INVESTIGATIONS ON THE RÔLE OF SILICON IN PLANT NUTRITION.

Part I. On the Nature of Interaction between Soil and Soluble Silicates.

By A. Sreenivasan, M.A.,
Department of Biochemistry, Indian Institute of Science, Bangalore.

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During recent years, there has been increasing evidence to show that many of the elements which have hitherto been regarded as "unessential" exercise profound influence on plant growth and metabolism. Some of these elements are essential to certain vital processes such as assimilation, while others impart general resistance and help to ward off a variety of plant diseases and insect pests. Many of these elements are normally present in useful quantities in most soils, but there are, nevertheless, vast tracts of land in which these elements are deficient and to which they must be supplied in some available form if healthy plant development is to be ensured. Among the various workers who have contributed to this important line of research, mention must be made of Bertrand and co-workers (1897, 1905, 1911, 1921, 1922), Mazé (1914, 1915, 1919), McHargue (1919, 1922, 1923, 1925, 1926, 1927), Brenchley and co-workers (1910, 1914, 1915, 1927), Warington (1923, 1926), Sommer (1926, 1928) and Haas and Reed (1927) who have shown that minute quantities of fluorine, iodine, zinc, aluminium, manganese and boron are essential to the normal growth of the plant. In spite of these useful advances, there are still some elements the precise rôle of which has not yet been properly understood. Silicon is perhaps the foremost among these.

Silicon occurs in all plant materials in quantities ranging from the merest trace to over 80 per cent. of the total ash (Crüger, 1857 ; Wicke, 1862 ; Wolff, 1880 ; Hattensaur, 1890 and many later workers). Several investigators (Sachs, 1862 ; Knop, 1861, 1862 ; Pierre, 1866 ; Honnel, 1877 ; Jodin, 1883, 1884 ; Pfeffer, 1900 ; Gregoire, 1911 ; Jennings, 1919 ; Sommer, 1926 ; Palladin, 1927 and others) have studied its physiological rôle, and although their findings are not always in agreement, it may, nevertheless, be concluded that (*a*) silicon cannot be placed in the category of essential elements such as nitrogen or phosphorus, and (*b*) it plays a useful secondary rôle by imparting general resistance to the plant and increasing the availability of other fertilising ingredients in the soil.

Kreuzhage and Wolff (1884) first drew attention to a probable relation between silicon and phosphorus in plant nutrition. The subsequent researches of Hall and Morison (1906), Shedd (1922), Schollenberger (1922), Lemmermann and co-workers (1922, 1925), Densch (1924), Duchon (1925), Gile and Smith (1925), Brenchley, Maskell and Warington (1927), Mange (1928), Seki (1928), Fisher (1929), Jensen and Lesch (1930), Arrhenius (1930), Reifenberg (1930) and others would point to the following:—(1) Silicate fertilisation increases the availability of phosphorus from soils which are either poor in that element or contain it in comparatively resistant forms such as rock-phosphates. Where phosphorus is present in a soluble or, at any rate, readily available form, the assimilation of the two elements seems to proceed independently of each other. (2) Silicon does not appear to be capable of wholly substituting phosphorus in plant economy, but its ability to do so at least partially is still an open question. (3) The seat of interaction between silicon and phosphorus is not well-defined, but is probably in the soil.

It may thus be seen that the precise nature of the relation between silicon and phosphorus is not fully understood. Further information is also required regarding the direct part played by silicon in plant metabolism. This would be of particular interest in regard to the nutrition of the rice plant, which is exceptionally rich in silicon (Nanji and Shaw, 1925) and flourishes best only under the conditions of the swamp soil. The present enquiry was, therefore, undertaken.

It has long been known that the soil possesses the remarkable property of absorbing basic radicles from solution (Thompson, 1850; Salomon, 1867; Biedermann, 1869; Frey, 1875 and others). Explanations of this have been offered by Way (1850, 1852), Liebig (1858), Knop (1868) and others, but it was Van Bemmelen who showed in a series of classical memoirs (1900, 1904) that the phenomena are similar to those shown by colloids. Among the acid radicles, the absorption of phosphate has been studied by a number of workers (Van Bemmelen, 1879; Rostworowski and Wiegner, 1912; Russell and Prescott, 1916; Prescott, 1916; Fisher, 1921; Harrison and Das, 1921; Gordon *et al*, 1922, 1923; Comber, 1925; Roszmann, 1927; Miller, 1928; Teakle, 1928; Wiedemann, 1928; Doughty, 1930; Ghosh and Bhattacharya, 1930; Ford, 1933; Scarseth and Tidmore, 1934; Dean, 1934; Floyd Heck, 1934; Ravikovitch, 1934 and others), but there is considerable difference of opinion regarding the manner in which phosphate is removed from solution. Absorption of other anions has been studied by Russell and Prescott (*loc. cit.*), Arrhenius (1922), Van der Spek (1922), and, more recently, by Mattson (1927, 1930, 1931), but very little is known regarding the retention of silicates in the soil. In view of this and the need for further knowledge regarding the nature of relation between silicon and phosphorus in the soil, the present study on the nature of interaction between soil and silicate was undertaken.

Experimental.

MATERIALS USED.—*Soils:* The major part of the present study was conducted with two soils, one a light clay and the other, a sandy loam. The samples were air-dried and ground to pass the 40-mesh sieve. *Sodium silicate.*—Kahlbaum's solution (25 per cent.) was diluted ten times and filtered. The filtrate was used in the present investigation. It was necessary to check the strength of the solution from time to time as it was found that silica tended to separate on prolonged standing.

METHODS.—*Estimation of Silica:* The quantities present in solution were determined by evaporation with hydrochloric acid to dryness on the water-bath followed by extraction with dilute hydrochloric acid and filtration. The precipitates thus obtained were ignited and weighed as silica (SiO_2). In each case, the filtrate was evaporated with fresh quantities of hydrochloric acid so as to include any silica that might have escaped precipitation during the first treatment.

Composition of sodium silicate.—The percentages of water and of total solids were determined by drying first over the water-bath and then in a hot air oven (105°) for 4-5 hours and weighing. Silica was determined by the method outlined above, while the proportion of Na_2O was estimated as follows:—10 c.c. of the stock solution was diluted largely (so that the hydrolysis may be complete) and titrated against decinormal sulphuric acid. The values thus obtained were checked by an indirect method. A known excess of the standard acid was added to the silicate and the mixture evaporated almost to dryness on the water-bath. After all the silica had separated out, the residue was extracted with water, filtered, washed well, and the filtrate and washings back-titrated against standard alkali. The results have been given in Table I.

TABLE I.

Sp. gravity	Per cent. solid in solution (by weight)	P_H	$\frac{SiO_2}{Na_2O}$ (Molecular ratio)	$\frac{SiO_2}{Na_2O}$ (Weight ratio)
1·021	3·80	10·6	2·71	2·64

It was observed that when a solution of sodium silicate was treated with excess of mineral acid, the mixture remained quite clear. Separation of silica commenced only after heating and was not complete unless the mixture was evaporated to dryness.

Effect of treatment with increasing quantities of silicate on soil reaction.—Samples (20 g.) of the clay soil were shaken with 50 c.c. each of a solution containing the equivalents of 1, 2, 3, 4, 5, 7, 9 and 10 c.c. respectively of the stock silicate and the P_H of the extracts determined colorimetrically using a Hellige Comparator outfit. The results have been presented in Table II.

TABLE II.

Volume (in c.c.) of silicate added	0	1	2	3	4	5	7	9	10
P_H of extract ..	7·4	7·5	7·6	7·6	7·8	8·0	8·4	9·2	9·8

It may be seen from the above that there is a steady shift in P_H towards the alkaline side as the concentration of sodium silicate is increased. The change is more rapid in the later stages than in the earlier ones. Thus, with an addition of 5 c.c. of sodium silicate, the reaction changes only from P_H 7·4 to 8·0 whereas addition of another 5 c.c. raises this to P_H 9·8. The observations would suggest that, in the early stages, the suspensions were buffered by some of the soil constituents. As the medium became increasingly alkaline, the buffering materials separated out, so that further additions of silicate solution led to rapid shift in P_H.

Extraction of soil-silicate mixtures.—Although the original soil itself yielded clear aqueous extracts, it was not possible to obtain similar extracts from suspensions to which silicate had been added. Even centrifuging at high speed (6000 R.P.M.) did not help to remove the suspended matter. This was found to be due to the action of alkali resulting from the hydrolysis of sodium silicate and consequent deflocculation of soil colloids. It was thought desirable therefore to treat the centrifugate with a suitable flocculant prior to filtering. No flocculant was added to the soil-silicate system itself so as to avoid interference with the initial reaction between soil and silicate. The following experiment was tried:—Samples (25 g.) of the clay soil were treated with 50 c.c. each of water, the mixtures well shaken and then centrifuged for 30 mins. at 6000 R.P.M. To the centrifugate obtained in each case was added 10 c.c. of silicate solution (equivalent to 261·0 mg. of SiO_2) followed by 5 drops of (1) normal hydrochloric acid solution, (2) normal sodium chloride solution, and (3) saturated lime water respectively. The mixtures were allowed to stand for one hour, then filtered, washed and the silica in the filtrate and washings estimated in the usual manner. The results were as follows:—

(1) 268·3 mg.; (2) 261·7 mg.; and (3) 202·4 mg. The sample of soil to which no silicate was added (control) yielded a value of 3·8 mg. It may be seen from the above that flocculation with hydrochloric acid yielded the most satisfactory results. The comparatively low recovery of silicate on treatment with lime water was probably due to the formation of the insoluble calcium-silicate complex.

Retention of silicate by the soil.—Samples (50 g.) of the soil were treated with varying quantities of the silicate solution and the suspensions allowed to stand for 10-15 minutes. Enough water was then added to make up the volume of suspensions to 200 c.c. in each case. They were then centrifuged, the centrifugates flocculated with dilute hydrochloric acid, then filtered and silica in aliquots of the filtrate determined (Table III).

TABLE III.

Silicate (as mg. of SiO_2) added	52·2	130·5	261·0	391·5	522·0
Silicate (as mg. of SiO_2) extracted	10·1	29·6	86·8	161·0	233·2
Per cent. of silicate retained by soil	80·7	77·3	66·7	58·9	55·3

It may be noted that, in all the cases, the major part of the added silicate was retained by the soil. The quantities thus retained increased with those of the silicate. The corresponding percentages tended however to decrease, thus showing that there was a fall in the efficiency of retention.

The above observations are similar to those recorded by some previous workers (*loc. cit.*) in regard to the retention of phosphorus in the soil.

Extraction of silica by different solvents.—To 50 g. lots of the clay soil were added 20 c.c. each of the silicate solution corresponding to 443·8 mg. of SiO_2. After standing for 10 mins., the soil-silicate pastes were extracted on the Buchner with successive small quantities of different solvents until aggregate leachates of about 400 c.c. each were obtained. In another set of experiments, the silicate treated soil was transferred to a shaking bottle, made with the extractant to 200 c.c. and shaken in an end-over-end shaker for a period of 6-8 hrs. (previous trials having shown that further shaking was unnecessary) and filtered. In each case the silica present in aliquots of the filtrate was determined and, from this, the total amounts in the extract calculated. The above experiments were also repeated with larger quantities (100 g.) of soil. Table IV gives the particulars relating to the extractants used as also the total amounts of silica recovered from solution when the soil-silicate mixture was (A) repeatedly leached and (B) shaken with each extractant.

The specimens treated with sodium carbonate solution did not filter easily. Centrifuging prior to filtration was somewhat helpful, but even then only small quantities of the filtrate could be obtained. The filtrates were dark coloured and contained humic matter which had been brought into solution by the alkali. The organic matter had to be destroyed by treatment with hydrogen peroxide before silica in solution could be determined.

It may be noted (Table IV) that the three acids extracted the maximum quantity of the silica while the buffer and sodium carbonate extracted considerably less. The quantities brought into solution by hydrochloric and citric acids were nearly the same while those by acetic acid were distinctly less. Attention may also be drawn to the fact that very nearly the same results were obtained by adopting either of the two methods of extraction except in the case of sodium carbonate. As the method of repeated leaching on the filter was a tedious process and occupied much time, the method of shaking with a known volume of solvent for 6-8 hours was, therefore, adopted in subsequent experiments.

TABLE IV.

Treatment	Solvent used for extraction									
	Citric acid (1 per cent.)		Acetic acid (1 per cent.)		Hydrochloric acid (1 per cent.)		Walpole's acetate buffer (P_H, 5·8)		Sodium carbonate (1 per cent.)	
	A	B	A	B	A	B	A	B	A	B
			Silicon	(as mg.	of SiO_2)	extracted.				
50 g. soil + silicate equivalent to 443·8 mg. of SiO_2 ..	283·5	302·0	..	..	280·0	273·2	169·6	177·2	86·6	136·2
100 g. soil + silicate equivalent to 443·8 mg. of SiO_2 ..	273·2	280·8	179·3	207·6	276·1	274·9	155·9	155·9	92·2	133·8

Influence of reaction (P_H) *of solvent on the extraction of silicate.*—The silicate solution (20 c.c.) was added to 100 g. lots of the two soils and the mixtures extracted with different solvents. The H-ion concentrations of the solvents as well as those of the extracts, as also the quantities of silica extracted in each case were determined (Table V).

TABLE V.

Extractant	P_H of solvent	Light Clay; P_H, 7·5				Sandy Loam; P_H, 7·2			
		Silicate (as SiO_2) added (in mg.)	Silicate (as SiO_2) recovered (in mg.)	Recovery per cent.	P_H of extract	Silicate (as SiO_2) added (in mg.)	Silicate (as SiO_2) recovered (in mg.)	Recovery per cent.	P_H of extract
Citric acid .. (1 per cent.)	2·2	443·8	279·2	62·9	3·0	449·1	270·5	60·3	3·2
Hydrochloric acid .. (1 per cent.)	$<$1·0	443·8	274·9	51·1	1·0	449·1	229·5	51·2	1·2
Sodium chloride .. (1 per cent.)	7·0	449·1	169·4	37·7	7·1	449·1	150·8	33·6	7·0
Acetic acid .. (1 per cent.)	2·4	449·1	214·4	57·4	2·8	449·1	169·0	37·6	3·0
Sodium carbonate .. (1 per cent.)	$>$10·6	443·8	133·9	30·2	..	449·1	100·8	22·4	..
Walpole's buffer ..	5·8	443·8	155·8	35·9	5·2	449·1	157·9	35·2	5·2
Citric acid .. (2 per cent.)	2·2	449·1	279·8	62·3	2·8	449·1	268·0	59·7	2·8

The above results do not show any relation between the reaction of the extractant and the extent of recovery of added silicate. Citric and hydrochloric acids extracted the largest amounts of silicate. With the available evidence it is difficult to explain why different solvents extracted varying quantities of the silicates.

Citric acid as extractant.—Extraction with water being slow and tedious, it was considered desirable to use an extractant which will act quickly and efficiently. The previous observations having shown that 1 per cent. citric acid meets the above requirements, some experiments were carried out comparing the results obtained by using that solvent with those extracted by water alone. Samples (50 g.) of the clay soil were treated with increasing quantities of the silicate solution. The pastes thus obtained were extracted by (*a*) water, the procedure involving preliminary centrifuging at 6000 R.P.M., and (*b*) citric acid, the suspension being shaken for 6 hrs., prior to filtration. The results thus obtained have been given in Table VI, correction being applied for the silicate extracted from the original soil by water (3·8 mg. as SiO_2) and citric acid (5·4 mg. as SiO_2) respectively.

TABLE VI.

Silicate added (as mg. of SiO_2) ..	52·2	130·5	261·0	391·5	522·0
Silicate recovered by water extraction (as mg. of SiO_2)	10·1	29·6	86·8	161·0	233·2
Silicate recovered by citric acid extraction (as mg. of SiO_2) ..	12·4	50·4	129·8	236·4	301·2

It would be seen from the above that although the quantities extracted by the two solvents are not identical, there is yet a close parallelism between the two. In addition to being rapid and yielding a clear solution, extraction with citric acid has also certain other features to recommend it. The acid is only slightly dissociated and, as a consequence, the P_H of the resulting extract will not be greatly altered. That acid has also found extensive use in the determination of available phosphorus in soils (Dyer, 1894). In view of these advantages, citric acid was used as the extractant in later studies.

Extraction with higher concentrations of citric and hydrochloric acids.—Samples (50 g.) of the clay soil were treated with known amounts of silicate solution and extracted with 1, 2 and 3 per cents. respectively of the two acids. More concentrated acid was not used as it was feared that it might affect the structural soil particles. The results are given in Table VII.

TABLE VII.

	Citric acid (per cent.)			Hydrochloric acid (per cent.)		
	1	2	3	1	2	3
SiO_2 recovered (in mg.) ..	128·0	129·4	127·5	130·0	129·4	142·6

Silicate originally added (as silica), 259·6 mg.

The results show that there is no appreciable improvement in the extraction of silica with increasing concentration. The apparently better extraction obtained with 3 per cent. hydrochloric acid was subsequently traced to the fact that the structural particles were themselves being attacked at that concentration.

Rate of extraction with water and citric acid.—To 50 g. lots of the clay soil known amounts of silicate solution were added. In one set of experiments each sample was centrifuged with 100 c.c. of water and the supernatant decanted out. The sediment was then stirred with 100 c.c. of water and centrifuged. The process was thus repeated 4 or 5 times. In each collection of centrifugate, silica was estimated in the manner outlined before. In another set of experiments, the soil-silicate mixture was treated on the Buchner with successive 100 c.c. portions of citric acid, the filtrates collected separately and the total silica in each lot determined. The results are given in Table VIII.

TABLE VIII.

	Silicate extracted (as mg. of SiO_2)	
	Water extract (centrifugate)	Citric acid extract (filtrate)
First 100 c.c... ..	77·6	109·2
Second „	10·4	16·8
Third „	3·8	8·4
Fourth „	3·2	6·0
Fifth „	3·6	5·4

Silicate originally added (as SiO_2), 259·8 mg.

It may be noted that the major part of the soluble silica was extracted by the first 100 c.c. in either case. After the third extraction, the quantities

TABLE IX.

Silicate added (as mg. of SiO_2)	Clay Soil		Loam Soil	
	Citric soluble silica (in mg.)	Percentage of silica retained	Citric soluble silica (in mg.)	Percentage of silica retained
44·8	11·6	74·1	10·6	76·4
67·3	14·2	78·9	16·2	75·9
112·1	49·2	56·1	45·6	59·3
224·2	123·2	45·1	119·3	46·8
448·4	289·5	35·4	268·7	40·1

extracted attained more or less steady, low values corresponding to those of the control, *i.e.*, the untreated soil itself. It would thus be seen that all the soluble silica was extracted in the first 200 c.c.

Effect of addition of increasing quantities of silicate on citric solubility.—To 50 g. lots of the clay or the loam soil known amounts of silicate were added, and the citric soluble silica estimated in each case. The results are given in Table IX.

As seen in the case of water extracted samples (Table III), while the total quantities of silicate retained by the soil increased, the corresponding percentages showed a marked decrease. The clay soil retained more of the silicate than the loam.

Influence of the nature of the soil on the extent of silicate retention.—Specimens (50 g. of each) of soils representing different types commonly met with in India and Ceylon were ground to pass the 40-mesh sieve, treated with known amounts of silicate and the amounts of citric soluble silica determined in each case. The description of the soils as also the recoveries and percentage retention of silica are given below (Table X):—

TABLE X.

Soil type	Silica recovered from solution mg.	Silica retained by soil mg.	Percentage retention
Sandy soil—Jaffna (Ceylon)	203·9	120·1	9·0
Clay soil—Bangalore	123·2	100·8	45·0
Red loam—Bangalore	119·2	104·8	46·8
Black cotton soil (clay)—Nagpur ..	46·4	178·0	79·3
Karl soil (clay)—Sholapur	53·7	170·3	76·0
Kalar soil (alkali)—Sind	103·1	120·9	54·0
Peat soil (acid)—Travancore	206·8	117·2	8·7

Silicate added (as mg. of silica), 224·0.

It would be seen from the above that the power of retaining silicates varies with the nature of the soil, being most in the clays and least in the sandy and peat soils. The rather high recovery from the peaty soil was partly due to its acid character (P_H 3·0) and partly to the fact that it was poor in clay. On the other hand, it appeared probable that the slightly alkaline character combined with the high buffering capacity of some of the other soils were responsible for the high retention in those cases. The reaction of the soil and that of the extract after treatment with 1 per cent. citric acid (P_H 2·8) in those cases are given below (Table XI) :—

TABLE XI.

Soil	P_H of soil	P_H of extract
Black cotton—Nagpur ..	7·4	6·4
Karl—Sholapur	7·6	6·8
Kalar—Sind	7·8	7·6

All the three soils, particularly the *Kalar*, have high buffering capacity. To obtain results comparable with those for other soils, separate extractions were carried out with these soils after addition of sufficient quantities of citric acid to bring the reaction to P_H 7·0 in each case. The added silica was then extracted with excess of 1 per cent. citric acid in the usual way (Table XII).

TABLE XII.

Soil	Silicate recovered (as mg. of SiO_2)	Silicate retention per cent.
Black cotton—Nagpur ..	54·6	75·6
Karl—Sholapur ..	70·4	68·6
Kalar—Sind	109·6	51·1

The above results are of about the same order as those obtained without pre-treatment with citric acid (Table X). It may be concluded therefore that the reaction and the buffering capacities are only of minor importance and that the retention of silicate is due to other agencies—probably the nature and mode of distribution of mineral constituents in the soil.

Effect of varying the quantities of soil and of silicate on citric soluble silica.—In the following experiments, the soil (clay) and silicate were mixed in varying proportions and then extracted with citric acid. The results are given in Table XIII.

TABLE XIII.

Weight of soil (in g.)	Silicate added as SiO_2 (in mg.)	Citric soluble SiO_2 (in mg.)	Per cent. retention of silica
100	443·8	280·8	36·7
100	221·9	117·5	47·1
100	112·3	46·0	59·1
50	443·8	299·5	32·5
50	224·6	123·2	45·1
50	112·3	52·4	53·3
25	449·8	341·7	24·0

As observed in one of the earlier experiments (Table IX), addition of increasing amounts of silicate to the same weight of soil led to decrease in the percentage of retention. When the same amount of silicate was added to increasing quantities of soil, there was correspondingly greater retention.

Effect of time of contact on retention of silicate by soil.—To 50 g. lots of clay soil aliquots of silicate solution, each corresponding to 224·0 mg. of SiO_2, were added. The suspensions thus obtained were extracted with citric acid at different intervals of time.

TABLE XIV.

Time of contact in hrs.	0	½	1	2	4	8	24
Citric soluble silica (as mg.) ..	123·4	123·2	123·6	122·8	121·2	123·6	122·4
Retention per cent.	45·0	45·1	44·9	45·2	45·9	44·9	45·4

The results (Table XIV) show that, as in the case of phosphates, (Roszmann, *loc. cit.;* Scarseth and Tidmore, *loc. cit.*) the reaction between soil and silicate is practically instantaneous. Even heating the soil-silicate mixture for a few minutes at the boiling temperature of water prior to extraction did not appreciably alter the extent of retention.

Effect of moisture content of soil on the extent of silicate retention.—The clay soil (in 50 g. lots) was adjusted to different levels of moisture and then treated with the same quantities of silicate. The resulting mixtures were then extracted with citric acid and the silica contents of the extracts determined (Table XV).

TABLE XV.

Percentage of moisture in the soil ..	0 (dried at 100°)	4	10	20	30	40	60	100
Citric soluble silica (in mg.)	129·7	123·2	124·9	127·4	130·8	133·1	139·0	141·5
Retention per cent. ..	42·2	45·1	44·3	43·2	41·7	40·7	38·0	36·9

Silicate added as mg. of silica = 224.2.

The results show that as the moisture content of the soil increases, there is perceptible decrease in the retention of silicate. As increasing moisture content of the soil will reduce the effective concentration of the added silicate, it would appear that the extent of dilution of the silicate is one of the factors determining the extent of retention by the soil. It may be further inferred that if the same quantity of silicate is applied to dry as well as swamp soil, the latter will contain more of soluble silica than the former. The oven-dried soil retains less silica than the one at 4 per cent. moisture. This may be due to partial loss of the power of retention on prolonged heating.

Effect of igniting the soil on its power of retaining silicate.—Samples (50 g.) of the two soils used in some of the previous studies were ignited for one hour at low red heat and then cooled. The products thus obtained were treated with known amounts of silicate and the citric extractable silica estimated.

TABLE XVI.

Silicate added (as mg. of silica)	Heavy Soil (ignited)		Light Soil (ignited)	
	Silicate recovered (as mg. of SiO_2)	Per cent. retention	Silicate recovered (as mg. of SiO_2)	Per cent. retention
224·0	222·2	0·8	219·0	2·2
448·0	439·6	1·9	436·8	2·5

The results (Table XVI) show that both the soils lose their power of retaining silicate on strong ignition.

Effect of soil organic matter on the retention of silicate.—The foregoing observations naturally suggested that the organic matter of the soil may be responsible for the retention of silica. In order to verify this, samples of soil (50 g.) were gently oxidised by repeated warming with small quantities of hydrogen peroxide (6 per cent.) until further addition of peroxide did not show any effervescence. The product thus obtained was treated with known quantities of silicate after which citric solubility was determined in the usual way (Table XVII).

TABLE XVII.

Silicate added (as mg. of SiO_2)	Heavy Soil (oxidised)		Light Soil (oxidised)	
	Silicate recovered (as mg. of SiO_2)	Per cent. retention	Silicate recovered (as mg. of SiO_2)	Per cent. retention
224·0	124·7	44·3 (45·0)	118·0	47·3 (46·8)
448·0	288·4	35·6 (35·4)	271·9	39·3 (40·1)

Bracketted figures are for the unoxidised soil (control).

It would be seen from the above that, if the organic matter is destroyed by a mild reagent that would not affect the ultimate structure of the soil, there is no appreciable change in the power of silicate retention. The reverse effect observed in the previous experiments should, therefore, be traced to the action of strong heat on the mineral constituents of the soil.

TABLE XVIII.

Silicate added as mg. of SiO_2	Fractions of Soil					
	Coarse		Silt		Fine	
	Silicate recovered (as mg. of SiO_2)	Per cent. retention	Silicate recovered (as mg. of SiO_2)	Per cent. retention	Silicate recovered (as mg. of SiO_2)	Per cent retention.
224·0	212·3	5·2	146·1	34·8	114·4	48·9

Silicate retention by the whole soil=45.0 per cent.

Retention of silicate by the textural separates of the soil.—By adopting the process of water sedimentation, the soil was divided into three main fractions, (*a*) the coarse one comprising coarse and fine sand, (*b*) the silt (including fine silt), and (*c*) the fine fraction consisting mostly of clay. 50 g. lots of the three different fractions were treated with known amounts of silicate solution and the citric soluble silica determined (Table XVIII).

It may be noted that very little of the added silicate was retained by the fraction consisting of coarse and fine sand, and that while fixation by the silt fraction was appreciable, it was maximum with the clay fraction. Since it has already been shown that the organic matter has practically no influence on silicate retention, it may be inferred that the mineral constituents of the finer fractions of the soil are responsible for that phenomenon.

Effect of addition of iron or aluminium oxide on the extent of silicate retention.—Since the finer fractions of the soil contain fairly large quantities of iron and aluminium oxides, some experiments were carried out adding varying quantities of those oxides to the clay soil (50 g.) prior to treatment with silicate solution. Citric soluble silica was then determined in the usual way (Table XIX).

TABLE XIX.

Ferric oxide added in g.	Silicate recovered as mg. of SiO_2	Recovery per cent.	Aluminium oxide added in g.	Silicate recovered as mg. of SiO_2	Recovery per cent.
0	123·2	55·0	0	123·2	55·0
1	117·6	52·5	1	116·6	52·1
2	111·0	49·6	2	110·0	49·1
5	105·6	47·2	5	98·1	43·8

Silicate added to soil (as SiO_2) = 224·0 mg.

In another set of experiments, the soil (50 g.) was well mixed with varying quantities of lemonite, hæmatite or bauxite. Silicate was then added and the citric soluble silica determined as before (Table XX).

It may be seen from the table that addition of the two oxides either as pure chemicals or as minerals does not appreciably increase the retention of silicate. Similar observations were also made when varying quantities of laterite (rich in iron and aluminium oxides) were added to the soil.

TABLE XX.

Mineral added and quantity	Silicate recovered as mg. of SiO_2			Recovery per cent.
	Soil + Mineral	Mineral alone (control)	Difference	
Lemonite (5 g.) ..	112·8	6·4	106·4	47·5
Hæmatite (5 g.) ..	109·2	7·8	101·4	45·3
Bauxite (5 g.) ..	121·4	14·5	105·9	47·3
,, (10 g.) ..	124·0	26·2	97·8	43·7

Silicate added as mg. of silica = 224·0.

The foregoing observations relate primarily to oxides which were present in the insoluble condition. Since the finer fractions of the soil contain fairly large quantities of iron and aluminium in the colloidal condition, it was considered necessary to conduct further trials to elucidate the rôle of those forms in the retention of silica by the soil.

Effect of previous leaching with hydrochloric acid on retention of silicate by soil.—Samples (50 g.) of the clay and the loam soils were leached on the Buchner with N. hydrochloric acid till about 500 c.c. of leachate was obtained in each case. It was expected that, by this treatment, a considerable part of the reactive iron and aluminium of the soil would be removed. The residues were air-dried, treated with known amounts of silicates and citric soluble silica estimated. The leachates were also analysed for their contents of silica and sesquioxides ($Fe_2O_3 + Al_2O_3$). The results are given in Table XXI.

TABLE XXI.

Soil	Leachate		Residue		
	Silicate as mg. of SiO_2	Sesqui-oxides (Fe_2O_3)	Silicate added as mg. of SiO_2	Silicate recovered as mg. of SiO_2	Percentage of retention
Light clay ..	55·0	41·0	224·0	139·6	37·8 (45·0)
Sandy loam ..	40·0	52·0	,,	134·2	40·1 (46·8)

The bracketted figures were obtained for the unleached soil (control.)

The observations show that partial removal of reactive minerals leads to appreciable reduction in the capacity of the soil to fix silicates.

Influence of lime on silicate retention.—Representative specimens (50 g.) of the clay soil were intimately mixed with 1 and 2 g. respectively of freshly ignited lime and then treated with known quantities (224·0 mg. each as SiO_2) of silicate. The mixtures were then extracted with citric acid using excess of the acid so as to neutralise the lime present. The results are given in Table XXII.

TABLE XXII.

Tretament	Silicate recovered as mg. of SiO_2	Percentage of retention
Soil (50 g.) alone (control)	123·2	45·0
„ + CaO (1 g.) ..	132·3	40·9
„ + CaO (2 g.) ..	140·6	37·2

Pre-treatment with lime is thus seen to reduce considerably the extent of silicate retention. This is probably due to a part of the added silicate combining with the lime to form a labile calcium complex. On treatment with citric acid, the complex is broken up and silica passes into the extract. The possible formation of the calcium complex receives support from the fact that when lime is added after the silicate has reacted with the soil, no improvement in extraction is obtained.

Mechanism of Retention of Silicate by the Soil.

Exchange of bases during interaction between soil and silicate.—The two soils (in 300 g. lots) used in the previous studies were treated as follows:—(*a*) with 500 c.c. of water alone, (*b*) 60 c.c. of silicate solution followed by 440 c.c. of water, and (*c*) 60 c.c. of sodium chloride solution containing 0·86 g. of the salt (the amount of exchangeable sodium being the same as that of the silicate solution used in *b*) followed by 440 c.c. of water. In each case, the suspension was allowed to stand overnight and then filtered. Clear filtrates were obtained from (*a*) and (*c*) but the filtrate from (*b*) had to be clarified by addition of a few drops of hydrochloric acid. Aliquots of the filtrates were then analysed for iron, aluminium and calcium. The determinations were carried out according to the A.O.A.C. methods (1930). The results have been presented in Table XXIII.

TABLE XXIII.

Treatment	Exchangeable iron as Fe_2O_3 (p.p.m.)	Exchangeable aluminium as Al_2O_3 (p.p.m.)	Exchangeable calcium as CaO (p.p.m.)
	SOIL—LIGHT CLAY.		
Soil untreated (control) ..	18	53	57
Soil + Sodium silicate ..	20	55	63
Soil + Sodium chloride ..	25	116	111
	SOIL—SANDY LOAM.		
Soil untreated (control) ..	24	37	26
Soil + Sodium silicate ..	29	27	32
Soil + Sodium chloride ..	43	97	78

It would be seen from the above that although treatment with silicate leads to slightly increased exchange with the different bases, the quantities are far less than those exchanged on addition of sodium chloride. The difference between the silicate treated samples and the controls is indeed so small that it may be stated that the sodium of the former does not behave in the normal manner.

Absorption of silicate by soil saturated with respect to different cations.—Samples (50 g.) of the clay soil were saturated with regard to hydrogen, sodium,

TABLE XXIV.

Soil used	Silicate extracted by water (as mg. of SiO_2)	Retention per cent.
Untreated (control) ..	86·1	66·8
H. Soil	106·9	58·8
Na. Soil	84·9	67·3
K. Soil	86·7	66·6
Ca. Soil	82·5	68·2

Silicate added to soil (as SiO_2) = 259·2 mg.

potassium and calcium ions by leaching on the Buchner with successive small quantities of N/2 solutions of the corresponding chlorides. In the later stages, washing was done with more dilute solutions with a view to avoiding, as far as possible, mechanical retention of the solutions by the soil. The specimens thus obtained were air-dried and treated with known amounts of silicate. The mixtures were then extracted with water and the silica in the extracts estimated. The results are given in Table XXIV.

The above results show that (except in the case of the hydrogen soil) the retention of silica is about the same in all the cases. The low retention by the hydrogen soil may be due to the acid nature of that sample which, as already observed, helps in the extraction of silicate from the soil.

Relation between concentration of added silicate and retention of silica by the soil.—Fifty gram lots of the clay soil were treated with silicate solutions (20 c.c. each) of different concentrations. They were then extracted with citric acid and the silica contents of the extracts determined.

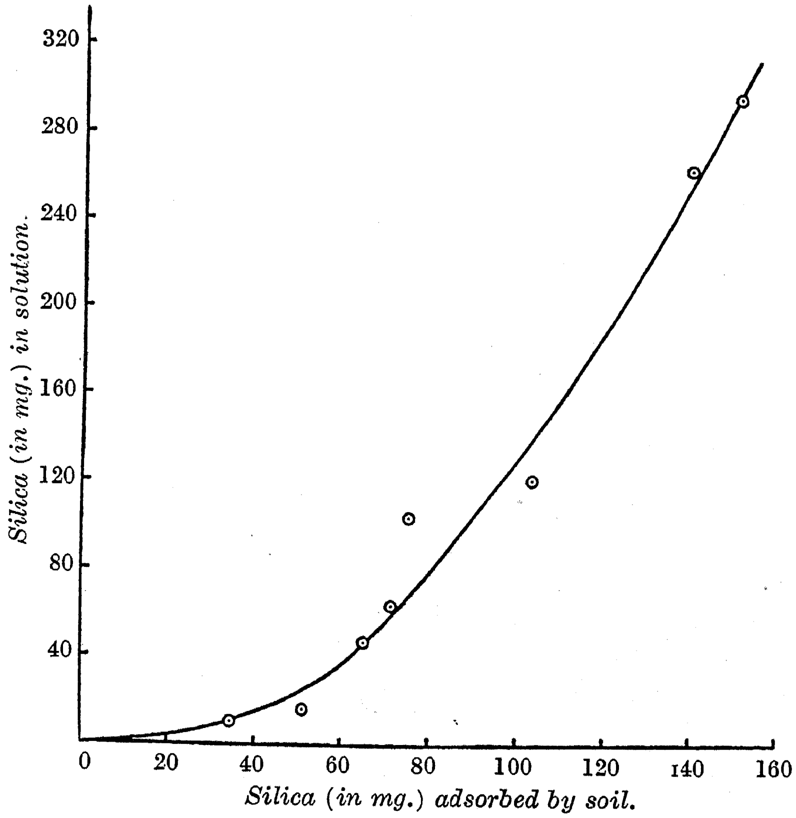

Fig. 1. Adsorption of Silicate by Soil.

When the amounts of silica present in solution are plotted against the corresponding quantities retained by the soil (Fig. 1), it is found that the former is logarithmically proportional to the latter. This observation, together with those of the previous experiments, would show that the retention of silicate is one of adsorption by the mineral colloids of the soil.

Effect of addition of silicate on the composition of the soil solution.—The two soils used in the previous studies were moistened to 60 per cent. saturation and then treated with sodium silicate (Kahlbaum's 25 per cent. solution) in quantities corresponding to 1·1 and 2·2 g. of SiO_2 respectively. They were then expressed in a hydraulic press at 4000 lbs. per square inch (Lipman, 1918). The untreated soils were also expressed likewise. The soil solutions (20-30 c.c.) thus obtained were filtered carefully and the total silica in 20 c.c. of the filtrate determined in each case. The related observations have been given in Table XXV.

TABLE XXV.

Treatment	Moisture per cent.		P_H of soil solution	Silica (in mg.) in 20 c.c. of soil solution
	Before pressing	After pressing		
Clay soil (500 g.) alone (control)	26·8	22·0	6·8	32
,, + silicate (equivalent to 1·1 g. of SiO_2) ..	27·2	20·5	7·2	30
,, + silicate (equivalent to 2·2 g. of SiO_2) ..	27·3	20·6	7·4	30
Loam soil (500 g.) alone (control)	14·9	8·1	..	26
,, + silicate (equivalent to 2·2 g. of SiO_2) ..	15·6	7·0	..	32

It is rather surprising to note that although fairly large quantities of silicate were added, the silica content of the soil solution was still not appreciably affected. The silicate had no doubt reacted with the soil as may be seen from the change in reaction. It has to be inferred, therefore, that the silicate ion or silicic acid (resulting from hydrolysis) had combined with the mineral colloids of the soil to form an insoluble complex. Extraction of a portion of the added silicate by leaching with either water or citric acid would therefore appear to be the result of a secondary reaction.

Discussion.

The results of the present enquiry have thrown much light on (*a*) the chemical nature and behaviour of silicates in solution, and (*b*) the mode of interaction between soil and silicate. Useful information regarding the extraction and general " availability" of silicon under a variety of conditions has also been obtained.

The silicate used in the present study (which is a well-known commercial brand) contained a high proportion of silicon and corresponded to the empirical formula $Na_3Si_4O_{10}$. It was completely hydrolysed by water and the solution behaved as a mixture of alkali and silica sol.

The reaction between soil and silicate would naturally resolve itself into interaction with dilute alkali on the one hand and colloidal silica on the other. The former would tend to make the soil somewhat alkaline but the quantities being small and the soil rich in buffering constituents, it is hardly probable that the application of the silicate would seriously affect the physical properties of the soil. The presence of the alkali should nevertheless be taken into consideration when evaluating the fertilising value of silicate. The silica sol behaves independently of the alkali and is adsorbed by the mineral colloids of the soil. The extent of retention of silicate by the soil is determined by a number of factors, the most important among which are (*a*) the moisture content and (*b*) the nature of the mineral constituents forming the clay fraction of the soil. The other changes attendant on the application of the silicate (especially in regard to the release of anions such as phosphate) are still awaiting systematic study, but it may be safely concluded that they would largely depend on the nature and extent of adsorption of the resulting silica sol. It would thus be seen that the process of silicate fertilisation is essentially an elegant method of applying colloidal silica to the soil.

The adsorption studies have already shown that the retention of silica by the soil proceeds largely in accordance with the laws of colloidal behaviour. Since the active mineral constituents of the soil are mostly composed of the oxides of iron, aluminium and silicon, it would be of interest to conduct further systematic studies with pure gels of those oxides. It may be expected that the enquiry would show as to which of the mineral constituents is most concerned in the adsorption of silica and the associated changes. It would also explain why, under the same conditions, different soils adsorb silica to such varying extents. Work on this aspect of the problem has already been completed and would form the subject of the next communication.

A part of the added silicate can be leached out from the soil by addition of either water or dilute acids, the most satisfactory among which is 1 per cent.

citric acid. The quantities thus extracted would naturally depend on the same factors as those responsible for the retention of silica in the soil. The soluble silica would correspond, at any rate approximately, to the quantities that may be taken up by the growing plant. It would thus come in the same class as phosphoric acid, the availability of which is an important factor in crop production. The precise significance of the availability of silica in field practice is still obscure, but it may be reasonable to assume that it will at least give an idea of the silica that may be taken up by the crop.

The nature of interaction between soil and silicate would suggest that it may assist in plant growth in one of the two following ways :—(*a*) by becoming directly available to the plant, and (*b*) by releasing from combination certain fertilising ingredients which may not otherwise be available to plant nutrition. A useful measure of the direct availability of silica would be provided by either water or citric solubility. The extent to which the added silicate increases the availability of other fertilising ingredients such as phosphates would depend on (1) the total amounts of such constituents in the soil, and (2) the capacity of the soil to retain silica and anions in general. In the former case the quantity of added silicate (above a certain minimum) will not appreciably increase its utility : in the latter, the availability of the other constituents (such as phosphates) would largely depend on the quantity of silicate applied. Further work along these lines is in progress and it is hoped that, before long, it will be possible to throw some light on this important aspect of the problem.

Attention has already been drawn to the low retention and consequently high availability of silica in presence of increasing quantities of water. It is also known that under the conditions of the swamp soil, decomposition of organic matter results in the formation of acid products (Subrahmanyan, 1929 ; Bhaskaran *et al*, 1934) which should further help in the extraction of silica. It may be naturally expected, therefore, that, under the conditions of the swamp soil, larger quantities of silica would be rendered available than under the corresponding dry conditions. This would naturally account for the high silica content of the rice plant as also certain other plant species (such as *Eragrotis cynosuroides*, *Saccharum spontaneum* and *Imperata arundinacea*) which are known to flourish under swamp conditions. Further research is needed, however, to show whether the greater intake of silica is directly related to the increased yield of crop which is always obtained under the swamp soil conditions.

Summary.

1. When soil is treated with a solution of alkali silicate, (*a*) the reaction of the mixture becomes slightly alkaline and (*b*) a considerable part of the

silicate is retained by the soil. As the concentration of the silicate is increased, the soil becomes increasingly alkaline (P_H 7·4 – 9·8) : larger quantity of the silicate is also retained though the percentage of retention is lowered (from 81 to 55).

2. The retention of silicate is not appreciably affected by the reaction of the soil. It occurs over a wide range of H-ion concentrations (P_H 1·0 – 10·6).

3. The procedure for extracting and estimating uncombined silica has been standardised. It has been found that extraction with 1 per cent. citric acid yields clearer extracts and more reliable estimates than that with water. Dilute solutions of other organic acids, as also mineral acids, are useful but not so efficient as citric acid. Increasing the concentration of citric acid beyond 1 per cent. does not also improve the extraction of silica.

4. The extent of silicate retention depends almost exclusively on the composition of the soil. The reaction and the buffering capacity of the soil do not appreciably affect the retention of the silicate.

5. The reaction between soil and silicate is almost instantaneous. The extent of silicate retention is not appreciably altered even after prolonged contact (24 hrs.) with the soil.

6. As the moisture content of the soil is increased (from 4 to 100 per cent.) there is perceptible decrease in the retention of silicate.

7. The soil continues to retain silicate even after oxidation of organic matter with hydrogen peroxide. On the other hand, ignition to low red heat deprives it of that property.

8. When the structural separates of the soil are treated with silicate, the coarse fractions (coarse and fine sand) show comparatively poor retention (5·2 per cent.), silt retains more (34·8 per cent.) and clay, the most (48·9 per cent.).

9. Addition of iron or aluminium oxide either as pure (precipitated), chemical or as mineral ore does not cause any marked increase in silicate retention. On the other hand, preliminary extraction of soil with dilute (4 per cent.) hydrochloric acid reduces the power of retention thereby showing that the active constituents are leachable.

10. Application of lime prior to addition of silicate reduces the extent of retention.

11. There is no cationic exchange following the treatment with silicate. Soils saturated with regard to different cations exhibit the same degree of silicate retaining capacity as unsaturated ones.

12. The relation between concentration of silicate and retention of silica is logarithmic, thereby showing that the interaction between soil and silica is mainly one of adsorption.

13. Application of silicate does not appreciably affect the concentration of silica in soil solution.

14. The significance of the above and allied observations has been discussed. The silicate solution behaves essentially as a mixture of alkali and silica sol. The alkali is responsible for the change in reaction while the silica sol is associated with the various adsorption phenomena recorded in the present study. A part of the silica is available for direct intake by plants, while the rest interacts with the mineral constituents of the soil. The possible relation of the latter to increased availability of fertilising ingredients such as phosphates is indicated. The mechanism of increased intake of silicon by the rice plant under swamp soil conditions is also discussed.

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REFERENCES.

A. O. A. C. .. .. *Methods of Analysis,* 1930.

Arrhenius, O. .. .. *J. Amer. Chem. Soc.,* 1922, **44**, 521.

. . . . *Z. Pflanz. Düng.,* 1930, **16A**, 94, 307.

Biedermann, R. .. . *Landw. Versuchs-Stat.,* 1869, **11**, 1.

Bertrand, G. .. .. *Compt. rend.,* 1897, **124**, 1032, 1355.

. . . . *Ibid.,* 1905, **141**, 1255.

. . ., and Javillier, M. .. *Ibid.,* 1911, **152**, 225.

. . ., and Rosenblatt, M. . *Ibid.,* 1921, **173**, 333, 1118.

. . . . *Ibid.,* 1922, **174**, 491.

Bhaskaran, T. R., *et al* . *Proc. Ind. Acad. Sci.,* 1934, **B1**, 155.

Brenchley, W. E. .. .. *Ann. Bot.,* 1910, **24**, 571.

. . . . *Ibid.,* 1914, **28**, 283.

. . . . *Inorganic Plant Poisons and Stimulants,* Second Edition, 1927.

. . ., Maskell, E. J., and Warington, K. .. *Ann. App. Biol.,* 1927, **14**, 45.

. . ., and Thornton, H. G. *Proc. Roy. Soc.,* 1925, **B98**, 373.

Comber, N. M. .. .. *Trans. Faraday Soc.,* 1925, **20**, 567.

Crüger, H. .. .. *Bot. Zeit.,* 1857, **15**, 281, 297.

Dean, L. A. .. .. *Soil Sci.,* 1934, **37**, 253.

Densch, A. .. .. *Landw. Jahrb.,* 1924, **60**, 142.

Doughty, J. L. .. .. *Soil Sci.,* 1930, **29**, 23.

Duchon, Fr. .. .. *Z. Pflanz. Düng.,* 1925, **4A**, 316.

Dyer, B. .. .. *J.C.S.,* 1894, **65**, 115.

Fisher, E. A. .. .. *Trans. Faraday Soc.,* 1921, **17**, 305.

Fisher, R. A. .. .. *J. Agric. Sci.,* 1929, **19**, 132.

Ford, M. C. .. .. *J. Amer. Soc. Agron.,* 1933, **25**, 135.

Frey, J. .. .. *Landw. Versuchs-Stat.,* 1875, **18**, 3.

Ghosh, J. C., and Bhattacharya, P. B. .. .. *Soil Sci.*, 1930, **29**, 311.

Gile, P. L., and Smith, J. G. .. *J. Agric. Res.*, 1925, **31**, 247.

Gordon, N. E., and Starkey, E. B. .. .. *Soil Sci.*, 1922, **14**, 1.

Gregoire, A. .. .. *Bull. Soc. Chim. Belg.*, 1911, **25**, **(ii)**, 85.

Haas, A. R. C., and Reed, H. S. *Bot. Gaz.*, 1927, **83**, 77.

Hall, A. D., and Morison, G. C. T. .. .. *Proc. Roy. Soc.* 1906, **B77**, 455.

Harrison, W. H., and Das, Sunder Lal .. .. *Mem. Dept. Agric. India, Chem. Ser.*, 1921, **9**, 195.

Hattensaur, G. .. .. *Ber. der Kais. Akad. der Wissenschaft Wien*, 1890, **99**, **IIB**, 29.

Heck, A. Floyd .. .. *Soil Sci.*, 1934, **37**, 343, 477.

. . . . *Ibid.*, 1934, **38**, 463.

Honnel .. .. *Heberlandts-wiss. prakt. Unters.*, 1877, **2**, 160.

Jennings, D. S. .. .. *Soil Sci.*, 1919, **7**, 201.

Jensen, W., and Lesch, W. .. *Z. Pflanz. Düng.*, 1930, **17A**, 48.

Jodin, V. .. .. *Ann. Agron.*, 1883, **9**, 385.

. . . . *Compt. rend.*, 1884, **97**, 344.

Knop, W. .. .. *Landw. Versuchs-Stat.*, 1861, **3**, 295.

. . . . *Ibid.*, 1862, **4**, 173.

. . . . *Lehrbuch der Agriculturchemie' Leipzig*, 1868.

Kreuzhage, C., and Wolff, E. . *Landw. Versuchs-Stat.*, 1884, **30**, 161.

Lemmermann, O., and Wiessmann, H. .. . *Z. Pflanz. Düng.*, 1922, **1A**, 185.

. . . . . . and Sammett, K. .. *Ibid.*, 1925, **4A**, 265.

Lichtenwalner, D. C., Flenner, A. L., and Gordon, N. E. . *Soil Sci.*, 1923, **15**, 157.

Liebig, J. von. .. .. *Ann. Chem. Pharm.*, 1858, **105**, 109.

. . . . *Ibid.*, 1858, **106**, 185.

Lipman, C. B. .. .. *Univ. Cal. Pub. Agric. Sci.*, Series 3, 1918, No. 7.

Mange, L. .. .. *Z. Pflanz. Düng.*, 1928, **8B**, 365.

Mattson, S. .. .. *Proc First Internat. Congr. Soil Sci.*, 1927, Comm. II, p. 199.

. . . . *Soil Sci.*, 1930, **30**, 459.

. . . . *Ibid.*, 1931, **32**, 343.

Mazè, P. .. .. *Ann. Inst. Pasteur*, 1914, **28**, 21.

. . . . *Compt. rend. Acad. Sci., Paris*, 1915, **160**, 211.

. . . . *Ann. Inst. Pasteur*, 1919, **33**, 139.

McHargue, J. S. .. .. *J. Ind. Eng. Chem.*, 1919, **11**, 332.

. . . . *J. Agric. Res.*, 1919, **16**, 183.

. . . . *J. Amer. Chem. Soc.*, 1922, **44**, 1592.

. . . . *J. Agric. Res.*, 1923, **23**, 395.

. . . . *Ibid.*, 1923, **24**, 781.

. . . . *Ibid.*, 1925, **30**, 193.

. . . . *J. Amer. Soc. Agron.*, 1925, **17**, 368.

. . . . *Ibid.*, 1926, **18**, 1076.

. . . . *J. Ind. Eng. Chem.*, 1927, **19**, 274.

Miller, L. B. .. .. *Soil Sci.*, 1928, **26**, 435.

Nanji, D. R., and Shaw, W. S. *J. Soc. Chem. Ind.*, 1925, **44**, 1T.

Palladin, V. I. .. .. *Plant Physiology*, 1927, p. 86.

Pfeffer, W. .. .. *Physiology of Plants*, 1900, **1**, 416, 435; **2**, 33, 55.

Pierre, I.	*Compt. rend. Acad. Sci., Paris,* 1866, **63**, 374.
Prescott, J. A.	*J. Agric. Sci.,* 1916, **8**, 111.
Ravikovitch, S.	*Soil Sci.,* 1934, **219**, 279.
Reifenberg, A.	*Z. Pflanz. Düng.,* 1930, **17A**, 1.
Rostworowski, S., and Wiegner, G.	*Journ. Landw.,* 1912, **60**, 223.
Roszmann, C. A.	*Soil Sci.,* 1927, **24**, 465.
Russell, E. J., and Prescott, J. A.	*J. Agric. Sci.,* 1916, **8**, 65.
Sachs, J. von.	*Flora,* 1862, p. 52.
Salomon, A.	*Landw. Versuchs-Stat.,* 1867, **9**, 351.
Scarseth, G. D., and Tidmore, J. W.	*J. Amer. Soc. Agron.,* 1934, **26**, 138, 152.
Schollenberger, C. J. ..	*Soil Sci.,* 1922, **14**, 347.
Seki, S.	*Chem. Abstracts,* 1928, **22**, 2803.
Shedd, O. M.	*Soil Sci.,* 1922, **14**, 233.
Sommer, A. L.	*Univ. Cal. Public. Agric. Sci.,* 1926, **5**, 57.
. . . .	*Plant Physiol.,* 1928, **3**, 217.
. . . ., and Lipman, C. B. ..	*Plant Physiol.,* 1926, **1**, 231.
Starkey, E. B., and Gordon, N. E.	*Soil Sci.,* 1922, **14**, 449.
Subrahmanyan, V.	*J. Agric. Sci.,* 1929, **19**, 627.
Teakle, L. J. H.	*Soil Sci.,* 1928, **25**, 143.
Thompson, H. S.	*J. Roy. Agric. Soc.,* 1850, **11**, 68.
Van Bemmelen, J. M. .. .	*Landw. Versuchs-Stat.,* 1879, **23**, 265.
. . . .	*Zeit. anorg. Chemie.,* 1900, **23**, 321.
. . . .	*Ibid.,* 1904, **42**, 314.
Van der Spek, Jac.	*Chem. Abstracts,* 1922, **16**, 4293.
Warington, K.	*Ann. Bot.,* 1923, **37**, 629.
. . . .	*Ibid.,* 1926, **40**, 27.
Way, J. T.	*J. Roy. Agric. Soc.,* 1850, **11**, 313.
. . . .	*Ibid.,* 1852, **13**, 123.
Wicke, W.	*Bot. Zeit.,* 1862, **20**, 76.
Wiedemann, A. G.	*Soil Sci.,* 1928, **26**, 281.
Wiley, R. C., and Gordon, N. E.	*Ibid.,* 1922, **14**, 441.
Wolff, E.	*Aschen-analysen,* 1880.