

# INVESTIGATIONS ON THE RÔLE OF SILICON IN PLANT NUTRITION.

Part III. On the Nature of Interaction of Soil or Hydrogels of Iron Oxide or Alumina with Mixtures of Phosphates and Silicates.

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EVER since the recognition that the colloidal fraction of the soil has the inherent property of converting soluble phosphates or phosphatic fertilisers into insoluble forms, various investigators (*vide*, Sreenivasan, 1935<sup>1</sup>) have attempted to clarify the behaviour of phosphates in the soil, but opinion is yet largely divided in regard to the exact mechanism of phosphate fixation. The principal functional fraction of the soil is made up of inter-related heterogeneous colloidal systems, the "ampholytes" (Mattson and Pugh, 1934) and as such phosphate retention by soils is complicated by a number of factors. Studies on phosphate adsorption with simpler systems of colloids have, in recent years, been carried out by a number of workers (Gordon *et al*, 1922, 1923; Miller, 1928; Ghosh and Bhattacharya, 1930; Mattson, 1927, 1930, etc.). More recently Demolon (1933), Demolon and Bastisse (1933, 1934), Ravikovitch (1934), Pugh (1934) and Bradfield *et al* (1935) have published papers dealing with the ionic exchange of phosphates.

In view of the earlier observations (Sreenivasan, *loc. cit.*) that soluble silicates interact with the soil in a manner similar to soluble phosphates, it was considered desirable to study the behaviour of solutions of phosphate and silicate together, when added to soil or pure gels of alumina or iron hydroxide. It was hoped that such a study may throw light on the mode of action of colloidal forms of silica in increasing phosphorus availability to cereal crops—an observation made by a number of independent workers, but on which highly conflicting views have been held, even upto recent times (Sreenivasan, 1934; Akhromeiko, 1934; and Dix and Rauterberg, 1934).

## *Experimental.*

*Materials: Soil.*—This was a red loam from an adjoining uncultivated tract of land. The soil was air dried and ground to pass the 40-mesh sieve.

*Silicate*.—Kahlbaum's 25 per cent. sodium silicate solution was filtered free of suspended impurities and used as such. Each c.c. of this solution was equivalent to 0.25 g. anhydrous silica. *Phosphate*.—A standard solution of pure potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , A.R.) was employed in place of the soluble phosphate. 1 c.c. of this solution corresponded to 1 mg. of  $\text{P}_2\text{O}_5$ .

The  $\text{P}_H$  of the soil, the silicate (aq.) and the phosphate (aq.) were 7.2, 10.6 and 4.6 respectively, as measured with the Hellige Comparator.

*Method*.—The quantities of silicon and phosphorus were estimated on the same samples, a special modified procedure being adopted for the purpose. The method may be outlined as follows:—The solution is evaporated to a small bulk on the water-bath and after cooling, spotted, with about 5 c.c. of pure concentrated sulphuric acid. It is again heated for a time (5 to 10 mins.) and then treated with about 10 c.c. of 95 per cent. alcohol. The mixture is allowed to remain on the water-bath for about 15 mins. after which it is diluted and filtered free of silica, the precipitate being washed well. To the filtrate and washings (about 100 c.c. in volume) is added enough solid ammonium nitrate to make it a 15–20 per cent. solution. It is then heated nearly to boiling and treated with 20 c.c. of a 10 per cent. solution of ammonium molybdate. The mixture is vigorously shaken and maintained near to boiling temperature for about 10 mins. The yellow precipitate is then filtered off, washed with cold water until free from acid and dissolved in standard alkali, excess of which is back titrated against acid with phenolphthalein as indicator. 1 c.c. normal alkali corresponds to 2.538 mg.  $\text{P}_2\text{O}_5$  (Cf. Neumann, 1902, 1904).

*Retention of Phosphate by the Soil*.—With a view to determining the quantities of phosphate retained by the soil used in the present study, samples (100 g.) of the latter were treated with varying quantities of the phosphate solution and the mixtures allowed to stand for 30 mins. Enough water was then added to make the volume of suspensions to 200 c.c. in each case. They were then shaken in an end-over-end shaker for a period of 2 hours (trials having shown that further shaking was unnecessary), filtered and the phosphate present in aliquots of the filtrate determined (Table I).

Considerable quantities of the added phosphate are retained by the soil (converted into insoluble forms). With increasing amounts of added phosphate, there is also an increase in the quantities retained. But there is a gradual decrease in the corresponding percentage retention. The observations are thus similar to the retention of soluble silicates by the soil (Sreenivasan, *loc. cit.*).

TABLE I.

Phosphate added (as p.p.m. of $P_2O_5$ )	0	20	50	100	150	200
Phosphate recovered (as p.p.m. of $P_2O_5$ )	Nil	5.22	17.95	45.92	71.39	103.5
Per cent. of Phosphate retained by soil	..	73.9	64.1	54.1	52.4	48.2
$P_H$ of extract	7.2	7.2	7.2	7.0	6.8	6.4

A study of the changes in the H-ion concentration of the soil extract shows that with small concentrations of phosphate, the soil reaction is practically unaffected (due to the buffering effect of the soil constituents) while, with increasing amounts, there is a steady shift in the  $P_H$  towards the acid side.

*Retention of Phosphate by the Soil in Presence of Sodium Silicate.*—In the following experiments, the soil (100 g. lots) was first treated with 5 c.c. of sodium silicate (corresponding to 1.25 g.  $SiO_2$ ) and allowed to stand for half an hour. Known amounts of phosphate solution were then added and the suspensions let stand for another half an hour after which they were extracted as before with water. The phosphate in solution was then determined in each case. (Table II.)

TABLE II.

Phosphate added (as p.p.m. of $P_2O_5$ )	0	20	50	100	150	200
Phosphate extracted (as p.p.m. of $P_2O_5$ )	..	7.1	20.9	53.0	78.5	111.7
Per cent. retention of Phosphate	..	64.5	58.2	47.0	47.7	44.2
$P_H$ of extract	8.0	8.0	7.8	7.8	7.4	7.2

From a comparison of the amounts of phosphate recovered with the corresponding figures in Table I, it will be seen that in the presence of the silicate greater quantities of phosphate are extracted from the soil. The percentage retention of phosphate in soils treated with sodium silicate is also less in the latter cases, the differences being more with small amounts of added phosphate. The H-ion concentration of the extract in the case of specimens

treated with silicate and phosphate are also less than in those treated with phosphate alone.

*Influence of Reaction on the Retention of Phosphate by the Soil.*—In the above experiments (Table II), the addition of sodium silicate to the soil has made the soil reaction somewhat alkaline and hence the extent of retention of phosphate by the soil with and without added silicate may not be strictly comparable. With a view to finding out the possible influence of the  $P_H$  of the soil or of the phosphate solution on phosphorus extractability, the following experiments were carried out in which the soil (100 g.) was adjusted to different initial  $P_H$  values by addition of varying amounts of normal hydrochloric acid or sodium hydroxide as the case may be, before treatment with a known amount (10 c.c.) of the phosphate solution. The recovery of phosphate in each case is given below (Table III).

TABLE III.

$P_H$ (adjusted) of soil	3.0	4.6	6.4	7.2	9.0	9.8
Phosphate extracted (as p.p.m. of $P_2O_5$ )	43.0	43.4	44.7	46.3	48.8	50.1

Phosphate originally added (as  $P_2O_5$ ) = 100.0 p. p. m.

In another set of experiments, the phosphate solution (10 c.c.) was adjusted to different initial  $P_H$  values by addition of acid or alkali (decinormal), as the case may be, and then added to 100 g. lots of the soil. The suspensions were then extracted in the usual way. (Table IV.)

TABLE IV.

$P_H$ (adjusted) of Phosphate solution	3.0	5.0	7.0	9.0	10.6
Phosphate extracted (as p.p.m. of $P_2O_5$ )	43.8	46.0	47.3	48.5	49.4

Phosphate added (as p. p. m. of  $P_2O_5$ ) = 100.0.

It may be observed that in either case (Tables III and IV) there is an increase in the amount of phosphorus recovered as the H-ion concentration decreases (*Cf.* Mattson, 1927, 1931; Gordon and co-workers, *loc. cit.*).

In view of the fact that with increased  $P_H$  there is also an increased recovery of added phosphate, it appeared probable that the influence of sodium silicate in increasing the amount of phosphorus in solution (Table II) may, in part at least, be due to the increased alkalinity brought about by

addition of silicate (Sreenivasan, *loc. cit.*). It was therefore thought desirable to overcome this influence of the sodium silicate on the soil reaction before the addition of phosphate. Accordingly, in the following experiments, 100 g. lots of the soil were mixed with 5 c.c. of the silicate solution. At the end of half an hour enough hydrochloric acid was added to neutralise the sodium silicate present and the soil suspension thoroughly mixed. (The quantity of acid necessary was determined by separate titration of the silicate solution against 1 per cent. HCl using phenolphthalein as indicator and found to be 1.6 c.c.). Known amounts of phosphate solution were then added to the soil suspension thus obtained and the quantities of phosphorus retained were then determined in the usual way. The results are given in Table V.

TABLE V.

Phosphate added (as (p.p.m. of $P_2O_5$ ))	20	50	100	150	200
Phosphate recovered (as p.p.m. of $P_2O_5$ )	5.4	19.3	50.5	78.6	110.6
Retention of Phosphate per cent.	73.0	61.4	49.5	47.6	44.7

It may be noted that the recovery of added phosphate is distinctly less than when the soil-silicate mixture was not neutralised before addition of phosphate (Table II). A comparison of the figures with the corresponding values obtained when the soil was treated with the phosphate alone (Table I) would, however, show that the quantities of phosphorus present in solution continue to be appreciably more in the presence of the silicate. In other words, the addition of the silicate to the soil results in an increase in the recovery of added phosphate due in part to the increased alkalinity and in part also to the silicate itself.

*Effect of Addition of Increasing Quantities of Silicate (aq.) on Phosphorus Recovery.*—To 100 g. lots of the soil were added varying amounts of sodium silicate. At the end of half an hour, the soil-silicate suspensions were divided into two halves and in one set of samples, they were thoroughly mixed with such quantities of 1 per cent. HCl as would be just enough to neutralise the sodium silicate present. All the samples were then treated with known amounts (10 c.c. and 20 c.c. respectively) of the phosphate solution and the amounts of extractable phosphate determined in each case. Table VI gives the results obtained :—

TABLE VI.

Sodium silicate added as mg. SiO <sub>2</sub>	Phosphate originally added (as p.p.m. of P <sub>2</sub> O <sub>5</sub> ) = 100		Phosphate originally added (as p.p.m. of P <sub>2</sub> O <sub>5</sub> ) = 200	
	Phosphate recovered as p.p.m. of P <sub>2</sub> O <sub>5</sub>			
	Without neutralisation of added silicate	After neutralisation of added silicate	Without neutralisation of added silicate	After neutralisation of added silicate
500	48.0	47.6	104.3	104.3
1250	53.0	50.5	111.7	110.6
2500	56.1	53.4	118.8	115.6
3750	58.7	55.1	123.6	119.0

It was found that in the experiments where the sodium silicate added was not neutralised with acid before treatment with phosphate, the extracts were highly coloured due to the soil organic matter having been brought into solution, especially where large amounts of silicate were employed. In such cases, the extracts were boiled with hydrogen peroxide to oxidise away the organic matter before removal of silica by treatment with sulphuric acid.

The results (Table VI) show that addition of increasing quantities of silica results in corresponding increase in the amounts of soluble phosphorus. The quantities present in solution are greater in the experiments where the silicate added was not neutralised. This is indeed to be expected, in view of the fact that the alkalinity of the silicate will decrease phosphate retention.

When the quantities of phosphorus in solution are plotted against the amounts of silicate added, a logarithmic curve (Fig. 1) is obtained.

These observations would suggest that the nature of interaction between the soil and a mixture of silicate (aq.) and phosphate is governed by the relative concentrations of the latter. It is possible that in presence of the silicate the soil adsorbing complex combines preferentially with the colloidal silica released as a result of addition of silicate so that the extent of phosphate adsorption decreases. As the amounts of added silicate increase, there is a corresponding decrease in phosphate adsorption.

*Effect of Addition of Sodium Silicate (aq.) to Soil treated with Phosphate (aq.).*—In the foregoing experiments the sodium silicate was added prior to treatment of the soil with phosphate. With a view to seeing whether

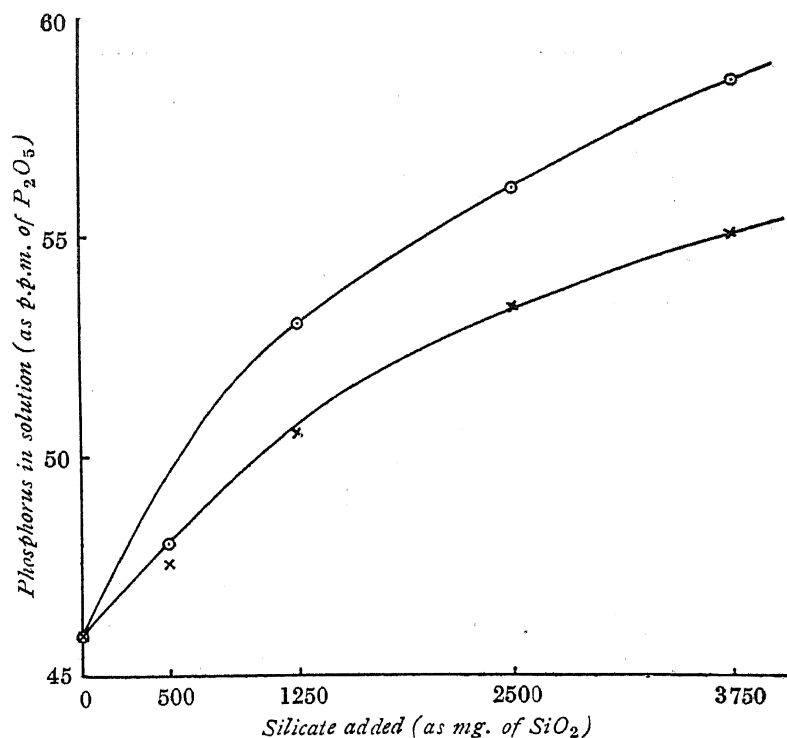


FIG. 1. Effect of Sodium Silicate (aq.) on Phosphorus Resorption.

○—○ without neutralisation of added silicate  
 ×—× after " " "

addition of silicate after treatment of the soil with phosphate brings about any change in the extent of recovery of the added phosphate, some experiments were carried out in which the soil (100 g.) was first treated with a known amount (10 c.c.) of phosphate solution. At the end of half an hour, varying quantities of silicate were added to the mixture, followed in one set of experiments, by enough hydrochloric acid (1 per cent.) to neutralise the sodium silicate. In either case, the phosphorus in solution was determined in the usual way after extraction with water (Table VII).

There does not appear to be any difference in the amounts of soluble phosphorus whether the silicate is added after or prior to treatment with phosphate. In other words, phosphate adsorbed by soil is released from combination by silicate addition, presumably as a result of preferential adsorption of silica resulting from the latter.

*Experiments with Silica Gel.*—It has been shown that the addition of sodium silicate to soil is in effect the same as treatment with colloidal silica (Sreenivasan, *loc. cit.*). It was further observed that the behaviour of phosphates and that of soluble silicates towards the soil are similar in character but whereas in the former case, it is adsorption of an anion, in the latter it is

TABLE VII.

Sodium silicate added as mg. SiO <sub>2</sub>	Phosphate extracted as p.p.m. of P <sub>2</sub> O <sub>5</sub>	
	Without neutralisation of added silicate	After neutralisation of added silicate
500	..	48.0
1250	52.2	50.9
2500	56.4	52.6
3750	..	56.4

Phosphate originally added (as p.p.m. of P<sub>2</sub>O<sub>5</sub>) = 100

adsorption of a negative colloidal complex. The behaviour of phosphate and silicate together towards the soil would appear to lend support to this view. With a view to observing whether the retention of phosphate by soil is affected in presence of colloidal silica as well, some experiments were carried out mixing soil (100 g.) with 10 g. of a silica gel (equivalent to 0.754 g. of SiO<sub>2</sub>) prepared by careful neutralisation of a dilute solution of sodium silicate with hydrochloric acid and dialysis of the mixture until free from chloride. Known amounts of phosphate solution were then added to the mixture and the phosphorus extracted was determined in each case as before (Table VIII).

TABLE VIII.

Phosphate added (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )	..	50	100	150	200
Phosphate extracted (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )		18.4	48.8	74.7	107.3
Per cent. retention	.. ..	63.2	51.2	50.2	46.3
P <sub>H</sub> of extract	.. ..	7.2	7.0	6.6	6.4

As distinct from the extracts obtained in the previous experiments with sodium silicate, it was observed that only very little of silica was extracted in the solution. A comparison of the results (Table VIII) with those in Table I would show that silica gel also increases the amount of water soluble phosphorus. Gile and Smith (1925) had observed that addition of 30 g. of silica gel increases somewhat the quantity of phosphoric acid brought into solution from rock phosphate by a mixed salt solution. Similar results



were obtained by Mattson (1922) on digesting a precipitated tricalcium phosphate with water suspensions of peat, ceramic clay and quartz flour.

*Effect of Addition of Increasing Quantities of Silica Gel on Phosphate Retention.*—100 g. lots of soil were thoroughly mixed with varying quantities of silica gel and the mixtures treated with a known amount (10 c.c.) of phosphate solution. The retention of phosphorus by the soil was then determined in the usual way. Results are given in Table IX.

TABLE IX.

Silica gel added (as mg. SiO <sub>2</sub> ) .. ..	377	754	1131	1508
Phosphate extracted (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )..	47.2	48.8	50.5	51.8

Phosphate added (as p.p.m. of P<sub>2</sub>O<sub>5</sub>) = 100.

It may be noted that as with sodium silicate, increasing quantities of silica gel increase the resorption of phosphorus.

A comparison of the figures for phosphorus in solution in the experiments with silica gel (Tables VIII and IX) with the corresponding values in the experiments with sodium silicate (Table VI) would show that the efficiency of phosphate resorption by the gel is somewhat less than that of the silicate solution. As shown in a subsequent section, silica gel itself has the power of adsorbing phosphate from solution although there is only slight adsorption. This adsorbed phosphate is, however, washed free from the adsorbing gel by the use of hot water. Since the extracts obtained in the above experiments with soil and silica gel were only cold water extracts, this adsorption of phosphate by silica gel might explain to some extent the lower values for phosphorus in solution obtained in these cases. Another explanation may be that the silica gel may not be as adsorptively active as the colloidal silica formed in the soil as a result of addition of sodium silicate. It is not unlikely that in the latter case the silica is formed in the *sol* condition and is hence more potent in regard to the release of phosphorus.

#### Absorption of Silica and of Phosphates in soluble forms by Colloidal Oxides of Iron and Aluminium.

Since the seat of interaction between the soil and silicate or phosphate is in the colloidal fraction, it was thought desirable to study the behaviour of mixtures of silicate and phosphate towards pure hydrous gels of iron oxide and alumina. The gels for the following studies were prepared as outlined previously (Sreenivasan, 1935<sup>2</sup>).

*Adsorption of Phosphate by Silica Gel.*—5 g. lots of hydrous silica gel (377 mg.  $\text{SiO}_2$ ) were treated in stoppered bottles with 100 c.c. of a solution containing different known amounts of phosphate. The mixture was, in each case, shaken repeatedly and let stand overnight. They were then filtered and the phosphorus in aliquots of the filtrate estimated as outlined before. The total phosphorus in solution was calculated, the water present in the gels being also taken into account so that the retention was expressed on the dry weight of the gel. The results are recorded in Table X.

TABLE X.

Phosphate added (as p.p.m. of $\text{P}_2\text{O}_5$ )	Phosphate in solution after adsorption (as p.p.m. of $\text{P}_2\text{O}_5$ )	Phosphate retained by gel (as p.p.m. of $\text{P}_2\text{O}_5$ )	Per cent. retention of $\text{P}_2\text{O}_5$	Retention of $\text{P}_2\text{O}_5$ per g. dry gel (p.p.m.)
20	18.4	0.6	3.0	1.6
50	48.0	2.0	4.0	5.3
100	96.4	3.6	3.6	9.6
200	193.5	6.5	3.3	17.3

It may be observed that only small quantities of phosphate are retained by the silica gel (*cf.* Gordon *et al.*, *loc. cit.*). As is to be expected, there is an increase in the quantity of phosphate retained, with increasing concentration of phosphate, but there is a decrease in the percentage retention.

With a view to seeing whether the adsorbed phosphate is firmly held by the silica gel and is therefore not leachable with hot water, the gel-silica complex in the last case (wherein 200 p.p.m. of phosphate as  $\text{P}_2\text{O}_5$  had been added to 5 g. of hydrous  $\text{SiO}_2$  gel) was treated with successive 100 c.c. portions of hot water and the phosphorus in the filtrates determined separately. The results are given in Table XI.

It would be seen from the above that even the small quantity of phosphate retained is practically completely leached out in the first one or two washings. This was further confirmed by taking a portion of the washed gel on the filter, decomposing it with dilute sulphuric acid and subsequently testing qualitatively for phosphate when a negative test was obtained.

*Effect of Addition of Different Quantities of Phosphate to Iron and Alumina gels.*—5 c.c. of each of the gels of iron oxide and alumina (containing respectively 164 and 116 mg. of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) were treated in stoppered bottles with 100 c.c. of a solution containing known amounts of phosphate.

TABLE XI.

Phosphate added as P <sub>2</sub> O <sub>5</sub>	= 200 p.p.m.
Phosphate recovered from solution (as P <sub>2</sub> O <sub>5</sub> )	= 193.5 p.p.m.
	P <sub>2</sub> O <sub>5</sub> (p.p.m.) in 100 c.c. wash water from gel-phosphate complex
First 100 c.c.	.. 3.97
Second 100 c.c.	.. 0.84
Third 100 c.c.	.. Nil

The mixtures were well shaken and allowed to attain equilibrium. (Usually they were left as such for 36-48 hrs. when steady values were obtained for the phosphate in solution.) They were then filtered and the phosphate in aliquots of the filtrate estimated. The total phosphorus in solution was calculated, the water in the gels being also taken into account so that minimum adsorption might be shown. The H-ion concentration of the phosphate solution before and after adsorption was also determined in each case colorimetrically. The results are given in Table XII.

TABLE XII.

Phosphate added (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )	Initial P <sub>H</sub> of phosphate solution	Iron hydroxide = 164.0 mg. Fe <sub>2</sub> O <sub>3</sub> . P <sub>H</sub> = 7.6				Alumina = 116.0 mg. Al <sub>2</sub> O <sub>3</sub> . P <sub>H</sub> = 8.0			
		Phosphate in solution after adsorption (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )	Retention of phosphate per cent.	P <sub>2</sub> O <sub>5</sub> retained per g. dry gel (p.p.m.)	P <sub>H</sub> of phosphate solution after adsorption	Phosphate in solution after adsorption (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )	Retention of phosphate per cent.	P <sub>2</sub> O <sub>5</sub> retained per g. dry gel (p.p.m.)	P <sub>H</sub> of phosphate solution after adsorption
20	7.0	6.7	66.5	81.1	7.2	6.3	68.5	118.1	7.6
50	6.8	16.7	66.6	203.1	7.0	16.3	67.4	290.5	7.6
100	6.8	33.4	66.6	406.1	7.0	38.4	61.6	531.0	7.4
150	6.8	54.7	63.6	581.2	7.0	64.3	57.2	738.7	7.2
200	6.6	82.2	58.9	718.5	7.0	100.2	49.9	860.2	7.0
300	6.4	138.4	53.9	985.4	6.8	156.6	47.8	1236.0	..

It may be seen from Table XII that adsorption similar to that with the soil takes place with the gels also (*cf.* Table I). Adsorption increases with increasing amounts of added phosphate, while there is a decrease in the percentage adsorption as the concentration increases.

*Effect of Addition of Sodium Silicate on Phosphate Adsorption by Gels.*—The gels (5 c.c. each) of iron oxide and alumina were first mixed with 10 c.c. of sodium silicate solution and then treated with varying quantities (in 90 c.c.) of phosphate solution as before. The phosphate solutions in one set of experiments contained enough hydrochloric acid (3.2 c.c. of 1 per cent.) as would neutralise the silicate present. The amounts of soluble phosphorus in solution at the end of 48 hours, with and without neutralisation, are recorded in Table XIII.

TABLE XIII.

Phosphate added as (p.p.m. of $P_2O_5$ )	Not neutralised for the alkalinity of sodium silicate				Neutralised for the alkalinity of sodium silicate		
	Phosphate in solution as p.p.m. of $P_2O_5$	Percentage retention of phosphate	$P_2O_5$ adsorbed per g. of dry gel (p.p.m.)	pH of phosphate solution after absorption	$P_2O_5$ in solution (p.p.m.)	Per cent. retention of phosphate	$P_2O_5$ adsorbed per g. of dry gel (p.p.m.)
Ferric hydroxide gel = 164.0 mg. $Fe_2O_3$							
20	8.4	58.0	70.8	9.5	7.9	60.5	73.8
50	21.5	57.0	173.8	9.4	19.4	61.2	186.6
100	39.9	60.1	366.5	9.2	38.6	61.4	374.4
150	69.9	53.4	488.4	9.0	61.4	59.0	540.3
200	95.6	52.2	636.6	9.0	89.3	55.4	674.8
300	154.9	48.4	884.9	8.6	147.0	51.0	933.0
Alumina gel = 116.0 mg. $Al_2O_3$							
20	8.4	58.0	100.0	..	7.5	62.5	107.7
50	22.3	55.4	238.8	9.8	19.2	61.6	265.6
100	52.2	47.8	412.0	9.8	45.1	54.9	473.3
150	76.0	49.4	637.8	9.6	69.7	53.6	692.1
200	118.0	41.0	706.8	9.4	109.6	45.2	779.3
300	175.6	41.5	1073.0	9.0	..	..	..

It would be seen from a comparison of the figures for soluble phosphorus in Tables XII and XIII, that the addition of sodium silicate has resulted in greater amounts of phosphorus being brought into solution. In the experiments where the effect of the added silicate on the reaction of the medium had been neutralised by addition of the requisite amount of acid, the increase is less than in the series where no acid was employed to neutralise the sodium silicate. But the  $P_H$  of the extracts in the latter cases are also very much towards the alkaline side.

*Order of Addition of Phosphate and Silicate.*—In the following experiments known amounts of the gels of iron oxide and alumina were first treated with 90 c.c. of a solution containing definite known amounts of phosphate. At the end of 24 hours they were treated with 10 c.c. of the silicate solution, followed by enough hydrochloric acid to neutralise the latter. The mixture was well shaken and set aside for another 24 hours after which the amounts of phosphate in solution were estimated as before (Table XIV).

TABLE XIV.

$P_2O_5$ originally present in solution (p.p.m.)	Ferric hydroxide gel = 164.0 mg. $Fe_2O_3$			Alumina gel = 116.0 mg. $Al_2O_3$		
	$P_2O_5$ in solution after adsorption (p.p.m.)	Retention per cent. of phosphate	$P_2O_5$ adsorbed per g. dry gel (p.p.m.)	$P_2O_5$ in solution after adsorption (p.p.m.)	Retention per cent. of phosphate	$P_2O_5$ adsorbed per g. dry gel (p.p.m.)
50	19.6	60.8	185.4	18.8	62.4	268.0
100	38.8	61.2	373.3	44.9	55.1	475.0
150	60.5	59.6	545.8	70.6	53.0	684.4
200	90.8	54.6	665.9	111.9	44.1	750.5

It was observed that as with the soil, there was not any significant difference in the values for soluble phosphorus by reversing the order of addition of silicate and phosphate. Irrespective of the order of addition of the two reagents, the presence of silica in solution definitely tends to increase phosphorus solubility.

*Effect of Addition of Increasing Quantities of Sodium Silicate.*—The gels (5 c.c. each) of iron oxide and alumina were treated with a known amount of a solution of phosphate and allowed to stand overnight. Different known quantities of sodium silicate were then added followed by 1 per cent. hydrochloric acid, just enough to neutralise the silicate. After thorough shaking,

the mixtures were let stand until equilibrium was attained. The phosphorus in solution was then determined in each case. Results are given in Table XV.

TABLE XV.

Silicate added as mg. of SiO <sub>2</sub>	Iron hydroxide gel = 164.0 mg. Fe <sub>2</sub> O <sub>3</sub>		Alumina gel = 116.0 Al <sub>2</sub> O <sub>3</sub>	
	P <sub>2</sub> O <sub>5</sub> in solution after adsorption (p.p.m.)	P <sub>2</sub> O <sub>5</sub> adsorbed per g. dry gel	P <sub>2</sub> O <sub>5</sub> in solution after adsorption (p.p.m.)	P <sub>2</sub> O <sub>5</sub> adsorbed per g. dry gel
0	33.4	406.1	38.4	531.0
500	34.9	397.0	40.1	516.3
1250	36.5	387.3	42.2	498.2
2500	38.8	373.3	44.9	475.0
3750	41.3	358.0	48.0	448.2
5000	44.7	337.2	50.1	430.1

Phosphate originally present in solution (as p.p.m. of P<sub>2</sub>O<sub>5</sub>) = 100.

*Effect of Addition of Silica Gel on Adsorption of Phosphate by Gels of Iron oxide and Alumina.*—In the following experiments 5 c.c. each of the gels of iron oxide and alumina were mixed with 20 g. of silica gel (hydrous) before treatment with varying known quantities of phosphate. The extent of phosphate adsorption was then determined in each case (Table XVI).

TABLE XVI.

Phosphate added (as p.p.m. of P <sub>2</sub> O <sub>5</sub> )	System: Iron hydroxide + Silica gel			System: Alumina + Silica gel		
	P <sub>2</sub> O <sub>5</sub> in soln. after adsorp- tion (p.p.m.)	Per cent. retention of phosphate	P <sub>2</sub> O <sub>5</sub> retain- ed per g. of Fe gel (p.p.m.)	P <sub>2</sub> O <sub>5</sub> in soln. after adsorp- tion (p.p.m.)	Per cent. retention of phosphate	P <sub>2</sub> O <sub>5</sub> retain- ed by g. of Al gel (p.p.m.)
50	17.6	64.8	197.5	18.4	63.2	272.4
100	36.4	63.6	387.9	41.6	58.4	503.4
200	86.8	56.6	690.4	103.4	48.3	832.8

(Silica gel added = 1504 mg. anhydrous SiO<sub>2</sub>).

It may be seen that addition of silica gel also aids resorption of phosphate although as already observed the efficiency of silica gel is less than that of an equivalent quantity of sodium silicate.

*Influence of H-ion Concentration on Phosphate Retention.*—In the experiments on the effect of addition of sodium silicate on phosphate retention

(Table XIII), it was found that in the cases where the reaction mixture was not neutralised for the alkalinity of the silicate, higher values for the phosphorus in solution were obtained. With a view to knowing the influence of H-ion concentration on phosphorus recovery from gels of alumina and iron hydroxide under the conditions of the experiments, the following experiments were carried out in which the gels (5 c.c. each) were treated with 100 c.c. of a solution containing a known amount of phosphate, but adjusted to different initial  $P_H$  values by use of decinormal acid or alkali as the case may be. After standing for 48 hours, the mixtures were filtered and the phosphate in aliquots of the solution determined in each case as before. (Table XVII.)

TABLE XVII.

Initial $P_H$ of phosphate soln.	Iron hydroxide gel = 164.0 mg. $Fe_2O_3$				Alumina gel = 116.0 mg. $Al_2O_3$			
	$P_H$ of solution after adsorption	Phosphate in solution (p.p.m. of $P_2O_5$ )	Phosphate retained per cent.	Phosphate retained per g. gel (p.p.m. of $P_2O_5$ )	Phosphate in solution (p.p.m. of $P_2O_5$ )	$P_H$ of solution after adsorption	Phosphate retained per cent.	Phosphate retained per g. gel (p.p.m. of $P_2O_5$ )
2.5	2.6	29.6	70.4	429.3	2.6	33.8	66.2	570.7
5.0	5.0	32.0	68.0	414.7	5.2	36.1	63.9	550.8
7.0	7.2	33.0	67.0	408.6	7.4	38.6	61.4	529.3
9.0	8.6	35.1	64.9	395.8	8.8	42.0	58.0	499.9
10.1	10.0	36.7	63.3	386.0	10.2	45.1	54.9	473.3

Phosphate added (as p.p.m. of  $P_2O_5$ ) = 100.0.

As has been observed already by Mattson (*loc. cit.*) and by Gordon and co-workers (*loc. cit.*), it may be seen that with increase in the  $P_H$  there is a decrease in the retention of phosphate. The changes are similar in character to those observed on the addition of sodium silicate of varying initial  $P_H$  values to gels of iron oxide and alumina (Sreenivasan, *loc. cit.*).

In another set of experiments, the gels were treated with 100 c.c. of a solution containing a known amount (10 c.c.) of phosphate together with 10 c.c. of silicate solution, the mixture having been initially adjusted to varying  $P_H$  values. The extent of phosphate adsorption in the several cases as determined in the usual way is recorded in Table XVIII.

A comparison of the values for phosphate in solution at any particular  $P_H$  with and without sodium silicate would show that addition of that reagent decreases phosphate adsorption by the gels. However, the extent of phosphate resorption is greater at low  $P_H$  than at high ones. Since at high

TABLE XVIII.

Initial P <sub>H</sub> of silicate phosphate mixture	Iron hydroxide gel = 164.0 mg. Fe <sub>2</sub> O <sub>3</sub>			Alumina gel = 116.0 mg. Al <sub>2</sub> O <sub>3</sub>		
	P <sub>2</sub> O <sub>5</sub> in solution (p.p.m.)	P <sub>2</sub> O <sub>5</sub> adsorbed (per cent.)	P <sub>2</sub> O <sub>5</sub> adsorbed per g. dry gel (p.p.m.)	P <sub>2</sub> O <sub>5</sub> in solution (p.p.m.)	P <sub>2</sub> O <sub>5</sub> adsorbed (per cent.)	P <sub>2</sub> O <sub>5</sub> adsorbed per g. dry gel (p.p.m.)
2.5	36.3	63.7	388.5	42.3	57.7	497.4
5.0	37.6	62.4	380.6	43.4	56.4	486.2
7.0	38.6	61.4	374.4	44.9	55.1	475.0
9.0	40.3	59.7	364.1	46.6	53.4	460.3
10.6	42.2	57.8	352.5	49.1	50.9	438.7

Phosphate originally present (as p.p.m. of P<sub>2</sub>O<sub>5</sub>) = 100. Silicate present (as mg. of SiO<sub>2</sub>) = 2500.

hydrogen-ion concentrations, the adsorption of silicate is most (Sreenivasan, *loc. cit.*), it would appear that phosphate resorption is the result of silicate adsorption. In other words, conditions which favour adsorption of silicates by the colloidal adsorbing complex result in maximum efficiency of the silicate in regard to release of phosphates from combination.

#### Discussion.

It has been stated in the previous communications (Sreenivasan, *loc. cit.*) that the reaction of soil or of colloidal oxide of iron or aluminium with alkali silicate resolves itself into interaction with dilute alkali on the one hand, and colloidal silica on the other. Both these reactions would naturally tend to alter the extent of retention of soluble phosphate by the soil adsorbing complex or the gels of iron oxide or alumina as the case may be. Although it has been known (*vide*, Voelcker, 1915, 1916; Russell, 1932) that the application of small quantities of alkali is beneficial to crop growth, it may yet be observed that in regard to the mode of action of sodium silicate in increasing phosphorus resorption, the effects of the silica formed—presumably in the *sol* condition—is far more than the cationic effect.

During recent years, evidence has been adduced to show that phosphate adsorption by soil colloids is an anion exchange phenomenon (Mattson, *loc. cit.*; Ravikovitch, *loc. cit.*; Pugh, *loc. cit.*; Scarseth, 1935; and others). It would, however, appear from the present enquiry that the behaviour of the soil towards silicate or phosphate in presence of varying concentrations of H-ion is different from its behaviour towards mixtures of phosphate and silicate in solution. Thus, in the former case, the extent



of adsorption of phosphate or of silica by the adsorbing complex decreases with increasing  $P_H$ . This would suggest that the nature of the adsorbing complex or its ability to retain varying amounts of phosphates or silicates from solution is altered by the H-ion concentration. On the other hand when phosphate and silicate are present together in solution, it would appear that the adsorbing colloid preferentially combines with the silicate, thereby resulting in greater amounts of phosphates being present in solution. Even when the silicate is added to the soil after treatment with phosphate, the latter is released from combination. In other words, the soil-silicate complex is more stable than the soil-phosphate complex, and hence, addition of silicate solution to the latter results in resorption of phosphate. Whether or not the quantities of phosphates thus exchanged correspond to the amounts of silica adsorbed is not known.

Although the direct effects of soluble silica in increasing the water-soluble phosphorus may only be small, yet it is not improbable that under field conditions and in presence of the growing plant, the actual amounts of phosphorus made available to the plant will be quite significant. Indeed as is evident from a number of earlier researches (Schollenberger, 1922; Lemmermann, Wiessmann and Sammett, 1925; Brenchley, Maskell and Warrington, 1927; and others), the increased availability of phosphorus to plants consequent on silicate fertilisation should be far more than what is indicated in the water extract. This would mean that silica, in some unknown manner, alters the nature of the unavailable phosphates in the soil whereby a part of the latter becomes available to the plant without its becoming water-soluble. For a fuller understanding of the precise mechanism by which silicate increases the intake of phosphorus by plants from the soil, it is necessary to have a reliable measure of the available phosphorus in soils.

The action of sodium silicate in increasing phosphorus resorption from soil would no doubt depend, on a number of factors, the most important among which are the nature of the soil and the relative proportions of the silicate and phosphate. Addition of sodium silicate to soil would tend to make the soil reaction alkaline, although when the quantities are small, the silicate may not seriously affect the physical properties of the soil, especially when the latter is rich in buffering constituents. It would be useful, however, to conduct large-scale field trials with silicate, either by itself, or in combination with other fertilisers, so as to determine the proportions which would give maximum beneficial effects, under all conditions, and with all types of soil without any injury to the soil itself.

*Summary.*

(1) When soil is treated with a solution of a phosphate a considerable part of the phosphate is retained by the soil. As the concentration of the phosphate is increased, the quantities of phosphate retained also increase, although there is a decrease in the percentage retention of phosphate.

(2) The extent of retention of phosphate by the soil decreases considerably when the soil is treated with a solution of sodium silicate prior to addition of phosphate. The reaction of the mixture however changes towards alkalinity.

(3) The extent of phosphate retention decreases with increase in  $P_H$  value of the medium. When soil is mixed with sodium silicate together with enough acid to neutralise the latter prior to treatment with phosphate solution, its power of retaining phosphate is somewhat more than when sodium silicate alone is added, but is still less than that of the soil alone.

(4) Addition of increasing quantities of silicate to soil prior to addition of phosphate decreases the extent of retention of the latter although the decrease is not in strict proportion to the quantities of silicate employed.

(5) Reversing the order of addition of silicate and phosphate to soil does not appreciably alter the extent of retention of phosphate by the soil.

(6) Addition of silica gel to soil results in similar decrease in phosphate retention although the effect is less marked than with corresponding quantities of sodium silicate.

(7) Silica gel has the power of adsorbing phosphate from solution only to a small extent and the adsorbed phosphate is practically completely leachable by hot water.

(8) The behaviour of sodium silicate and of phosphate in solution in presence of hydrogels of iron oxide and alumina is very similar to that with the soil. The effect of sodium silicate in decreasing phosphate retention by the colloid is likewise more pronounced when the silicate is not neutralised for its alkaline reaction.

(9) Study of the influence of hydrogen-ion-concentration of silicate-phosphate mixtures on phosphate retention by gels of iron oxide and alumina shows that there is a decrease in the extent of retention of phosphate by the gel in presence of silicate at all  $P_H$  values. The decrease is greater at low  $P_H$  values than at high ones.

(10) Based on the foregoing and other observations, the mechanism of the increased resorption of phosphorus consequent on application of silicate has been discussed. The nature of further work relating to (a) the standardisation of a suitable procedure for measuring the available

phosphates in soil, and (b) its application in the elucidation of the mode of action of colloidal silica in increasing phosphorus availability is discussed.

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