and ^{32}P was determined by Cherenkov counting. Sufficient solution was passed through the filter before collecting the filtrate for counting to avoid losses due to adsorption. The final phosphate concentration and amount adsorbed were calculated by means of the $^{31}\text{P} : ^{32}\text{P}$ ratio of the original solution used. The solid : solution ratio was $0.0021 \text{ g goethite ml}^{-1}$.

Desorption experiments

After each adsorption period, samples of the adsorption suspensions were pipetted into polythene bottles containing large known volumes of solutions, at various conditions of pH and temperature, but always at the same ionic strength as in the adsorption experiment. The resulting 'desorption suspensions' had a solid : solution ratio from 17 to 3000 times less than in the adsorption experiments.

From these 'desorption suspensions' samples were taken at various times and filtered through Millipore filters. The phosphate concentration and the amount remaining on the oxide were determined as described for the adsorption experiments.

All suspensions were shaken in an orbital shaker at 180 r.p.m., except those in which the reaction time was less than 5 min, which were shaken by hand.

In some experiments, LiCl was used instead of NaCl as indifferent electrolyte. The experiments at very high pH were made in polythene bottles wrapped with aluminium foil to reduce contamination with CO_2 . For reasons that will be explained later, polycarbonate bottles were sometimes used instead of polythene. To find out whether the technique had an influence upon the amount adsorbed or desorbed, some experiments were made by the adsorption-desorption technique used by Hingston *et al.* (1974).

Results

Effect of the dilution on the amount remaining adsorbed

In these series of experiments two initial phosphate concentrations were used, 3.45×10^{-4} and $5.76 \times 10^{-4} \text{ M}$, and the conditions were pH 5.6, ionic strength 0.1 M NaCl, and temperature 25°C throughout. After three different times of adsorption (0.25, 1 and 23 h) the 'adsorption suspensions' were diluted from 17 to 3000 times, and samples of the resulting 'desorption suspensions' measured after 0.5 h to 6 days.

The plots of concentration against time for the 'desorption suspensions' usually showed no significant variation of the concentration after 1-2 days. For example,

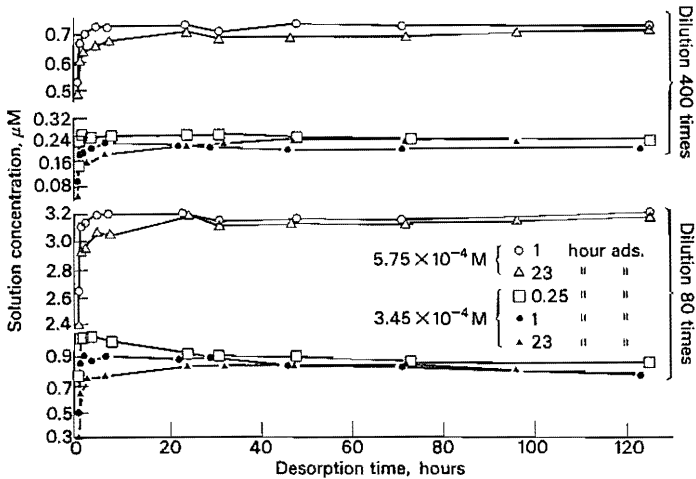


FIG. 1. Variation of the solution concentration with desorption time, 2 dilutions (80 and 400 times), after various adsorption times and initial concentrations; ionic strength, 0.1 M NaCl.

Fig. 1 shows the results for two dilutions, 80 and 400 times. Results for the other dilutions are similar and are not shown here. In the first 24 h the behaviour differed according to which time had been allowed for adsorption. There is a rapid increase in the solution concentration, which seems to pass through a maximum at small adsorption times and dilutions. After 24 h there is little or no significant difference for the various adsorption times especially when compared with the concentrations at zero desorption time. These results, comparable with those from other authors (e.g. Munns and Fox, 1976), suggest that such 'readsorption' is the effect of a slow component of the adsorption reaction. For desorption times long compared with the adsorption time there is no effect of the latter on the adsorbed amount.

When the amount remaining adsorbed after 5–6 days of desorption for the various dilutions is plotted against the corresponding solution concentration, a 'desorption isotherm' is obtained. As can be seen in Fig. 2, the results lie within a region narrow enough to be considered a single curve, regardless of the adsorption conditions (initial phosphate concentration and time), although the points are scattered at low concentrations. In this region sampling errors, contamination with micro-organisms etc. are likely to have a large effect on the phosphate concentration, and this, combined with the magnifying effect of the large dilution on the experimental errors of the concentrations when calculating the adsorbed phosphate, could be the reason for the scatter of the points for concentrations below 5×10^{-7} M.

Effect of adsorption and desorption conditions

Since the error in the determination of the amount adsorbed seems to increase markedly for dilutions of 800 times or greater, a standard dilution of 700 times, just below this limit, was chosen in order to investigate the influence of various conditions of adsorption and desorption on the amount desorbed.

Adsorption suspensions were made up at 3 different pH values (4, 7, 10) and 3 different initial phosphate concentrations (4.61×10^{-4} , 6.91×10^{-4} and 9.22×10^{-4} M). After 3 adsorption times (0.25, 1 and 24 h) they were diluted 700 times

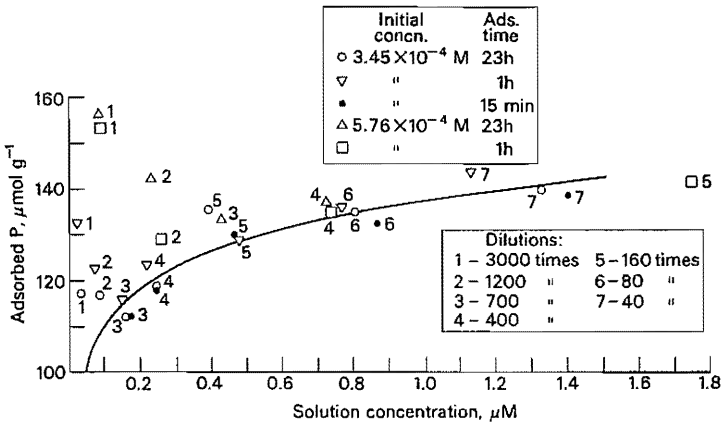


FIG. 2. Variation of the phosphate adsorbed after 5–6 days of desorption with solution concentration, for various dilutions and adsorption conditions; pH 5.6; ionic strength 0.1 M NaCl. Full line: theoretical isotherm at pH 5.6 calculated using the procedures of Bowden *et al.* (1973, 1974, 1977) and the following parameters of the model (Bowden *et al.*, 1977), $pzc = 8.0$; maximum number of adsorption sites (N_T) = 3×10^{-10} moles/cm². Electrical capacitance (G) = 2×10^{-12} equiv. cm⁻² mvolt⁻¹. Binding constants; $K_{H_2PO_4^-} = 0$, $K_{HPO_4^{2-}} = 10^4$ l/mole⁻¹, $K_{PO_4^{3-}} = 10^4$ l/mole⁻¹. These parameters were obtained at high phosphate concentrations where time effects would be small. The Nernst equation was used to calculate the surface potential (ψ_s) since it has been shown to be a good approximation when the surface coverage is not too large (Bowden *et al.*, 1977).

under various desorption conditions of pH, temperature and ionic strength. In some of these experiments LiCl was used instead of NaCl as electrolyte.

For a given set of desorption conditions and for a given initial phosphate concentration, a group of graphs was obtained as in Fig. 3. After 1–2 days of desorption, the adsorbed phosphate seems to reach an 'equilibrium' value, unique

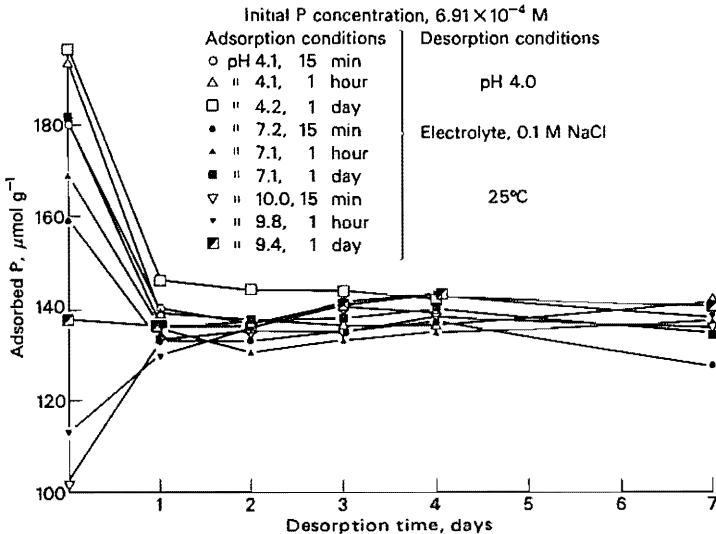


FIG. 3. Examples of the variation of the adsorbed phosphate with desorption time, for various adsorption conditions.

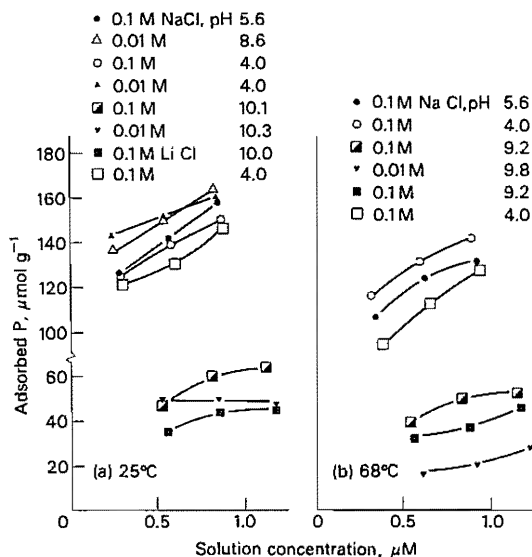


FIG. 4. Plot of average adsorbed phosphate against average solution concentration after 5–6 days of desorption, various desorption conditions: a) 25 °C; b) 68 °C.

for each of these groups, which does not depend upon the time or the pH of adsorption. Those suspensions with less adsorbed phosphate (at desorption time = 0) than this unique value adsorb phosphate during the first day after dilution, and those with more phosphate adsorbed than the 'equilibrium' value desorb part of it. The average 'equilibrium' values after 5–6 days of the amount of phosphate remaining on the oxide are plotted in Fig. 4 against the corresponding average solution concentrations for various desorption conditions.

Adsorption and desorption at very short reaction times

Some adsorption suspensions were diluted after short adsorption times (1–5 min), and samples of the corresponding desorption suspensions were also taken at short times, from 1 min up to 1 h with a final sample after 1 day. Fig. 5 shows the results for experiments at 68 °C. The experiments at 25 °C gave a similar pattern and are not shown here.

The behaviour was similar to the one described in the preceding section: the samples either desorbed phosphate or adsorbed more, depending upon whether they had more or less phosphate adsorbed at desorption time = 0 than the 'equilibrium' adsorption. The approach to this 'equilibrium' adsorption seemed to be similar to the experiment in Fig. 1 for 15 min of adsorption and large dilution: there was a very rapid desorption within the first few minutes, slowing down later, so that the variation between 1 and 24 h was small in most cases. The maximum in the desorption reported for some results in Fig. 1 was not found here, probably because the slow re-adsorption was reduced by the 700 fold dilution used.

Desorption by 'steps'

The purpose of this experiment was to establish whether the desorption resulting from an increase in pH was comparable in speed to that resulting from dilution at

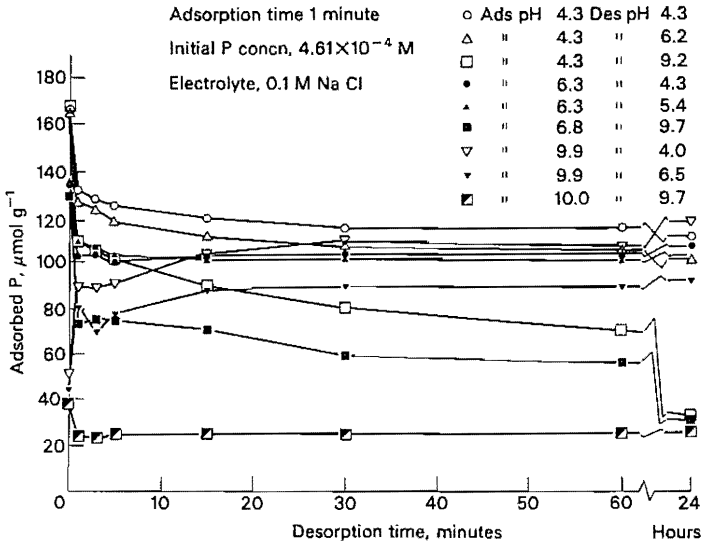


FIG. 5. Examples of the variation of the adsorbed phosphate with desorption time, short-term experiments.

constant pH. In these experiments, the pH of the desorption suspension was not constant throughout the whole desorption time, but was increased every few days, and samples were taken 1 h, 6 h, 1 day and 2–3 days after each change in pH (Fig. 6, means of eight experiments). The initial phosphate concentration was 4.61×10^{-4} M the adsorption pH and the initial desorption pH were 4.0, and the electrolyte was 0.1 M NaCl.

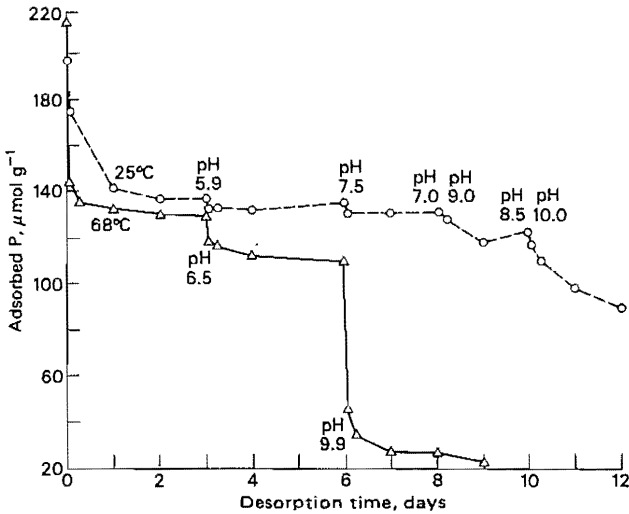


FIG. 6. Variation of the adsorbed phosphate with desorption time following changes in pH; ionic strength 0.1 M NaCl.

It can be seen that after each pH change the amount adsorbed decreased sharply within the first hour, and later, as happened in the experiments described in previous sections, the rate of desorption decreased markedly. The sharp decrease in the amount adsorbed after each pH change is particularly noticeable for the experiments at 68 °C.

In some cases, probably due to contamination with CO₂, the pH decreased again after some time, and in such cases the amount of phosphate adsorbed increased accordingly.

Experiments at very low concentrations

If a slow component of the adsorption process is responsible for the difference between adsorption and desorption isotherms, it would be likely to produce small variations in the 'equilibrium' concentrations which would be more noticeable at very low concentrations. For that reason and to minimise experimental errors due to dilution noted for the results reported in Fig. 1, some experiments were made with low initial solution concentrations (1.84×10^{-4} and 2.30×10^{-4} M) to give equilibrium concentrations equal to or less than 10^{-7} M. Desorption suspensions were prepared from suspensions by diluting 100 and 200 times after 3 days of adsorption. Samples were taken from both adsorption and desorption suspensions at various times up to 20 days.

Preliminary experiments in this series showed that the polythene bottles themselves produced a small decrease in solution concentration of phosphate. The decrease was not detectable for higher concentrations. With polycarbonate containers little change in the concentration of phosphate was observed over 3 days and they were used in this series of experiments instead of polythene bottles.

Fig. 7 shows that the solution concentrations for both adsorption and desorption slowly decrease, so that all points tend to approach the 'theoretical' isotherm. For this reason, comparison of desorption and adsorption points corresponding to similar *total* periods of reaction, *i.e.* desorption points for 3 days and adsorption points for 6 days (since the desorption experiments were prepared after 3 days of adsorption) show that the apparent discrepancy between both adsorption and desorption points is much less marked. Fig. 8 summarizes adsorption and desorption results at pH 4 from the various series described above. The desorption points have been chosen so that the total time of reaction (adsorption plus desorption) is the same as for the adsorption points, 24 h, except the desorption point A, which corresponds to 24 h of desorption *after* 24 h of adsorption. The results can again be fitted into a single line if the total reaction time is the same. This conclusion was already reached from Fig. 7 for longer reaction times and very low concentrations, and is consistent with results from other authors (*e.g.* White and Taylor, 1977).

Effect of the adsorption-desorption technique

Centrifugation has been widely used for separating solid from solution in the adsorption suspensions before adding the desorbing solution. Since this technique may cause the formation of aggregates which could make the solid surface partly inaccessible and decrease or slow down the subsequent desorption, a series of experiments was carried out to test such hypothesis. The same procedure described by Hingston *et al.* (1974) was used, and after adding the desorbing solution the oxide was redispersed by different means including ultra-sonic dispersion. If the hypothesis was correct, the more energetic the redispersion the more phosphate would be desorbed. Little or no difference was observed.

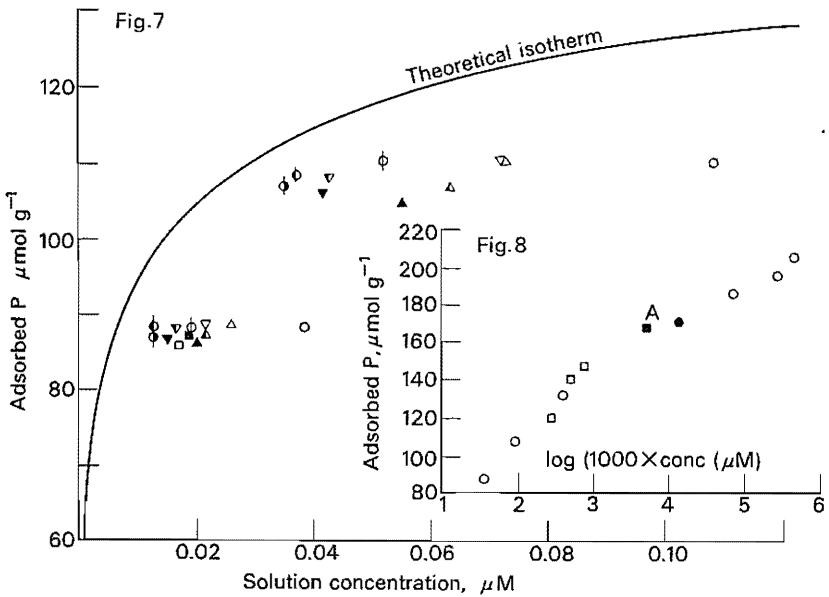


FIG. 7. Position of adsorption and desorption points for various reaction times. Adsorption pH 4; desorption pH 4; ionic strength 0.1 M NaCl. Theoretical isotherm calculated using parameters given for Figure 2.

Adsorption		Desorption	
○	3d	(▲ 3d. dilution 100. ■ 7d ▼ 10d ◊ 16d	
△	6d	(▲ 3d. dilution 200. □ 7d ▼ 10d ◊ 16d	
▽	13d		
◊	19d		

FIG. 8. (Inset in Fig. 7). Comparison of various adsorption and desorption results at pH 4, ionic strength 0.1 M NaCl.

○	Adsorption	● } Desorption, technique
□	Desorption	■ } of Hingston <i>et al.</i> (1974)

Discussion

Even though the results obtained here suggest that, given enough time, adsorption is both reversible (Figs. 2, 7, 8) and in accord with the Stern model (Bowden, 1973), extremely high dilutions may be required to desorb completely the phosphate. For example, given a point on the theoretical isotherm of solution concentration C_1 $\mu\text{mol.ml}^{-1}$ and adsorbed phosphate X_1 $\mu\text{mol.g}^{-1}$ for a solid : solution ratio A g.ml^{-1} , the volume of phosphate-free solution that has to be added to 1 ml of the system in order to reach a second point of composition C_2 and X_2 is, in ml,

$$V = \frac{(X_1 - X_2)A + C_1}{C_2} - 1$$

For the system used here $C_1 = 3.45 \times 10^{-5}$ M, $X_1 = 194.9$ $\mu\text{mol.g}^{-1}$, and $A = 0.0021$ g goethite ml^{-1} . Thus, after a dilution of 100 000 times (much higher than

the maximum dilution of 3000 used here) the solid still retains 50 per cent of the amount adsorbed at the starting point.

The above findings do not exclude the possibility of adsorbing sites being heterogeneous, as results of isotopic exchange have suggested (Atkinson *et al.*, 1972). In fact, the maximum observed in some plots of the solution concentration against desorption time after times of adsorption shorter than 1 day (Fig. 1) suggests the occurrence of more than one process during both the adsorption and desorption reactions, ranging from the very fast to the very slow. The results in Figs. 5 and 6 also demonstrate the existence of a range of desorption rates, while Fig. 9 shows that a range exists for adsorption. These figures show that a large proportion of the reactions are fast. Adsorption is extremely fast and is faster the lower the pH. At pH 4.0 at least 90 per cent of the adsorption at 24 h is complete after one min and hence is too fast to measure.

Some authors have suggested that the slow process could be related to diffusion of phosphate into the solid (Ryden *et al.*, 1977), or, in the case of soils, into the soil aggregates. This last hypothesis may well be true for experiments with un-

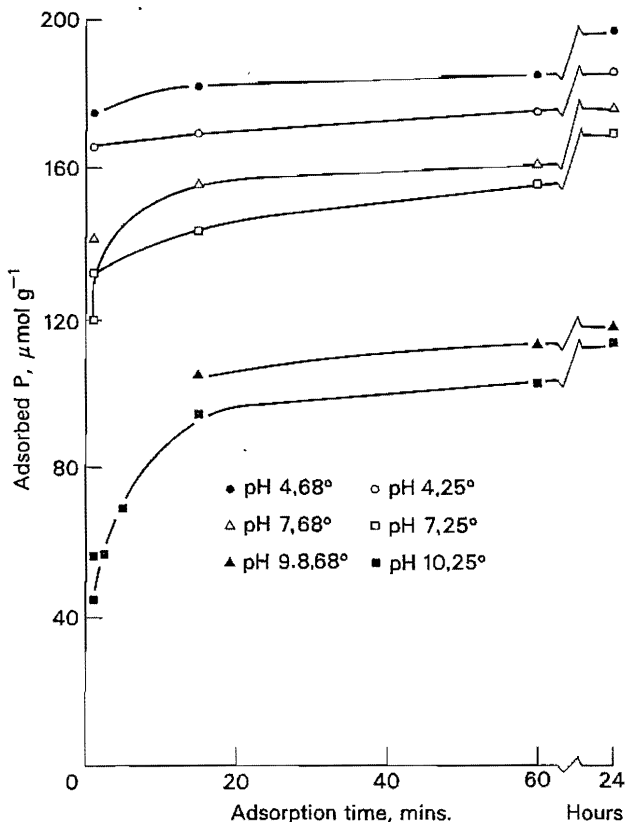


FIG. 9. Variation of the adsorbed phosphate with adsorption time for various adsorption conditions; ionic strength 0.1 M NaCl.

shaken soils, but it is very unlikely in the present experiments, where the goethite is strongly dispersed and is not allowed to settle at any time during the experiments.

Fig. 6 shows that there is a very rapid approach to a new equilibrium each time the pH is raised, the speed of which is comparable to the adsorption process (Fig. 9). If the desorption in each step was related to some kind of diffusion process out of the lattice, the change in pH should not increase the rate so sharply. Thus, if there is a diffusion component in the process, its contribution is negligible for times shorter than a few days.

The fact that there is no marked difference between desorption experiments after 1 min or 15 min of adsorption (cf. Figs. 1 and 5) suggests that any slow process has little effect for times shorter than 15 min.

Results in Fig. 4 have some features which are worth noting.

I) For a given ionic strength, the amount of phosphate remaining on the oxide decreases as the pH increases. The exceptions are the curves for pH 4 and 5.6, which cross each other for ionic strength 0.01 M.

II) At pH values below the pzc e.g. pH 4.0 and 5.6, 0.01 M NaCl leaves more phosphate on the oxide than 0.1 M NaCl, and the opposite is true for pH values above the pzc; e.g. compare pH 10.1 and 10.3 (Fig. 4a) and also pH 9.2 and 9.6 (Fig. 4b).

III) The amount of phosphate remaining on the oxide is greater at 25 °C than at 68 °C, with the exception of LiCl at pH 10, which does not show a significant difference between the two temperatures (compare Figs. 4a and b). Nevertheless, this exception can be due to the small difference in pH between both series of experiments.

IV) All other conditions being equal, LiCl leaves less phosphate adsorbed than NaCl (see Fig. 4a and b).

The features I) and II) are fully compatible with the effect of pH and ionic strength on the adsorption isotherms calculated by the Stern model. The greater desorption with increasing pH results from an increase in competition from hydroxyl ions, and the decrease in positive charge or increase in negative charge on the surface resulting in a lessening of the attraction or a repulsion, respectively, between the surface and the anion. This effect is further amplified if the anion increases its negative charge as the pH is increased.

At pH values below the pzc, increasing the ionic strength depresses the positive diffuse double layer potential and hence reduces the attraction between the anion and the surface, hence adsorption is decreased. Above the pzc raising the ionic strength decreases the negative diffuse double layer potential which reduces the repulsion between the negative surface and the anion, hence adsorption is increased.

REFERENCES

- ATKINSON, R. J., POSNER, A. M. and QUIRK, J. P. 1972. Kinetics of heterogeneous isotopic exchange reactions. Exchange of phosphate at the α -FeOOH-aqueous solution interface. *J. inorg. nucl. Chem.* 34, 2201-11.
- BARROW, N. J. and SHAW, T. C. 1975. The slow reactions between soil and anions: 5. Effects of period or prior contact on the desorption of phosphate from soils. *Soil Sci.* 119, 311-20.
- BOWDEN, J. W. 1973. Models for ion adsorption on mineral surfaces. Ph.D Thesis, Univ. Western Australia.
- HINGSTON, F. J., POSNER, A. M. and QUIRK, J. P. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23, 177-92.
- 1974. Anion adsorption by goethite and gibbsite. II. Desorption of anions from hydrous oxide surfaces. *Ibid* 25, 16-26.

- KAFKAFI, U., POSNER, A. M. and QUIRK, J. P. 1967. Desorption of phosphate from kaolinite. *Proc. Soil Sci. Soc. Am.* 31, 348-53.
- MULJADI, D., POSNER, A. M. and QUIRK, J. P. 1966. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. *J. Soil Sci.* 17, 212-47.
- MUNNS, D. N. and FOX, R. L. 1976. The slow reaction which continues after phosphate adsorption: kinetics and equilibrium in some tropical soils. *Proc. Soil Sci. Soc. Am.* 40, 46-51.
- NEOH, L. S. 1975. Desorption of phosphate from goethite. Ph.D. Thesis, Univ. Western Australia.
- RYDEN, J. C. and SYERS, J. K. 1977. Desorption and isotopic exchange relationships of phosphate sorbed by soils and hydrous ferric oxide gels. *J. Soil Sci.* 28, 596-609.
- McLAUGHLIN, J. R. and SYERS, J. K. 1977. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. *Ibid.* 28, 585-95.
- WHITE, R. E., and TAYLOR, A. W. 1977. Reactions of soluble phosphate with acid soils: the interpretation of adsorption-desorption isotherms. *Ibid.* 28, 314-28.

(Received 7 October 1978)