SOME FACTORS AFFECTING THE SOLUBILITY OF PHOSPHORUS IN SOILS

Thesis for Degree of M. S.

Russell Hayden Austin

1925

This opportunity is taken
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The solution of the problem of insolubility of phosphorus in the soil and of phosphorus applied, whether the soil is acid, neutral, or alkaline, would be of inestimatable value to the science of agriculture. Until more is known about these factors and also the chemical constitution of soils, the practice of phosphorus fertilization or, infact, any kind of fertilization will continue along the uncertain route of the past.

When soluble phosphorus is applied to the soil, it is subjected to all of the chemical and physical factors of that soil, which factors doubtless act along varying lines or directions of force. The resultant of these various soil factors, in reality, is the real determining factor of the solubility of the applied phosphorus. Of the many contributing factors, those that have been considered as the most important are the compounds of iron, aluminum, and silicon, organic matter, the phenomena of adsorption, and the reaction of the soil. Until more is learned regarding the effect and behavior of these contributing factors, little can be ascertained regarding the resultant of these factors. Considerable work has been done upon the problem, although the greater part of the work has been hot-house and field plot work interpreted in terms of crop response or yields. This is very good, and in reality, is the final objective of investigational work in the field of agriculture, but such methods add practically nothing to the too meager knowledge of the chemical constitution of soils.

In the following studies, an attempt was made to learn something regarding the chemical constitution of the soil. The studies and determinations have been of a chemical and physical nature. First a study was made of some chemical reactions between phosphorus compounds and several alkalis and the resulting effect on the solubility of the phosphorus in water solution was noted. In connection with these reactions, the effect of the presence of aluminum and iron as hydroxide was studied. Tests were made also regarding the effect of time upon the reaction. A microscopic study of the precipitates formed in all of the reactions studies revealed some important information regarding the reversion of acid phosphate to di-calcium and tri-calcium phosphates. Following these studies, similar experiments were conducted with soil samples taken from the profile of a light and also a heavier type of soil. Experiments were also conducted with silicic acid, rock flour, and the fine portion of soils in order to determine if the acquired data would coincide with the adsorption isotherm graph. Reaction, character of precipitates, and phosphorus content by analysis were the points considered in the interpretation of results.

Experimental

The behavior of acid phosphate, under a change of reaction only, is best made in water solutions. Time being a factor in such reactions, the first titrations were made in a minimum elapse of time. The hydrogen electrode (70) was used in making the readings of pH values. Additions of alkali (½ or 1 cc.) were made at 5 minute intervals and the readings of pH values were made just prior to each succeeding addition of alkali, thus giving the reaction time to become somewhat stabilized. To minimize any outside influences a cork cover was placed over the container with openings for the mechanical stiring device and the hydrogen electrode, and the calomel cell, containing a porous plug in the salt arm to prevent diffusion, was fitted into the cork and kept in the solution throughout the titration. Neutral distilled water was used in all of the work. The initial volume of these first titrations was 200 cc., but with the several additions of alkali the final volume was about 240 cc. The ratio of $CaH_4(PO_4)_2$ to alkali was the same in all of these immediate titrations. The end points or equivalent points are on the points of 10, 20, and 30 cc. of alkali. The specific concentration of phosphorus was varied and is given in the tables with the other data.

The first titration of $CaH_4(PO_4)_2$ (table 1) was made with 0.1 normal KOH. $CaHPO_4$ first appeared as a precipitate when 8.5 cc. of KOH had been added at a pH value of 6.1. The depression of the pH value with the precipitation of $CaHPO_4$ is shown in curve A, fig. 1, table 2 and curve B, fig. 1 contains the data of this titration repeated with double the concentration of solution used in the first titration; table 3 and curve C fig.1 with 4 times the concentration of solution; table 4 and curve D fig. 1 with 6 times the concentration of solution; and finally table 5 and curve E fig. 1 with 8 times the concentration of solution as was used in the first titration. The point of precipitation of the $CaHPO_4$ was advanced by the increase in concentration of solution; the solubility product of $CaHPO_4$ being exceeded earlier in the course of the titration. This earlier precipitation of $CaHPO_4$ was accompanied by a lowering of the

Table 1.

Titration of $CaH_4(PO_4)_2$ with 0.1N. KOH

0.2522 gms. $CaH_4(PO_4)_2$ (1.26 gms. per L) in 200 cc. neutral distilled water

Time Hr.min.	cc. 0.1 N. KOH	pH	notes	Time Hr.Min.	cc.0.1 N. KOH	pH	notes
0		2.94		2:10	13	6.39	precipitate
5		3.08		2:15	14	6.48	"
10		3.23		2:20	15	6.58	"
15	0.0	3.29		2:25	16	6.68	"
20	0.5	3.45		2:30	17	6.78	"
25	1.0	3.67		2:35	18	6.86	"
30	1.5	4.07		2:40	19	6.98	"
35	2.0	4.77		2:45	20	7.06	"
40	2.5	5.29		2:50	21	7.20	"
45	3.0	5.56		2:55	22	7.32	"
50	3.5	5.75		3:00	23	7.47	"
55	4.0	5.87		3:05	24	7.66	"
1:00	4.5	5.97		3:10	25	7.91	"
1:05	5.0	6.07		3:15	26	8.27	"
1:10	5.5	6.15		3:20	27	8.83	"
1:15	6.0	6.20		3:25	28	9.65	"
1:20	6.5	6.27		3:30	29	10.30	"
1:25	7.0	6.34		3:35	30	10.62	"
1:30	7.5	6.39		3:40	31	10.80	"
1:35	8.0	6.44		3:45	32	10.92	"
1:40	8.5	6.14	precipitate	3:50	33	11.02	"
1:45	9.0	6.07	appeared.	3:55	34	11.09	"
1:50	9.5	6.10	increased	4:00	35	11.17	"
1:55	10	6.14	with	4:05	36	11.24	"
2:00	11	6.20	KOH	4:10	37	11.27	"
2:05	12	6.29		4:15	38	11.33	"

pH value.

$CaH_4(PO_4)_2$ was also treated in like manner with $Ca(OH)_2$ and with the same proportion of phosphorus to base, but in a less concentrated solution, as $Ca(OH)_2$ is, at best, only about 0.04 normal. The general trend of the curve (fig. 2) is similar to that obtained by titrating $CaH_4(PO_4)_2$ with KOH, the difference probably being due mainly to the

Table 2

Titration of $CaH_4(PO_4)_2$ with 0.2 N KOH

0.5044 gm. $CaH_4(PO_4)_2$ (2.52 gm. per L.) in 200 cc. neutral distilled water

Time Hr.Min	cc 0.2 N KOH	pH	notes	Time Hr.Min	cc 0.2 N KOH	pH	notes
5		3.01		2:15	16	6.80	precipitate
10		3.18		2:20	17	6.95	"
15		3.23		2:25	18	7.08	"
20	0	3.23		2:30	19	7.24	"
25	1	3.62		2:35	20	7.41	"
30	2	4.65		2:40	21	7.61	"
35	3	5.52		2:45	22	7.93	"
40	3.5	5.68		2:50	23	8.48	"
45	4	5.82		2:55	24	9.65	"
50	4.5	5.92		3:00	25	10.45	"
55	5	5.91	precipitate	3:05	26	10.80	"
1:00	5.5	5.50	formed.	3:10	27	11.02	"
1:05	6	5.55	increased	3:15	28	11.14	"
1:10	6.5	5.61	with	3:20	29	11.23	"
1:15	7	5.65	KOH	3:25	30	11.33	"
1:20	7.5	5.68	additions	3:30	31	11.39	"
1:25	8	5.71	"	3:35	32	11.46	"
1:30	8.5	5.75	"	3:40	33	11.51	"
1:35	9	5.75	"	3:45	34	11.56	"
1:40	9.5	5.80	"	3:50	35	11.60	"
1:45	10	5.83	"	3:55	36	11.63	"
1:50	11	6.02	"	4:00	37	11.68	"
1:55	12	6.17	"	4:05	38	11.70	"
2:00	13	6.35	"	4:10	39	11.73	"
2:05	14	6.51	"	4:15	40	11.77	"
2:10	15	6.66	"				

lower concentration of the latter solution. The precipitate of $CaHPO_4$ (table 6) is later in appearing due to the same factor.

Table 3

Titration of $CaH_4(PO_4)_2$ with 0.4 N KOH

1.0088 gm. $CaH_4(PO_4)_2$ (5.04 gm. per L) in 200 cc. neutral distilled water

Time Hr.Min.	cc 0.4 N KOH	pH	Notes	Time Hr.Min.	cc 0.4 N KOH	pH	Notes
5		2.98		2:05	10	5.50	Precipitate
10		3.01		2:10	11	5.83	"
15		3.06		2:15	12	6.15	"
20		3.09		2:20	13	6.41	"
25		3:11		2:25	14	6.59	"
30		3.12		2:30	15	6.76	"
35	0	3.13		2:35	16	6.91	"
40	0.5	3.26		2:40	17	7.08	"
45	1	3.50		2:45	18	7.21	"
50	1.5	3.97		2:50	19	7.49	"
55	2	4.70		2:55	20	7.79	"
1:00	2.5	5.19		3:00	21	8.50	"
1:05	3	5.41		3:05	22	10.14	"
1:10	3.5	5.50	precipitate	3:10	23	10.82	"
1:15	4	5.29	appeared	3:15	24	11.06	"
1:20	4.5	5.00	increasing	3:20	25	11.23	"
1:25	5	4.92	with	3:25	26	11.36	"
1:30	5.5	4.90	KOH	3:30	27	11.46	"
1:35	6	4.90	additions	3:35	28	11.55	"
1:40	6.5	4.90	"	3.40	29	11.61	"
1:45	7	4.92	"	3:45	30	11.68	"
1:50	7.5	4.95	"	3:50	31	11.73	"
1:55	8.	5.02	"	3:55	32	11.80	"
2:00	9	5.22	"				

Table 4

Titration of $CaH_4(PO_4)_2$ with 0.6 Normal KOH

1.5132 gm. $CaH_4(PO_4)_2$ (7.57 gm. per l) in 200 cc. neutral distilled water

Time Hr.Min	cc 0.6 N KOH	pH	Notes	Time Hr.Min	cc 0.6 N KOH	pH	Notes
5		2.84		2:00	12	6.17	Precipitate
10		2.94		2:05	13	6.42	"
15		3.01		2:10	14	6.59	"
20		3.03		2:15	15	6.78	"
25	0	3.04		2:20	16	6.93	"
30	0.5	3.21		2:25	17	7.10	"
35	1	3.45		2:30	18	7.27	"
40	1.5	3.94		2:35	19	7.51	"
45	2	4.75	Pt. forms but	2:40	20	7.84	"
50	2.5	5.11	disappears	2:45	21	8.74	"
55	3	5.19	Pt. persists.	2:50	22	10.43	"
1:00	3.5	4.62	"	2:55	23	10.92	"
1:05	4	4.46	"	3:00	24	11.14	"
1:10	4.5	4.41	"	3:05	25	11.31	"
1:15	5	4.41	"	3:10	26	11.43	"
1:20	5.5	4.43	"	3:15	27	11.53	"
1:25	6	4.45	"	3:20	28	11.61	"
1:30	6.5	4.48	"	3:25	29	11.68	"
1:35	7	4.55	"	3:30	30	11.75	"
1:40	8	4.70	"	3:35	32	11.87	"
1:45	9	4.90	"	3:40	36	12.05	"
1:50	10	5.26	"	3:45	40	12.19	"
1:55	11	5.78	"				

Table 5
Titration of $CaH_4(PO_4)_2$ with 0.8 Normal KOH

2.0176 gm. $CaH_4(PO_4)_2$ (10.09 gm. per l) in 200 cc. neutral distilled water

Time Hr.Min	cc 0.8 N KOH	pH	Notes	Time Hr.Min	cc 0.8 N KOH	pH	Notes
5		2.82		1:45	13	6.37	precipitate
10		2.86		1:50	14	6.58	"
15	0	2.89		1:55	15	6.73	"
20	0.5	3.06	Pt. for 20 sec.	2:00	16	6.90	"
25	1	3.33	Pt. for 25 sec.	2:05	17	7.05	"
30	1.5	3.79	" " 30 "	2:10	18	7.22	"
35	2	4.58	" " 40 "	2:15	19	7.44	"
40	2.5	4.99	" persists.	2:20	20	7.74	"
45	3	4.35	"	2:25	21	8.54	"
50	3.5	4.24	"	2:30	22	10.33	"
55	4	4.18	"	2:35	23	10.87	"
1:00	4.5	4.16	"	2:40	24	11.12	"
1:05	5	4.16	"	2:45	25	11.29	"
1:10	6	4.23	"	2:50	26	11.43	"
1:15	7	4.33	"	2:55	28	11.63	"
1:20	8	4.48	"	3:00	30	11.80	"
1:25	9	4.70	"	3:05	32	11.92	"
1:30	10	5.04	"	3:10	36	12.14	"
1:35	11	5.67	"	3:15	40	12.27	"
1:40	12	6.12	"	3:20	50	12.56	"

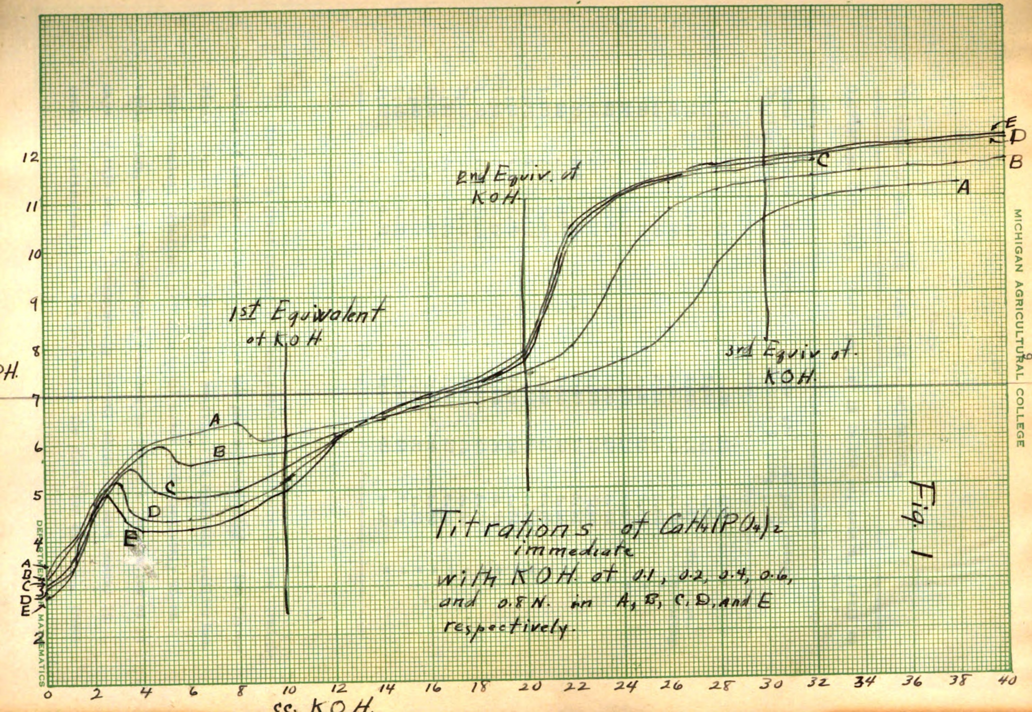


Fig. 1

Titrations of $CaH_4(PO_4)_2$ immediate with KOH. of 0.1, 0.2, 0.4, 0.6, and 0.8 N. in A, B, C, D, and E respectively.

Table 6

Titration of $CaH_4(PO_4)_2$ with 0.04 Normal $Ca(OH)_2$

0.09988 gm. $CaH_4(PO_4)_2$ (2.016 gm. per 1L) in 200 cc. neutral distilled water

Time Hr.Min	cc 0.04 N KOH	pH	Notes	Time Hr.Min	cc 0.04 N KOH	pH	Notes
5		3.01		1:55	10	6.70	
10		3.28		2;00	11	6.76	
15		3.40		2;05	12	6.83	Pt. faint.
20		3.55		2;10	13	6.06	" increasing
25	0	3.60		2;15	14	6.83	"
30	0.5	3.79		2;20	15	6.49	"
35	1	4.06		2;25	16	6.42	"
40	1.5	4.53		2;30	17	6.44	"
45	2	5.07		2;35	18	6.48	"
50	2.5	5.46		2;40	19	6.51	"
55	3	5.71		2;45	20	6.56	"
1;00	3.5	5.88		2;50	21	6.59	"
1;05	4	6.00		2;55	22	6.63	"
1;10	4.5	6.09		3;00	23	6.66	"
1;15	5	6.19		3;05	24	6.73	"
1;20	5.5	6.26		3;10	25	6.76	"
1;25	6	6.31		3;15	26	6.83	"
1;30	6.5	6.36		3;20	27	6.88	"
1;35	7	6.42		3;25	28	6.93	"
1;40	7.5	6.46		3;30	30	7.10	"
1;45	8	6.51		3;35	34	7.61	"
1;50	9	6.61		3;40	40	8.39	"

Time is a great factor in these chemical reactions.and the straightening of the curves, and calls for the partial repeating of the titrations in such a manner to permit the reactions to approach equilibrium. These chemical reactions probably would never come absolutely to an equilibrium, but it was thought feasible to select a time factor of 14 days for this work. Consequently several solutions were needed in order to determine the points desired in the titration curves. These

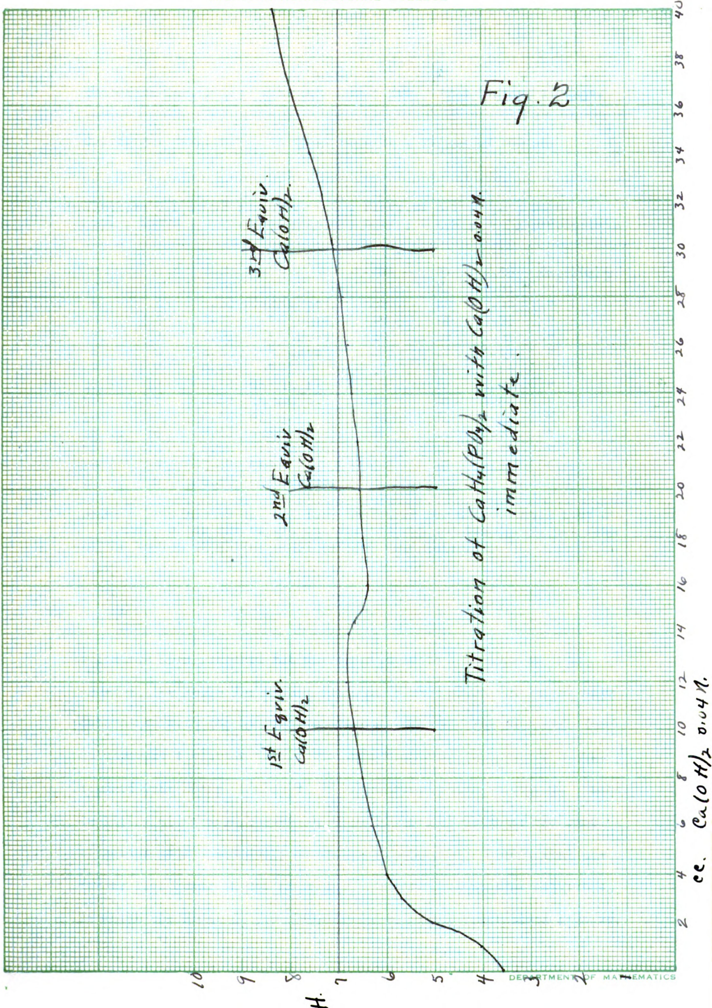


Fig. 2

Titration of $CaH_4(PO_4)_2$ with $Ca(OH)_2$ 0.04 N.
immediate.

Table 7

Titration $CaH_4(PO_4)_2$ with 0.1 normal KOH. Time factor, 14 days.

0.2582 gm. $CaH_4(PO_4)_2$ in flask made to a volume of 200 cc.

Flask no.	cc 0.1 N KOH	pH	Notes precipitate	Flask no.	cc 0.1 N KOH	pH	Notes precipitate
0	0	3.30		20	20	6.78	$Ca_3(PO_4)_2$
2	2	4.82		21	21	6.81	"
4	4	5.35	$CaHPO_4$ pct.	22	22	7.03	"
6	6	5.28	" more	24	24	7.19	"
7	7	5.31	" most	26	26	7.41	"
8	8	5.36	" less	27	27	7.69	"
9	9	5.21	" "	28	28	7.98	"
10	10	5.53	$Ca_3(PO_4)_2$	29	29	9.23	"
11	11	5.58	in no. 4	30	30	9.64	"
12	12	5.55	with	32	32	10.18	"
14	14	5.83	increase	34	34	10.80	"
16	16	5.95	to no. 14,	36	36	10.96	"
18	18	6.49	then	40	40	11.26	"
19	19	6.63	ddecreases.				

Note; Precipitate did not form in flasks no. 4 to 7 until 1 or 2 hours after the experiment was set up, and $CaHPO_4$ did not form in the bottom of flasks until several days later.

solutions were prepared and additions made in titrating as is shown in the table for each titration. Some of the pH values were determined with the hydrogen electrode (70) and some with the the quinhydrone electrode (69). The effect of more time on the titration of $CaH_4(PO_4)_2$ (table 7) is shown graphically in fig. 3. There is little difference between this curve and the curve of the same titration made immediately at this concentration, except that the former lies lower in the pH range. In more concentrated solutions, in which the break in the curve when the $CaHPO_4$ precipitate appears

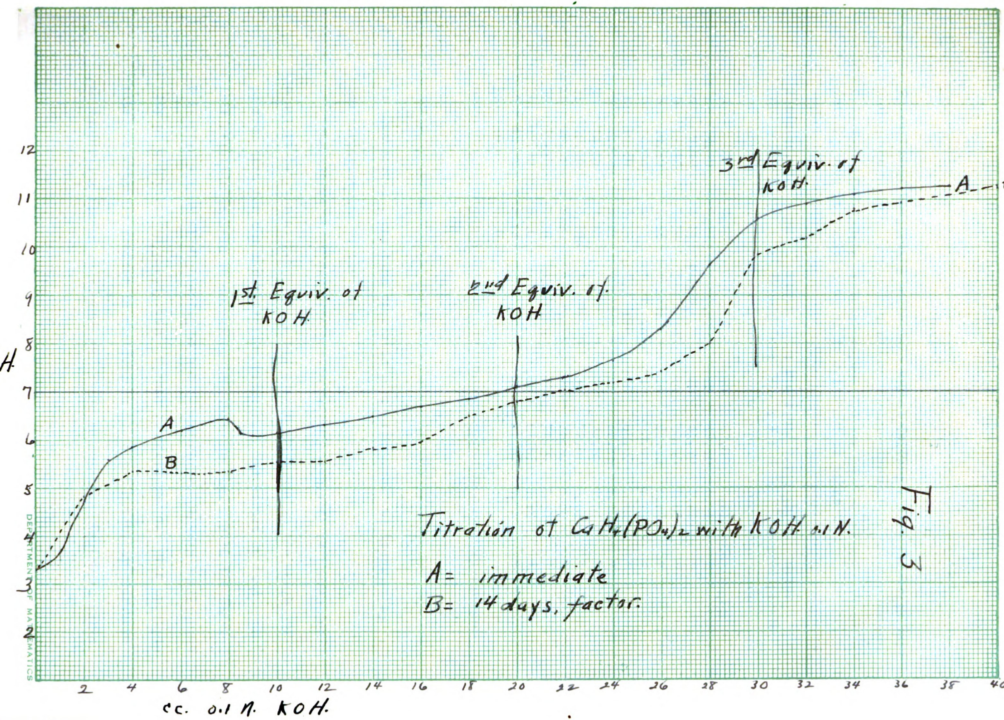


Fig. 3

Titration of $CaH_4(PO_4)_2$ with KOH 0.1 N.

A = immediate
B = 14 days, factor.

Table 8

Titration of $CAH_4(PO_4)_2$ with 0.04 Normal $Ca(OH)_2$. Time factor 14 days

0.25[illegible]2 gm. $CaH_4(PO_4)_2$. Total volume 200 cc.
$Ca(OH)_2$ used in quantity equal to 0.1 N KOH in table 7

Flask no.	cc. 0.1 N KOH	pH	Notes precipitate	Flask no.	cc. 0.1 N KOH	pH	Notes precipitate
0	0	3.23		20	47.00	5.21	$Ca_3(PO_4)_2$
2	4.70	4.77		21	49.35	5.21	"
4	9.40	5.11	$CaHPO_4$	22	51.70	5.25	"
5	11.75	5.18	" more	24	56.40	5.30	"
6	14.10	5.16	" less	26	61.10	5.33	"
7	16.45	5.11	" " Ca_3-	27	63.45	5.38	"
8	18.80	5.18	" "$(PO_4)_2$	28	65.80	5.43	"
9	21.15	5.21	" " "	29	68.15	5.45	"
10	23.50	5.21	" " "	30	70.50	5.50	"
11	25.85	5.23	" " "	31	72.85	5.52	"
12	28.20	5.20	" " "	32	75.20	5.50	"
14	32.40	5.18	$Ca_3(PO_4)_2$	34	79.90	5.60	"
16	37.60	5.20	"	36	84.60	5.76	"
18	42.30	5.18	"	40	94.00	6.05	"
19	44.65	5.20	"				

is more marked , the time factor is more pronounced as is shown by the straightening of the curve.

The titration of $CaH_4(PO_4)_2$ with $Ca(OH)_2$ (table 8) in quantities equal to 0.1 normal KOH gives a curve much different in the range of pH from that for the KOH titration (fig.4). The effect of time on this reaction is seen in comparing the curve in fig. 2 with the curve B in fig. 4, by a straightening of the former curve. A very small quantity of a crystaline precipitate formed in flask no. 4. This precipitate was slightly greater in quantity in no. 5 but gradually decreased in succeeding flasks until none was found in no. 14. $Ca_3(PO_4)_2$ first

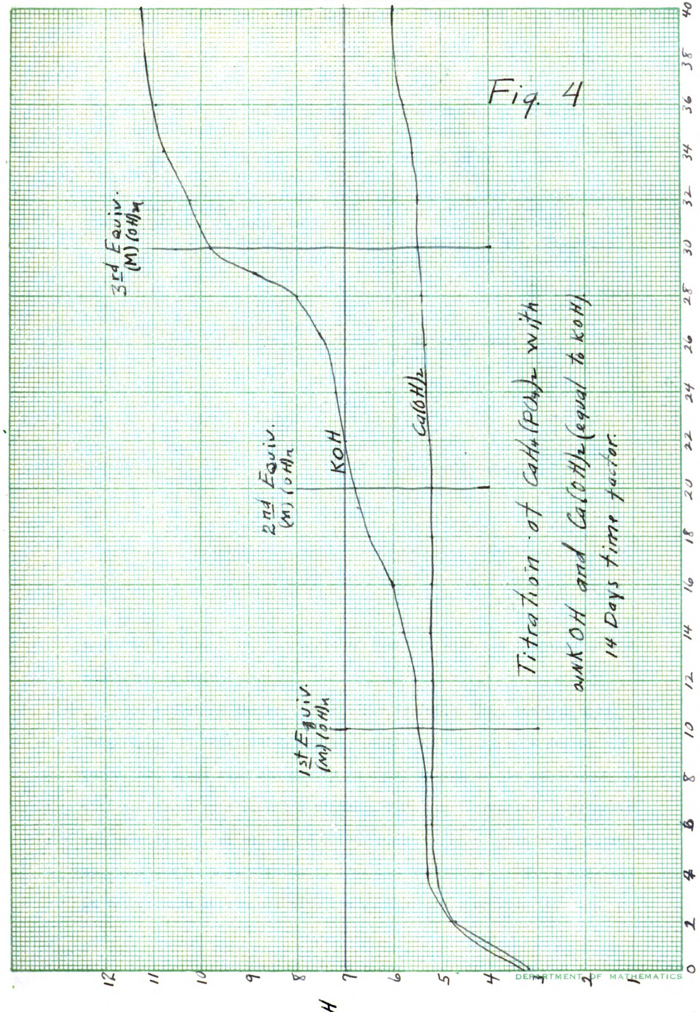


Fig. 4

Titration of $CaH_4(PO_4)_2$ with

and KOH and $Ca(OH)_2$ (equal to KOH)

14 Days time factor.

Table 9

Titration of $CaCO_3$ with $CaH_4(PO_4)_2$. Time factor of 14 days.

0.3009 gm. $CaCO_3$ in each tube. Total volume of 50 cc. each.
$CaH_4(PO_4)_2$ solution contained 21.02 gm. per liter.
6

Tube no.	$CaH_4(PO_4)_2$ cc.	Proportion $CaCO_3$ to $CaH_4(PO_4)_2$	pH	Precipitates $CaHPO_4$	Precipitates $Ca_3(PO_4)_2$
1	3	$3:\frac{1}{4}$	8.45		greatest amt.
2	6	$3:\frac{1}{2}$	8.49		less
3	9	$3:\frac{3}{4}$	8.42		"
4	12	3:1	8.54	greatest amt.	"
5	15	$3:1\frac{1}{4}$	8.54	less	"
6	18	$3:1\frac{1}{2}$	8.47	"	"
7	21	$3:1\frac{3}{4}$	8.23	"	"
8	24	3:2	8.12	"	"
9	27	$3:2\frac{1}{4}$	7.91	"	"
10	30	$3:2\frac{1}{2}$	7.07	"	"
11	33	$3:2\frac{3}{4}$	4.67	"	crystaline
12	36	3:3	4.48	small amt.	"
13	39	$3:3\frac{1}{4}$	4.13		"
14	42	$3:3\frac{1}{2}$	3.94		"
15	45	$3:3\frac{3}{4}$	3.80		"
16	48	3:4	3.70		"

appeared in tube 7 and increased in quantity with the increase in the additions of $Ca(OH)_2$.

The effect of the solid materials as $CaCO_3$, CaO, and MgO upon $CaH_4(PO_4)_2$ in water solution was studied by setting up a series of large test tubes each containing an equal amount of the solid material with additions of a solution of $CaH_4(PO_4)_2$ in increasing increments and made to a total volume of 50 cc. each. These tubes were allowed to,stand for 14 days with daily shaking, at the end of which time the pH values were determined with the quinhydrone electrode (69) and a

Table 10

Titration of CaO with $CaH_4(PO_4)_2$. Time factor of 14 days.

0.168 gm. CaO in each tube. Total volume of each tube 50 cc.
$CaH_4(PO_4)_2$ solution contained 21.02 gm. per liter.

Tube no.	$CaH_4(PO_4)_2$ cc.	Proportion CaO to $CaH_4(PO_4)_2$	pH	Precipitates $CaHPO_4$	Precipitates $Ca_3(PO_4)_2$
1	3	3: 1/4	12.15		$Ca_3(PO_4)_2$
2	6	3: 1/2	11.63	$CaHPO_4$	"
3	9	3: 3/4	6.24	"	"
4	12	3:1	5.26	"	"
5	15	3:1 1/4	5.09	"	"
6	18	3:1 1/2	4.78	crystaline	"
7	21	3:1 3/4	4.50	"	"
8	24	3:2	4.28	"	"
9	27	3:2 1/4	4.02	"	"
10	30	3:2 1/2	3.82	"	"

microscopic examination made of the solid material in each tube. There was an amorphous precipitate in tubes 1 to 12 (table 9), and since it is probable that $CaCO_3$ can not exist at a pH of 4.5, it must be $Ca_3(PO_4)_2$. There is also a crystaline precipitate in tubes 4 to 16 which must be either $CaH_4(PC_4)_2$ or $CaHPO_4$. It is without doubt $CaHPO_4$ in tubes 4 to 10 since $CaH_4(PO_4)_2$ would not exist at a pH of 7. It is thought that $CaHPO_4$ exists in tubes 11 to 16 also and that the low pH reading is due to the liberated CO_2 from $CaCO_3$ which had reacted with H_3PO_4 from the splitting up of $CaH_4(PO_4)_2$ into $CaHPO_4$ and H_3PO_4.

To compare with the $CaCO_3$ results the titration was repeated using CaO. The formation of precipitates of $CaHPO_4$ and $Ca_3(PO_4)_2$ was very much as with the $CaCO_3$, but the pH range is greater in the

Table 11

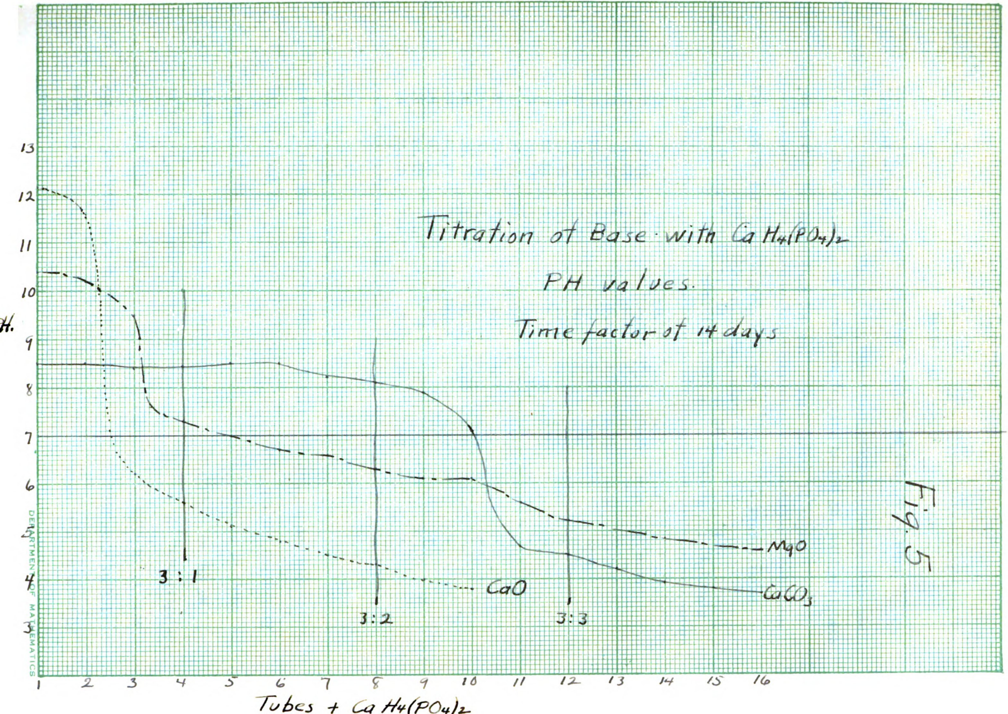
Titration of MgO with $CaH_4(PO_4)_2$. Time factor of 14 days.

0.121 gm. MgO in each tube. Total volume of each tube 50 cc. $CaH_4(PO_4)_2$ solution contained 21.02 gm. per liter.

Tube no.	$CaH_4(PO_4)_2$ cc.	Proportion MgO to $CaH_4(PO_4)_2$	pH	Precipitaes $CaHPO_4$	$Ca_3(PO_4)_2$
1	3	3; $\frac{1}{4}$	10.40	none	none
2	6	3; $\frac{1}{2}$	10.15	"	"
3	9	3; $\frac{3}{4}$	9.50	"	"
4-2	10		7.62	"	"
4	12	3;1	7.32	"	"
5	15	3;1$\frac{1}{4}$	7.03	"	"
6	18	3:1$\frac{1}{2}$	6.73	"	"
7	21	3:1$\frac{3}{4}$	6.58	"	"
8-2	22		6.48	"	"
8-1	23		6.32	"	"
8	24	3;2	6.34	"	"
8±1	25		6.24	"	"
8±2	26		6.14	"	"
9	27	3;2$\frac{1}{4}$	6.07	"	"
10	30	3;2$\frac{1}{2}$	6.07	"	"
11	33	3;2$\frac{3}{4}$	5.65	"	"
12-2	34		5.68	"	"
12-1	35		5.68	"	"
12	36	3;3	5.21	"	"
12±1	37		5.23	"	"
12±2	38		5.46	"	"
14	42	3;3$\frac{1}{2}$	4.87	"	"
16	48	3;4	4.62	"	"

titration of the CaO (table 10 and fig. 5), changing from pH 12, at the beginning, to 6.3 with the addition of 9 cc. of the solution of $CaH4(PO_4)_2$, or a change in proportion from 3;0 to 3;$\frac{3}{4}$. There was little change in pH until 27 cc. of the $CaH4(PO_4)_2$ solution had been added to the $CaCO_3$ titration. Again the titration was repeated using MgO (table 11), but no precipitates were formed, which is probably due

Fig. 5



Titration of Base with $CaH_4(PO_4)_2$

PH values.

Time factor of 14 days

Table 12

Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ When Titrated with $Ca(OH)_2$

0.05916 gm. $CaH_4(PO_4)_2$ in each flask (equiv. to 100 lb. acid phosphate per acre). Volume of each 250 cc. Time factor 14 days.

Flask no.	$Ca(OH)_2$ cc.	Proportion $CaH_4(PO_4)_2$ to $Ca(OH)_2$	P_2O_5 mgm. per 100 cc. In Solution	P_2O_5 mgm. per 100 cc. Loss	pH	Precipitates $CaHPO_4$	Precipitates $Ca_3(PO_4)_2$
x	--	--	13.50	--	--	--	--
1	3.23	1: $\frac{1}{4}$	13.50	0.00	5.57	none	none
2	6.46	1: $\frac{1}{2}$	13.43	0.07	--	"	"
3	9.69	1: $\frac{3}{4}$	9.46	4.04	6.31	some	"
4	12.92	1:1	7.62	5.88	6.23	"	some
5	16.15	1:1$\frac{1}{4}$	5.42	8.08	6.31	"	more
6	19.38	1:1$\frac{1}{2}$	3.78	9.72	6.50	none	"
7	22.61	1:1$\frac{3}{4}$	2.11	11.39	6.79	"	"
8	25.85	1:2	1.16	12.34	--	"	"
9	29.07	1:2$\frac{1}{4}$	0.17	13.33	--	"	"
10	32.30	1:2$\frac{1}{2}$	0.11	13.39	--	"	"
11	35.53	1:2$\frac{3}{4}$	0.06	13.44	8.36	"	"
12	38.76	1:3	0.03	13.47	8.60	"	"
13	41.99	1:3$\frac{1}{4}$	trace	13.50-	8.65	"	"
14	45.22	1:3$\frac{1}{2}$	"	"	9.02	"	"
15	48.45	1:3$\frac{3}{4}$	"	"	9.06	"	"
16	51.68	1:4	"	"	9.21	"	"

to the fact that the phosphorus compounds of magnesium are more soluble than the phosphorus compounds on calcium, and the solubility product of the magnesium compounds have not been exceeded in these titrations. The effect of the additions of $CaH_4(PO_4)_2$ on the pH is not as great as on the CaO but is greater than on the $CaCO_3$(fig. 5).

The application of discovered facts to field conditions is the goal of the soil chemist and in order to approach this goal in this work the assumption is made that an acre 6-inches of soil contains 12 percent of moisture, on the weight basis of 2,000,000 pounds, in which

Table 13

Solubility of Phosphorus in Water solution of $CaH_4(PO_4)_2$ when Titrated with $Ca(OH)_2$.

0.11832 gm. $CaH_4(PO_4)_2$ in each flask (equiv. to 200 lb. acid phosphate per acre). Volume of each 250 cc. Time factor 14 days.

Flask	$Ca(OH)_2$	Proportion $CaH_4(PO_4)_2$ to $Ca(OH)_2$	P_2O_5 mgm. per 100 cc.		pH	Precipitates	
no.	cc.		in solution	loss		$CaHPO_4$	$Ca_3(PO_4)_2$
X	--	--	27.00	--	--	--	--
1	6.46	$1:\frac{1}{4}$	25.50	1.50	6.35	none	none
2	12.92	$1:\frac{1}{2}$	20.80	6.13	5.99	some	"
3	19.38	$1:\frac{3}{4}$	17.30	9.70	5.92	doubtful	some
4	25.84	1:1	15.79	11.21	5.96	none	more
5	32.30	$1:1\frac{1}{4}$	10.90	16.10	6.09	"	"
6	38.76	$1:1\frac{1}{2}$	7.24	19.76	6.31	"	"
7	45.22	$1;1\frac{3}{4}$	4.24	22.76	6.52	"	"
8	51.68	1:2	1.68	25.32	6.88	"	"
9	58.14	$1:2\frac{1}{4}$	1.69	25.31	7.20	"	"
10	64.60	$1:2\frac{1}{2}$	0.25	26.75	8.34	"	"
11	71.06	$1;2\frac{3}{4}$	0.25	26.75	8.78	"	"
12	77.52	1:3	0.20	26.80	9.01	"	"
13	83.98	$1:3\frac{1}{4}$	not		9.19	"	"
14	90.44	$1:3\frac{1}{2}$	analyzed		9.43	"	"
15	96.90	$1;3\frac{3}{4}$			9.58	"	"
16	103.36	1;4			9.58	"	"

the phosphorus of the soil, or applied phosphorus, may become dissolved. A series of titrations were made on this basis with concentrations of $CaH_4(PO_4)_2$ equivalent to 100, 200, 300, and 400 pounds of acid phosphate per acre respectively. The proportion of $CaH_4(PO_4)_2$ to $Ca(OH)_2$ was the same in each series. Erhlenmeyer flasks were used in this experiment and the volumes were made to 250 cc. each. The time allowed for the chemical reactions in these series was also 14 days.

The end points or equivalent points in each of these series occur in flasks numbers 4, 8, and 12 of each series alike (tables 12 to 15).

Table 14

Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ when Titrated with $Ca(OH)_2$.

0.17748 gm. $CaH_4(PO_4)_2$ in each flask (equiv. to 300 lb. acid phosphate per acre). Volume of each 250 cc. Time factor 14 days.

Flask no.	$Ca(OH)_2$ cc.	Proportion $CaH_4(PO_4)_2$ to $Ca(OH)_2$	P_2O_5 mgm. per 100 cc. in solution	loss	pH	Precipitates $CaHPO_4$	$Ca_3(PO_4)_2$
X	--	--	40.50	--	--	--	--
1	9.69	1: ¼	36.20	4.30	6.25	some	none
2	19.38	1: ½	31.10	9.50	5.89	none	some
3	29.07	1: ¾	26.00	14.50	5.79	"	"
4	38.76	1:1	21.00	19.50	5.82	"	"
5	48.45	1:1¼	15.41	25.09	5.96	"	"
6	58.14	1:1½	10.19	30.31	5.45	"	"
7	67.83	1:1¾	5.44	35.06	6.37	"	"
8	77.52	1:2	1.39	39.11	6.48	"	"
9	87.21	1:2¼	0.23	40.27	7.13	"	"
10	96.90	1:2½	0.06	40.44	8.68	"	"
11	106.59	1:2¾	trace	40.50-	9.11	"	"
12	116.28	1:3	"	"	9.21	"	"
13	125.97	1:3¼	"	"	9.52	"	"
14	125.66	1:3½	not analyzed		9.55	"	"
15	145.35	1:3¾			9.60	"	"
16	155.04	1:4			9.75	"	"

In flask number 4 the equivalent proportion of $CaH_4(PO_4)_2$ to $Ca(OH)_2$ was 1 : 1, in no. 8 1:2, and in no. 12 1:3. $CaHPO_4$ was found in the bottom of flasks 3, 4, and 5, and $Ca_3(PO_4)_2$ in flasks 4 to 16 with the amounts increasing with the increase in the amount of additions of $Ca(OH)_2$, in the titration of $CaH_4(PO_4)_2$ equivalent to 100 pounds of acid phosphate per acre. If the concentration was doubled (table 13) very much the same results were secured except that the precipitation occured earlier in the series. Even the greater concentrations used behaved in the same manner (tables 14 and 15).

Table 15

Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ When Titrated with $Ca(OH)_2$.

0.23664 gms. $CaH_4(PO_4)_2$ in each flask (equiv. to 400 pounds acid phosphate per acre). Volume of each 250 cc. Time factor 14 days

Flask no.	$Ca(OH)_2$ cc.	Proportion $CaH_4(PO_4)_2$ to $Ca(OH)_2$	P_2O_5 mgm. per 100 cc. in solution	P_2O_5 mgm. per 100 cc. loss	pH	Precipitates $CaHPO_4$	Precipitates $Ca_3(PO_4)_2$
X	--	--	54.00	--	--	--	--
1	12.92	1: ¼	41.38	12.62	5.79	some	none
2	25.84	1: ½	39.84	14.16	5.77	none	some
3	38.76	1: ¾	34.96	19.06	5.67	"	more
4	51.68	1:1	26.19	27.81	5.70	"	"

On analyzing for phosphorus in solution in the clear liquid in each flask of these series marked differences were found. The amount of phosphorus in solution decreased with additions of $Ca(OH)_2$ and the decrease is very marked as the reaction approaches the neutral point, the solubility being very low in the alkaline solutions. In the more concentrated solutions the earlier appearance of a precipitate was accompanied by an earlier drop in the curve of the pH values (fig. 6); while in the alkaline range, the pH curve for the more concentrated solutions was higher in the pH scale. The reaction and the amount of phosphorus in the solution was greatly influenced by the quantity of $Ca(OH)_2$ added.

In a titration of $Ca(OH)_2$ and $Fe(OH)_3$ together with $CaH_4(PO_4)_2$ the excess of $Fe(OH)_3$ present made the study of precipitates difficult. The quantity of phosphorus taken from the solution increased with the additions of $CaH_4(PO_4)_2$ but the increases were not in proportion to the

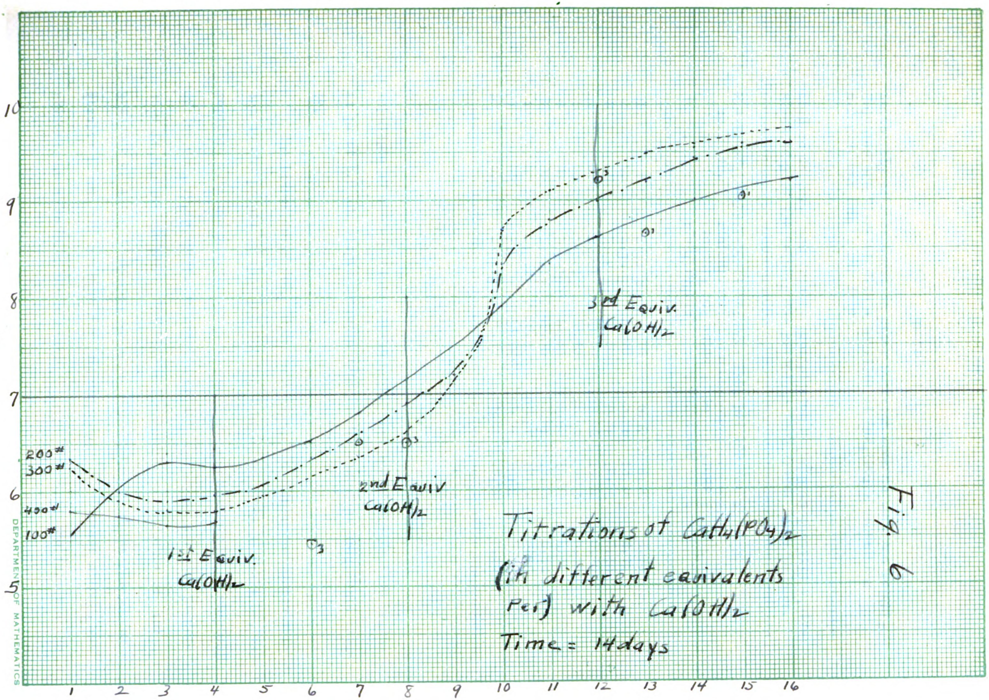


Fig. 6

Titrations of $CaH_4(PO_4)_2$ (in different equivalents Per) with $Ca(OH)_2$

Time = 14 days

Table 16

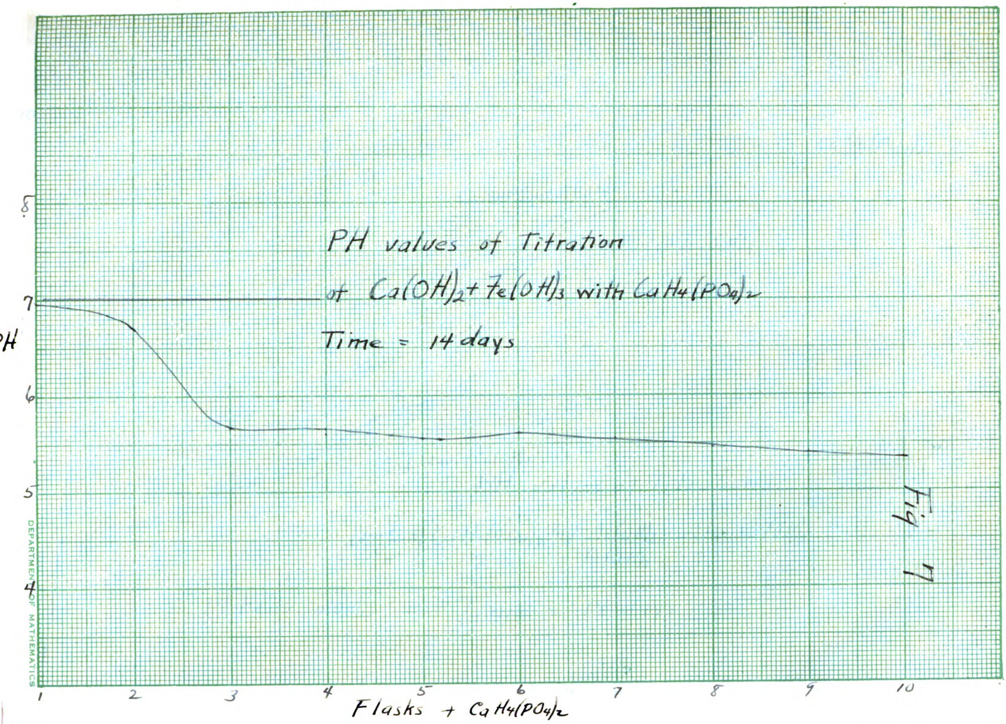
Solubility of Phosphorus in Water Solution when $Ca(OH)_2$ and $Fe(OH)_3$ Together are Titrated With a Solution of $CaH_4(PO_4)_2$ containing 6.3 gms. $CaH_4(PO_4)_2$ per Liter.

25.5 cc $Ca(OH)_2$ and freshly precipitated $Fe(OH)_3$ in quantity equivalent to $\frac{1}{2}$ of the $Ca(OH)_2$ was placed in each flask. Time 14 days.

Flask no.	$CaH_4(PO_4)_2$ cc.	Proportion $Ca(OH)_2$ to $Fe(OH)_3$ to $CaH_4(PO_4)_2$	mgm. P_2O_5 per 100 cc.			pH
			added	in solution	loss	
1	5	$1:\frac{1}{2}:\frac{1}{4}$	7.10	0.20	6.90	6.93
2	10	$1:\frac{1}{2}:\frac{1}{2}$	14.20	0.56	13.64	6.71
3	15	$1:\frac{1}{2}:\frac{3}{4}$	21.30	5.39	15.91	5.63
4	20	$1:\frac{1}{2}:1$	28.40	11.54	16.86	5.65
5	25	$1:\frac{1}{2}:1\frac{1}{4}$	35.50	19.46	16.04	5.55
6	30	$1:\frac{1}{2}:1\frac{1}{2}$	42.60	25.63	16.97	5.61
7	35	$1:\frac{1}{2}:1\frac{3}{4}$	49.70	30.02	19.68	5.56
8	40	$1:\frac{1}{2}:2$	56.80	37.68	19.12	5.46
9	45	$1:\frac{1}{2}:2\frac{1}{4}$	63.90	45.09	18.81	5.39
10	50	$1:\frac{1}{2}:2\frac{1}{2}$	71.00	51.82	19.18	5.34

magnitude of the additions (table 16). The curve of titration begins at pH of 6.9 and slopes downward with the additions of $CaH_4(PO_4)_2$ (fig. 7).

The titration of $CaH_4(PO_4)_2$ with $CaCO_3$ in concentration equivalent to 200 pounds of acid phosphate per acre, as given in table 13, was repeated with the addition of $Fe(OH)_3$, in amounts equivalent to one-half of the $CaH_4(PO_4)_2$ used, in one series and $Al(OH)_3$ in the same proportion in another series. These results showed the influence of the presence of $Al(OH)_3$ and $Fe(OH)_3$ upon the solubility of the phosphorus (tables 17 and 18) and upon the reaction (fig. 8). Where $Al(OH)_3$ was present, less $Ca(OH)_2$ was required to raise the pH of the solution to



PH values of Titration
of $Ca(OH)_2 + Fe(OH)_3$ with $CaH_4(PO_4)_2$
Time = 14 days

Fig 7

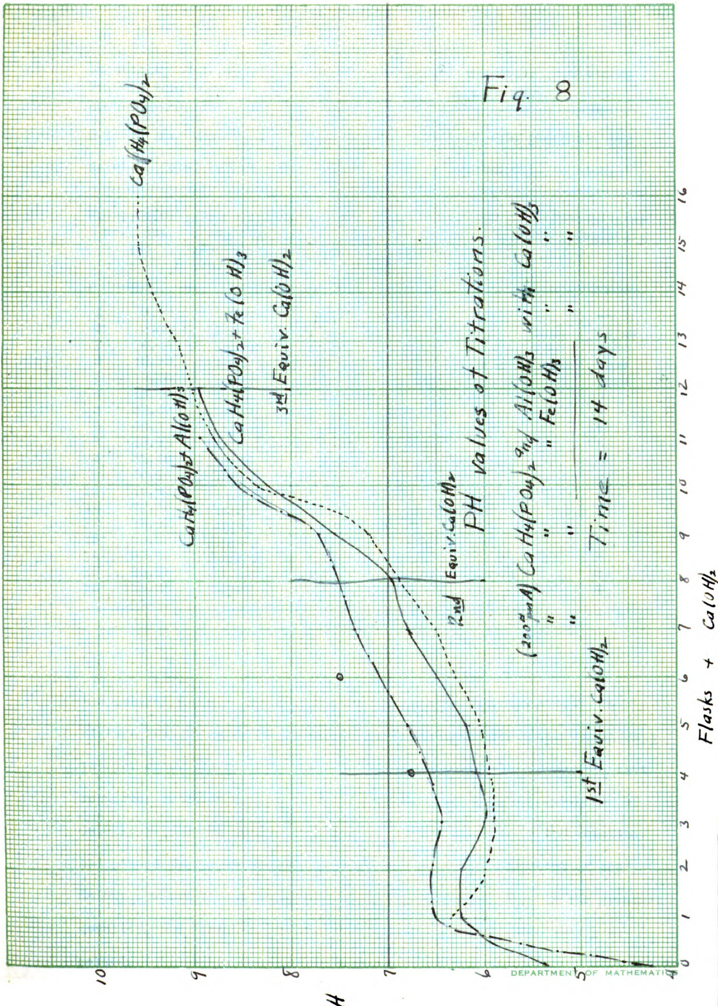


Fig. 8

PH values of Titrations.

(200 p.p.m. A) CaH$_4$(PO$_4$)$_2$ and Al(OH)$_3$ with Ca(OH)$_2$
" " " Fe(OH)$_3$ " "

Time = 14 days

Table 17

Solubility of Phosphorus in water solution of $CaH_4(PO_4)_2$ containing $Fe(OH)_3$ equivalent to ½ the $CaH_4(PO_4)_2$. Time 14 days.

0.11832 gm. $CaH_4(PO_4)_2$ (equiv. to 200 pounds of acid phosphate per acre). Total volume was 250 cc. 25.65 mgm. $Fe(OH)_3$ to each.

Flask no.	$Ca(OH)_2$ cc.	Proportion $CaH_4(PO_4)_2$: $Fe(OH)_3$: $Ca(OH)_2$	mgm. P_2O_5 per 100 cc. in solution	loss	pH	Precipitates $CaHPO_4$	$Ca_3(PO_4)_2$
X	0.00	1:0:0	27.00	--	--	--	--
0	0.00	1:½:0	23.47	3.53	5.33	none	none
1	6.46	1:½:¼	21.86	5.14	6.24	some	"
2	12.92	1:½:½	17.14	9.86	6.24	none	some
3	19.38	1:½:¾	13.85	13.17	6.00	"	More
4	25.84	1:½:1	9.99	17.01	6.10	"	"
5	32.30	1:½:1¼	7.10	19.90	6.20	"	"
6	38.76	1:½:1½	4.32	22.68	6.49	"	"
7	45.22	1:½:1¾	1.66	25.34	6.81	"	"
8	51.68	1:½:2	0.32	26.68	6.95	"	"
9	58.14	1:½:2¼	0.12	26.88	7.57	"	"
10	64,60	1:½:2½	--	--	8.25	"	"
11	71.06	1:½:2¾	--	--	8.77	"	"
12	77.52	1:½:3	--	--	8.96	"	"
13	83.98	1:½:3¼	0.11	26.89	--	"	"
14	90.44	1:½:3½	0.04	26.96	--	"	"
15	96.90	1:½:3¾	0.06	26.94	--	"	"
16	103.36	1:½:4	--	--	--	"	"

the neutral point. $Fe(OH)_3$ had some influence upon the pH of the mixture but the raise in pH was not as great as it was where the $Al(OH)_3$ was present. In the presence of $Fe(OH)_3$ 2 equivalents of $Ca(OH)_2$ were required to raise the pH of the mixture as high as 1½ equivalents of $Ca(OH)_2$ raised the pH in the presence of $Al(OH)_3$. After the reaction had passed the point of the addition of the second equivalent of the $Ca(OH)_2$, which is the field of pH where $Ca_3(PO_4)_2$ exists in the greatest quantity, the effect of either $Al(OH)_3$ or $Fe(OH)_3$ was not nearly so marked.

Table 18

Solubility of Phosphorus in water solution of $CaH_4(PO_4)_2$ containing $Al(OH)_3$ Equivalent to one-half of the $CaH_4(PO_4)_2$. Time 14 days.

0.11832 gm. $CaH_4(PO_4)_2$ (equiv. to 200 pounds of acid phosphate per acre). Total volume was 250 cc. 0.05604 gms $Al(OH)_3$ to each.

Flask no.	$Ca(OH)_2$ cc.	Proportion; $CaH_4(PO_4)_2$; to $Fe(OH)_3$; to $Ca(OH)_2$	mgm. P_2O_5 per 100 cc in solution	mgm. P_2O_5 per 100 cc loss	pH	Precipitates $CaHPO_4$	Precipitates $Ca_3(PO_4)_2$
X	0.00	1:0:0	27.00	--	--	--	--
0	0.00	1:½:0	26.25	0.75	4.26	none	none
1	6.46	1:½:¼	21.86	5.14	6.49	some	"
2	17.92	1:½:½	16.24	10.76	6.57	none	some
3	19.38	1:½:¾	11.86	15.14	6.47	"	"
4	25.84	1:½:1	8.71	18.29	6.78	"	"
5	32.30	1:½:1¼	4.80	22.20	6.78	"	"
6	38.76	1:½:1½	3.61	23.39	7.52	"	"
7	45.22	1:½:1¾	.75	26.25	7.35	"	"
9	58.14	1:½:2¼	.62	26.38	7.69	"	"
10	64.60	1:½:2½	.31	26.69	8.57	"	"
11	71.06	1:½:2¾	.30	26.70	8.94	"	"
12	77.52	1:½:3	.18	26.82	---	"	"
13	83.98	1:½:3¼	.12	26.88	---	"	"
14	90.44	1:½:3½	.15	26.85	---	"	"
15	96.90	1:½:3¾	trace	27.00-	---	"	"
16	103.36	1:½:4	"	"	---	"	"

The effect of $Fe(OH)_3$ and $Al(OH)_3$ upon the solubility of $CaH_4(PO_4)_2$ was studied in 2 series where each was used alone. The concentrations were reduced to an equivalent of 50 pounds of acid phosphate per acre, with the proportions of the $CaH_4(PO_4)_2$ to the $Fe(OH)_3$ or the $Al(OH)_3$ of 1 to 0 up to 1 to 400 in terms of equivalents. In these series the $Fe(OH)_3$ was found to have a greater influence upon the solubility of the phosphorus, causing it to become less soluble , (tables 19 and 20), and also the $Fe(OH)_3$ increased the pH of the solution more than the

Table 19

Effect of $Fe(OH)_3$ on the Solubility of Phosphorus in a Water Solution of $CaH_4(PO_4)_2$.

0.02958 gms. of $CaH_4(PO_4)_2$ (equivalent to 50 pounds of acid phosphate per acre). Total volume of each flask was 250 cc. Time 14 days.

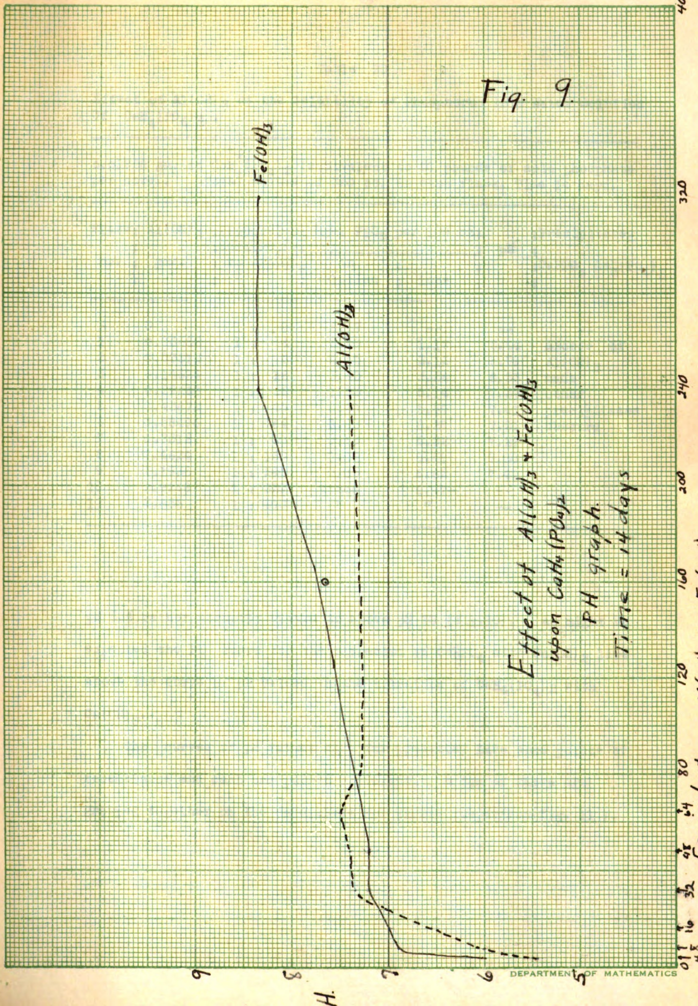
Flask no.	$Fe(OH)_3$ gms.	Proportion $CaH_4(PO_4)_2$ to $Fe(OH)_3$	mgm. P_2O_5 per 100 cc		pH	Precipitates $CaHPO_4$; $Ca_3(PO_4)_2$
			in solution	loss		
0	0	1:0	6.67	--	--	-----
1	0.05013	1:4	2.71	3,96	6.02	$Fe(OH)_3$
2	0.10026	1:8	1.27	5.40	6.88	obscured
3	0.20052	1:16	0.12	6.55	7.00	other
4	0.40104	1:32	trace	6.67-	--	precipitates
5	0.60156	1:48	"	"	7.19	
6	0.80208	1:64	"	"	--	
7	1.0026	1:80	not analyzed		--	see
8	2.0052	1:160			7.66	note
9	3.0078	1:240			8.34	
10	4.0104	1:320			8.37	
11	5.0130	1:400			--	

Note : Tests were made for iron with KCNS, with very faint test for iron in clear solution in no.4 and slightly increasing to no. 11, but there was only a small amount even in no. 11.

$Al(OH)_3$ did (fig. 9).

In the foregoing titrations of $CaH_4(PO_4)_2$ with alkalies the $CaHPO_4$ is formed when the pH is raised above 5.6 by additions of $Ca(OH)_2$. In the next titration presented a nearly saturated solution of $CaHPO_4$ was titrated with $Ca(OH)_2$ in the same manner as the $CaH_4(PO_4)_2$ in the 100 pound acid phosphate equivalent reported in table 12. The titration of $CaHPO_4$ with $Ca(OH)_2$ forms $Ca_3(PO_4)_2$ which is insoluble and precipitates from the solution as is shown in table 21. The curve of the pH values of this titration rises from

Fig. 9.



Effect of $Al(OH)_3$ + $Fe(OH)_3$ upon $CaH_4(PO_4)_2$

PH graph.

Time = 14 days

Table 20

Effect of Al(OH)$_3$ on the Solubility of Phosphorus in a Water Solution Of $CaH_4(PO_4)_2$.

0.02928 gm. of $CaH_4(PO_4)_2$ (equivalent to 50 pounds of acid phosphate per acre). Total volume of 250 cc. in each flask. Time 14 days.

Flask no.	Al(OH)$_3$ gms.	Proportion $CaH_4(PO_4)_2$ to Al(OH)$_3$	mgm. P_2O_5 per 100 cc in solution	mgm. P_2O_5 per 100 cc loss	pH	Precipitates $CaHPO_4$ $Ca_3(PO_4)_2$
X	0	1 : 0	6.67	--	--	--
1	0.03656	1 : 4	5.50	1.17	5.44	excess of Al(OH)$_3$ made other precipitates obscure
2	0.07312	1 : 8	4.55	2.12	5.99	
3	0.14624	1 : 16	3.43	3.24	6.53	
4	0.29248	1 : 32	1.53	5.14	7.37	
5	0.43872	1 : 48	0.80	5.87	7.41	
6	0.58496	1 : 64	0.40	6.27	7.51	
7	0.7312	1 : 80	0.15	6.52	7.29	
8	1.4624	1 : 160	0.06	6.61	7.30	
9	2.1936	1 : 240	0.05	6.62	7.42	
10	2.9248	1 : 320	trace	6.67-	--	
11	3.656	1 : 400	"	"	--	

pH 6.5 rather abruptly upward to above pH 10 (fig.10). As might be expected the PH curve for the titration of $CaHPO_4$ with $Ca(OH)_2$ lies above the curve of pH values in the titration of $CaH_4(PO_4)_2$ with $Ca(OH)_2$.

The curves of pH values thus far presented have some points of resemblance and each has points different. A few of these are grouped together on the same sheet for direct comparison(fig. 11).

Table 21

Titration of $CaHPO_4$ with $Ca(OH)_2$.

0.04038 gms. $CaHPO_4$ in solution in each flask. Total volume 250 cc.
Time factoe of 14 days. Time factor 14 days.

Flask no.	$Ca(OH)_2$ cc.	Proportion $CaHPO_4$ to $Ca(OH)_2$	Mgm. P_2O_5 per100 cc		pH	Precipitates	
			in solution	loss		$CaHPO_4$	$Ca_3(PO_4)_2$
X	0	1:0	8.43	--	--	--	--
1	3.23	1:$\frac{1}{4}$	6.18	2.25	6.49	some	none?
2	6.46	1:$\frac{1}{2}$	3.83	4.60	6.52	none	some
3	9.69	1:$\frac{3}{4}$	2.78	5.65	6.69	none	more
4	12.92	1:1	0.80	7.63	6.86	"	"
5	16.15	1:1$\frac{1}{4}$	0.15	8.28	6.89	"	"
6	19.38	1:1$\frac{1}{2}$	0.12	8.31	7.23	"	"
7	22.61	1:1$\frac{3}{4}$	0.15	8.28	8.57	"	"
8	25.84	1:2	trace	8.43-	--	"	"
9	29.07	1:2$\frac{1}{4}$	"	"	10.28	"	"

Two soil profiles and a very acid sandy surface soil were selected from which to secure samples of soil for a continued study of phosphorus fixation upon a soil medium. The procedure of study was as near as possible like the foregoing studies.

The soil in 100 gram portions was placed in jelly glasses. The soil had been passed through a 2-mm. mesh sieve. These were given varying treatments of CaO and made to optimum moisture content with neutral distilled water. These soil mixtures were stirred daily for 7 days, when equal additions were made to each of the soil samples, at the rate of 200 pounds of acid

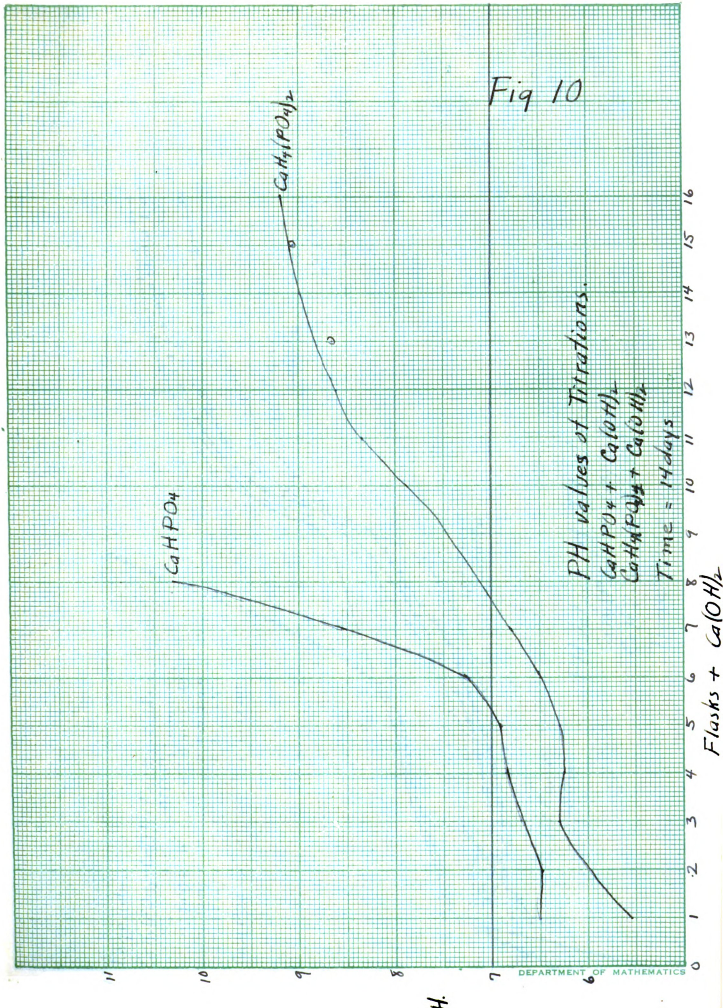


Fig 10

PH values of Titrations.
$CaHPO_4 + Ca(OH)_2$
$CaH_4(PO_4)_2 + Ca(OH)_2$
Time = 14 days
$CaHPO_4$
$CaH_4(PO_4)_2$
Flasks + $Ca(OH)_2$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
11
10
9
8
7
6
H.

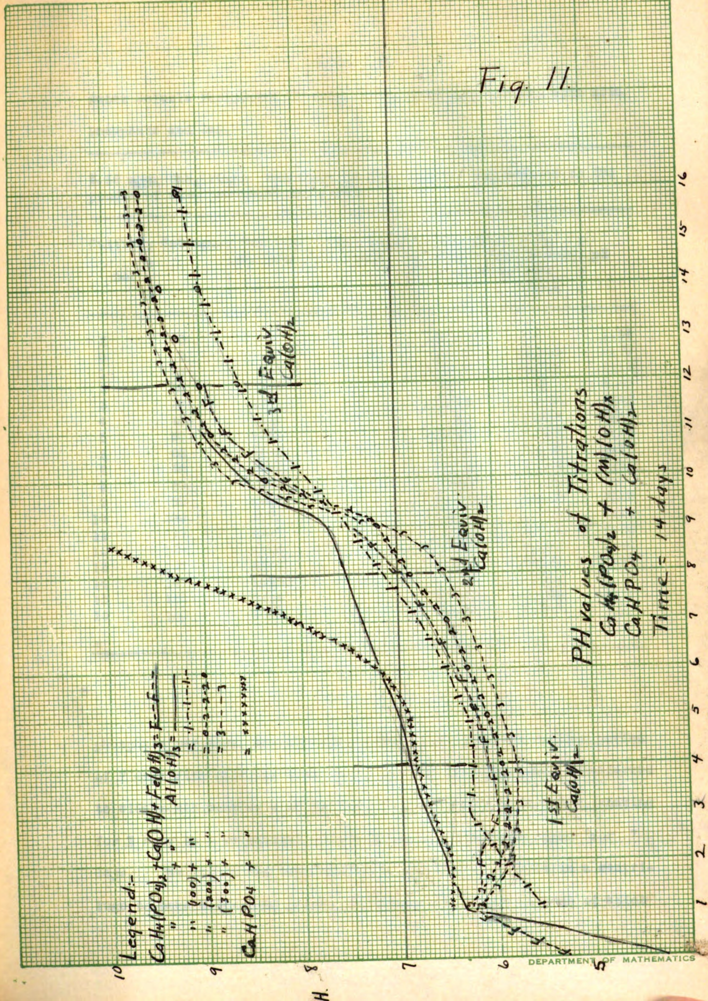


Fig. 11.

PH values of Titrations
$CaH_4(PO_4)_2$ + $(M)(OH)_x$
$CaHPO_4$ + $Ca(OH)_2$
Time = 14 days

Table 22

Water Soluble Phosphorus in Acid Sandy Loam When Treated With Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre).

Culture no.	CaO mgm.	CaO lbs per acre	mgm. P_2O_5 added	Mgm. P_2O_5 soluble in 250 cc. H_2O	P_2O_5 increase over check	pH
X	0	--	0	0.232	----	5.89
0	0	--	3.2	0.927	0.695	5.70
1	10	357	"	0.270	0.038	6.13
2	20	714	"	--	--	6.30
3	30	1071	"	0.292	0.060	6.49
4	40	1428	"	0.332	0.100	6.55
5	50	1785	"	0.310	0.078	6.60
6	60	2142	"	0.350	0.118	6.77
7	70	2499	"	0.462	0.230	6.69
8	80	2857	"	0.350	0.118	--
9	90	3213	"	0.270	0.038	7.03
10	100	3570	"	0.385	0.153	7.12
11	110	3927	"	0.310	0.078	7.22
12	120	4285	"	0.385	0.153	7.34
13	130	4642	"	0.350	0.118	7.52
14	140	4999	"	0.425	0.193	7.59
15	150	5356	"	0.462	0.230	7.76
16	160	5714	"	0.502	0.270	7.95

phosphate per acre, and the whole allowed to stand for another period of 7 days with stirring each day. At this time they were transferred to wide mouth bottles with 250 cc. of neutral distilled water, shaking for 1 hour on a mechanical shaker, and then allowed to stand for 7 days. The liquid was then carefully poured off, whirled in a centrifuge to make clear, and placed in Erlenmeyer flasks to each of which

Table 23

Water Soluble Phosphorus in Miami Loam A1 Horizon when Treated with Acid phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre).

Soil Culture	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc. H_2O	increase over X	pH
X	0	--	0	0.115	--	5.31
0	0	--	3.2	0.207	0.092	5.31
1	10	357	3.2	0.247	0.132	5.34
2	20	714	3.2	0.370	0.255	5.51
3	30	1071	3.2	0.347	0.232	5.49
4	40	1428	3.2	0.310	0.195	5.64
5	50	1785	3.2	0.347	0.232	5.74
6	60	2142	3.2	0.310	0.195	---
7	70	2499	3.2	0.232	0.117	5.93
8	80	2857	3.2	0.155	0.040	5.98
9	90	3213	3.2	0.077	--	5.91
10	100	3570	3.2	0.077	-	6.18
11	110	3927	3.2	0.170	0.055	6.26
12	120	4285	3.2	----	---	6.24
13	130	4642	3.2	0.140	0.025	6.28
14	140	4999	3.2	---	--	6.49
15	150	5356	3.2	0.215	0.100	6.66
16	160	5714	3.2	---	---	---

which was added 1 cc. of a nearly saturated solution of $MgSO_4$ to complete the clearing of the solution. After standing over night a a determination of phosphorus was made on the solution from each flask. The reaction of each solution was determined with the quinhydrone electrode (69).

The results with the acid sandy loam soil (table 22) indicates

Table 24

Water Soluble Phosphorus in Miami Loam A3 Horizon when Treated with Acid Phosphate and CaO.

5.68 mgm, $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre.).

Soil Culture	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc water	Increase over check	pH
X	0	--	0	0.155	--	6.28
0	0	--	3.2	0.115	-	6.23
1	10	357	3.2	0.077	-	6.45
2	20	714	3.2	0.170	0.015	6.65
3	30	1071	3.2	0.155	0	6.86
4	40	1428	3.2	0.207	0.052	7.05
5	50	1785	3.2	0.277	0.122	7.25
6	60	2142	3.2	0.247	0.092	7.37
7	70	2499	3.2	0.200	0.045	7.58
8	80	2857	3.2	0.170	0.015	7.65
9	90	3213	3.2	0.122	--	7.73
10	100	3570	3.2	0.155	0	7.83
11	110	3927	3.2	0.247	0.092	7.90
12	120	4285	3.2	0.232	0.077	7.98
13	130	4642	3.2	--	--	--
14	140	4999	3.2	0.155	0	7.99
15	150	5356	3.2	0.077	--	8.07

little except that the soil is extremely retentive of acid phosphate, unless it can be interpreted htat the additions of CaO reduces the quantity of phosphorus in solution.

The results from the A2 and A3 horizons, which are acid, and the C horizon, which is alkaline, of the Miami Loam soil tend to indicate a les degree of solubility of the phosphorus in this soil than in the other soils studied (tables 23, 24 and 25).

Table 25

Water Soluble Phosphorus in Miami Loam C Horizon when Treated with Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre.).

Soil culture no.	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc. H_2O	increase over check	pH
X	0	---	0	0.088	--	8.06
0	0	---	3.2	0.132	0.044	8.10
6	60	2142	3.2	0.114	0.026	8.22
16	160	5356	3.2	0.191	0.103	8.41

The Fox Soil profile was also selected for these studies. The results which are given in tables 26 to 30 are very much the same as in the other soils. The virgin surface released less of the phosphorus into solution than the cultivated surface. More phosphorus was found in solution in Fox C horizon than in any of the other. The reactions of these soils as treated are plotted in fig. 12. The results obtained in this set of experiments with the soil profiles do nor warrant any definate conclusions because of the fluctuations and small differences among them. In order to approach field conditions the quantities of phosphorus taken from the determinations were too small and hence the experimental error became proportionately too large to be able to get satisfactory results.

The Theory of Adsorption in connection with phosphorus fixation in soils is receiving much attention at the present time particularly in the study of soil colloids as well as in many other fields of

Table 26

Water Soluble Phosphorus in Fox Sandy Loam Cultivated Surface When Treated With Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre).

Soil culture no.	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc. H_2O	increase over check	pH
X	0	--	0	0.232	--	5.89
0	0	--	3.2	0.257	0.025	6.06
1	10	357	3.2	0.299	0.067	6.34
2	20	714	3.2	0.283	0.051	6.51
3	30	1071	3.2	0.293	0.061	6.70
4	40	1428	3.2	0.391	0.159	6.72
5	50	1785	3.2	0.283	0.051	6.89
6	60	2142	3.2	0.257	0.025	6.99
7	70	2499	3.2	0.216	-	7.14
8	80	2857	3.2	0.257	0.025	7.09
9	90	3213	3.2	0.257	0.025	7.33
10	100	3570	3.2	0.257	0.025	7.39
11	110	3927	3.2	0.257	0.025	7.50
12	120	4285	3.2	0.690	0.458	7.46
14	140	4999	3.2	0.273	0.041	--
15	150	5356	3.2	---	---	7.78
16	160	5714	3.2	0.293	0.061	7.80

Table 27

Water Soluble Phosphorus in Fox Sandy Loam Virgin Surface When Treated with Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each culture (equivalent to 200 pounds of acid phosphate per acre.).

Soil culture no.	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc. H_2O	increase over check	pH
X	0	--	0	2.780	--	5.84
0	0	--	3.2	0.880	-	6.35
2	20	714	3.2	1.290	-	6.50
4	40	1428	3.2	1.130	-	6.48
6	60	2142	3.2	0.720	-	6.54
8	80	2857	3.2	0.177	-	6.52
10	100	3570	3.2	0.620	-	6.61
12	120	4285	3.2	0.570	-	6.86
14	140	4999	3.2	0.770	-	6.94
16	160	5714	3.2	0.680	-	6.84

Table 28

Water Soluble Phosphorus;Fox Sandy Loam A2 Horizon When Treated With Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each soil culture (equivalent to 200 pounds of acid phosphate per acre.).

Soil culture no.	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 250 cc. H_2O	increase over check	pH
X	0	--	0	0.308	--	6.80
0	0	--	3.2	0.437	0.129	6.73
1	10	357	3.2	0.463	0.155	6.78
2	20	714	3.2	0.566	0.258	6.98
3	30	1071	3.2	0.386	0.078	7.11
4	40	1428	3.2	0.566	0.258	7.23
5	50	1785	3.2	0.463	0.155	7.38
6	60	2142	3.2	0.257	-	7.45
7	70	2499	3.2	0.437	0.129	7.60
8	80	2857	3.2	0.455	0.145	7.63
9	90	3213	3.2	0.412	0.104	7.75
10	100	3570	3.2	0.412	0.104	7.86
11	110	3927	3.2	0.360	0.052	7.88
12	120	4285	3.2	0.720	0.412	7.93
13	130	4642	3.2	---	---	7.96
14	140	4999	3.2	0.391	0.083	8.00
15	150	5356	3.2	---	---	8.08
16	160	5714	3.2	0.350	0.042	8.18

Table 29

Water Soluble Phosphorus in Fox Sandy Loam B Horizon when Treated With Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each soil culture (equivalent to 200 pounds of acid phosphate per acre).

Soil culture no.	CaO mgm.	CaO lbs. per acre	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 100 gm soil	increase over check	pH
X	0	--	0	0.494	--	7.16
0	0	--	3.2	0.546	0.052	7.10
1	10	357	3.2	0.463	---	7.23
2	20	714	3.2	0.628	0.134	7.40
3	30	1071	3.2	0.679	0.185	7.55
4	40	1428	3.2	0.772	0.278	7.67
5	50	1785	3.2	0.716	0.222	7.70
6	60	2142	3.2	0.618	0.124	7.60
7	70	2499	3.2	0.643	0.149	7.97
8	80	2857	3.2	0.705	0.211	7.87
9	90	3213	3.2	0.443	--	7.94
10	100	3570	3.2	0.515	0.021	8.03
11	110	3927	3.2	0.483	-	8.07
12	120	4285	3.2	0.386	-	8.07
14	140	4999	3.2	0.412	-	8.10
16	160	5714	3.2	0.283	-	8.13

Table 30

Water Soluble Phosphorus in Fox Sandy Loam C Horizon When Treated With Acid Phosphate and CaO.

5.68 mgm. $CaH_4(PO_4)_2$ was added to each soil culture (equivalent to 200 pounds of acid phosphate per acre.).

Soil culture no.	CaO mgm. added	CaO lbs. per acre.	mgm. P_2O_5 added	mgm. P_2O_5 soluble in 100 gm. soil	increase over check	pH
X	0	--	0	0.154	--	7.85
0	0	--	3.2	0.489	0.335	7.78
1	10	357	3.2	0.479	0.325	7.85
2	20	714	3.2	0.577	0.423	8.14
3	30	1071	3.2	0.469	0.335	8.17
4	40	1428	3.2	0.479	0.325	8.26
6	60	2142	3.2	0.607	0.453	8.26
8	80	2857	3.2	0.592	0.483	8.29
10	100	3570	3.2	0.582	0.428	8.35
12	120	4285	3.2	0.668	0.514	8.31
14	140	4999	3.2	0.628	0.474	8.43
16	160	5356	3.2	0.649	0.495	8.29

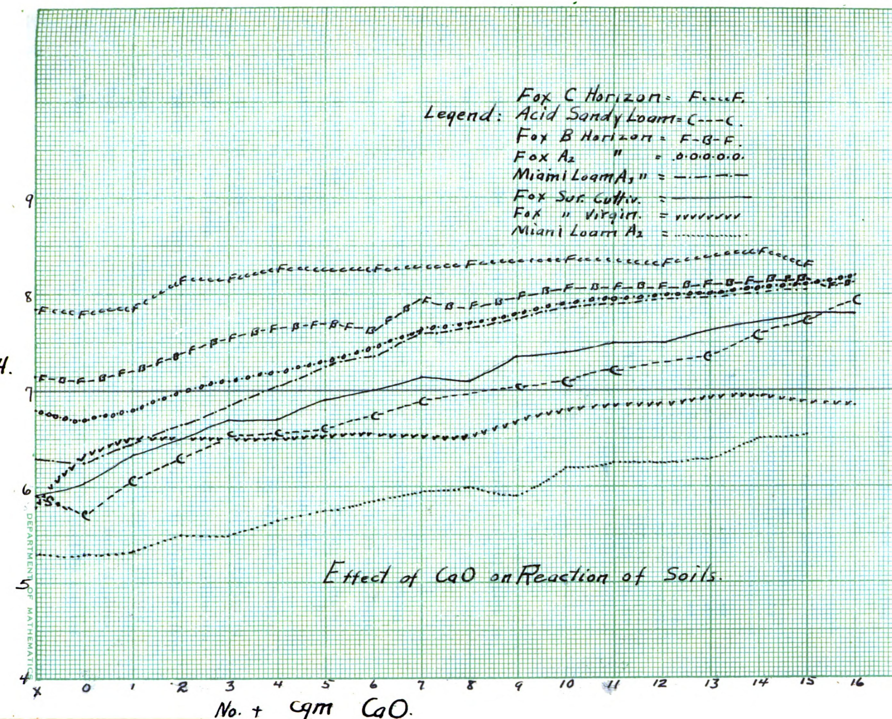


Fig. 12

Effect of CaO on Reaction of Soils.

Table 31

Effect of H_2SiO_3 on the Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ of Several Concentrations.

Flask no.	mgm. P_2O_5 per 100 cc. original	final	loss	mgm. P_2O_5 loss per flask.	pH	Ca per 250 cc. original	final	loss
1	8	7.68	0.14	0.35	4.33	--	--	--
2	12	11.79	0.21	0.53	4.15	--	--	--
3	24	23.10	0.90	2.25	3.65	--	--	--
4	64	62.07	1.93	4.83	3.54	45.04	41.00	4.04
5	128	123.96	4.04	10.10	3.11	90.07	83.75	6.32
6	192	186.10	5.90	14.75	3.14	135.11	124.50	10.61
7	320	313.46	6.54	16.35	3.10	225.19	202.12	23.07

research. The equasion for the adsorption isotherm for solutions is written (72),

$$(X/M)^n = KC$$

in which X is the amount adsorbed by M units of solid adsorbing agent, C is the concentration of the solution, K is an adsorbent constant and n is also an adsorbent constant. The approximate accuracy of the formula has been shown by Freundlich (73).

A series of experiments were conducted with H_2SiO_3 and a natural silicious deposit, commonly called rock flour, which had a reaction of 4.9 pH. Ten gram samples of the solid were placed into erlenmeyer flasks containing 250 cc. of solutions of $CaH_4(PO_4)_2$ of several different concentrations, shaken constantly and vigorously for 10 minutes and allowed to stand over night. The final concentrations of phosphorus were determined and the results, X/M and C plotted and the

Table 32

Effect of "Rock Flour" on the Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ of Several Concentrations.

Flask no.	mgm. P_2O_5 per 100 cc. original	mgm. P_2O_5 per 250 cc. original	mgm. P_2O_5 per 100 cc. final	mgm. P_2O_5 per 250 cc. final	mgm. P_2O_5 per 10 gm. rock flour loss	pH
1	2	5	.95	2.38	2.62	4.28
2	4	10	2.09	5.24	4.76	4.16
3	8	20	5.50	13.74	6.26	4.08
4	12	30	9.02	22.54	7.46	3.84
5	16	40	12.30	30.76	9.24	3.96
6	24	60	20.02	50.05	9.95	3.76
7	32	80	27.79	61.47	10.53	3.59
8	64	160	56.98	142.45	17.55	3.47
9	128	320	118.22	295.55	24.45	3.34
10	192	480	179.94	449.85	30.15	3.24
11	320	800	306.66	766.65	33.35	3.17
12	640	1600	614.80	1537.00	63.00	--
13	1280	3200	1247.60	3119.00	81.00	--

curves compared with the adsorption isotherm curve.

The results from H_2SiO_3 on the solubility of phosphorus in the water solution of $CaH_4(PO_4)_2$, and also with the rock flour, (tables 31 and 32, and figs. 13 and 14) somewhat approach the adsorption isotherm curve.

This study was repeated using soil particles as the adsorbing agent. A 500-gram sample of the acid sandy loam was thoroughly shaken in water to cause deflocculation and, after standing for 1 hour, the suspension was poured off, continueing the process until the water remained

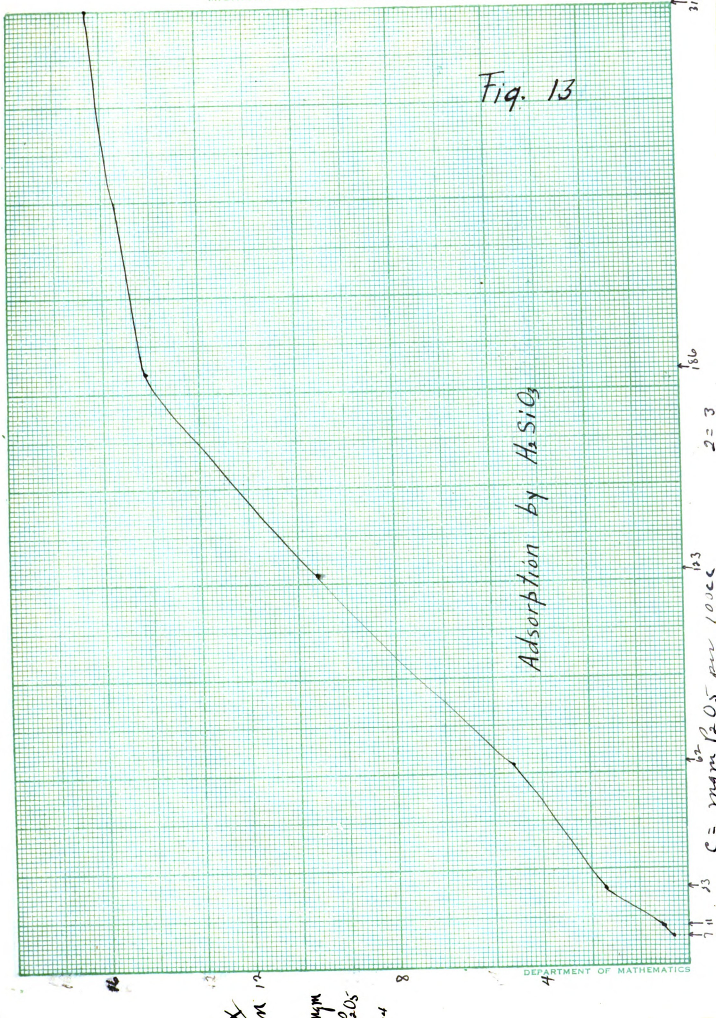


Fig. 13

Adsorption by H_2SiO_3

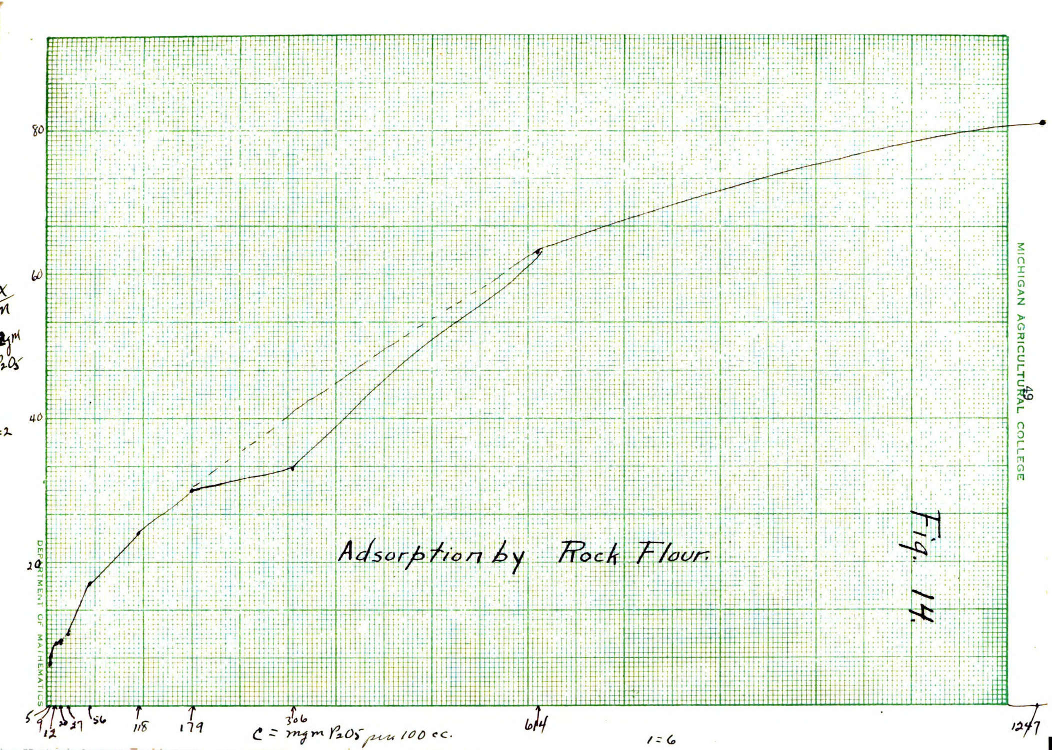


Fig. 14.

Adsorption by Rock Flour.

Table 33

Effect of Different Size Soil Particles on the Solubility of Phosphorus in Water Solution of $CaH_4(PO_4)_2$ from the standpoint of Adsorption.

Sample no.	size of particles	Rate per acre on 500 gm. soil acid phos.	Mgm. P_2O_5 per 150 cc. water added	 final	 loss
10	colloid	500	40	13.55	26.45
11	clay	500	40	5.40	34.60
12	sand & silt	500	40	10.25	29.75
20	colloid	1000	80	35.85	44.15
21	clay	1000	80	15.90	64.10
22	sand & silt	1000	80	37.05	42.95

nearly clear. This soil suspension was passed through a super centrifuge thus seperating the soil material which collected in the cylinder with the larger size particles near the intake, and the finest particles, distributed along the sides of the cylinder. The portions of the soil thus secured, namely, the finest patticles from the centrifuge, termed colloid, the less fine particles from the centrifuge, termed clay, and the bulk of the 500-gram sample, mostly mostly sand and silt, were placed in solutions of $CaH_4(PO_4)_2$ equivalent to 500 pounds of acid phosphate per acre. A second set was also set up in solutions of double this strength. These were shaken constantly and vigorously for 10 minutes, allowed to stand over night and the phosphorus concentrations determined.

There was a marked loss of phosphorus from the solutions (table 33) in each case, but being much greater per unit adsorbing agent for the

Table 34

Adsorption Of Phosphorus By The Fine Portion Of A Very Acid Sandy Loam.

Flask no.	mgm. P_2O_5 per 100 cc. original	mgm. P_2O_5 per 250 cc. original	Final concentration mgm. P_2O_5 per 100 cc.	Final concentration 250 cc.	mgm. P_2O_5 per 250 cc. loss	pH
1	24	60	9.98	24.95	35.05	4.16
2	32	80	15.56	38.91	41.09	4.11
3	64	160	45.03	112.57	47.43	3.96
4	128	320	104.14	260.35	59.65	3.89
5	192	480	163.92	409.80	70.20	3.57
6	320	800	284.86	712.15	87.85	3.47

colloid and clay as they were only a very small part of the original 500 grams of soil. There probably was not over 20 grams of the clay and colloid portions thus obtained.

The finer particles of the soil were separated from other portions of soil by shaking for a short time, using 200 grams of soil in 300 cc. of water and allowing it to settle for 2 minutes and then pouring off 250 cc. of the suspension, which contained about 50 grams of the fine soil particles, into erhlenmeyer flasks. To the flasks thus prepared was added $CaH_4(PO_4)_2$ in varying amounts. When the $CaH_4(PO_4)_2$ had been given time to dissolve, the the flasks were shaken constantly and vigorously for 10 minutes, allowed to stand over night and the final phosphorus concentrations determined.

The acid sandy loam soil, and the A2 horizon of the Miami Loam soil, which was acid, were used in this experiment. The data (tables

Table 35

Adsorption of Phosphorus by the Fine Portion of the A2 Horizon of the Miami Loam

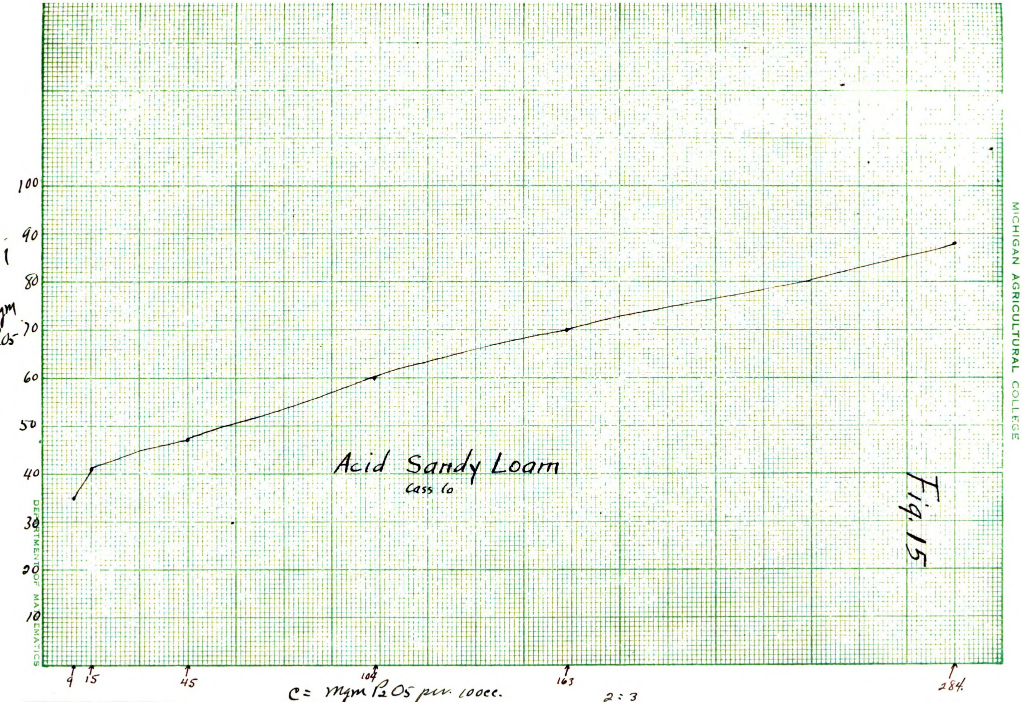
Flask no.	Original concentration mgm. P_2O_5 per 100 cc.	Original concentration mgm. P_2O_5 per 250 cc.	Final concentration mgm. P_2O_5 per 100 cc.	Final concentration mgm. P_2O_5 per 250 cc.	Loss per 250 cc.
1	24	60	10.33	25.82	24.18
2	32	80	11.86	29.65	50.35
3	64	160	35.36	88.40	71.60
4	128	320	88.14	220.35	99.65
5	192	480	133.48	333.70	146.30
6	320	800	260.10	650.25	149.75

34 and 35) were plotted as shown in figures 15 and 16. They do not have any great resemblence to the adsorption isotherm curve although a general resemblence in shape to that curve exists.

The data in table 16 were plotted to show the adsorption curve. This curve (fig. 17) also somewhat resembles the adsorption isotherm curve.

No general conclusions can be drawn from these curves in view of the fact that chemical reactions are probably present in many cases in these soil studies, and any very close adherence to the adsorption isotherm probably would not be obtained in the presence of chemical reactions. However, where there is a solid- liquid interface there probably is adsorption and with reactible compounds also present there probably is chemical reaction, both of which are doubtless functioning in the soil.

Fig. 15


MICHIGAN AGRICULTURAL COLLEGE
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Acid Sandy Loam
Cass Co
100
90
80
70
60
50
40
30
20
10
9
15
45
104
163
284
C = Mgm P_2O_5 per 100cc.
2 : 3

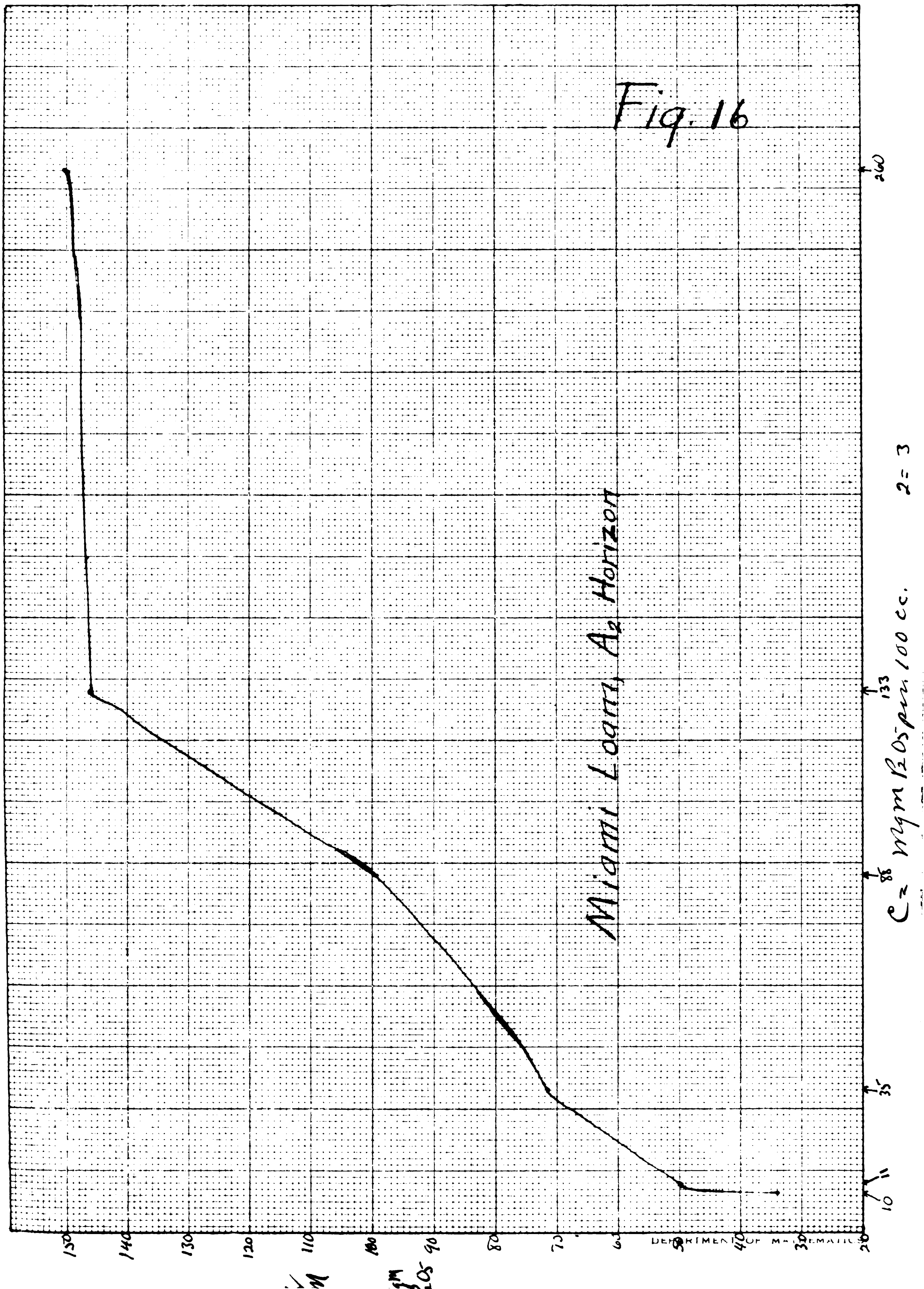

Fig. 16

Miami Loam, A_2 Horizon
C = mgm P_2O_5 per 100 cc.
2 = 3
260
133
88
35
11
10
150
140
130
120
110
100
90
80
70
60
50
40
30
20
DEPARTMENT OF MATHEMATICS

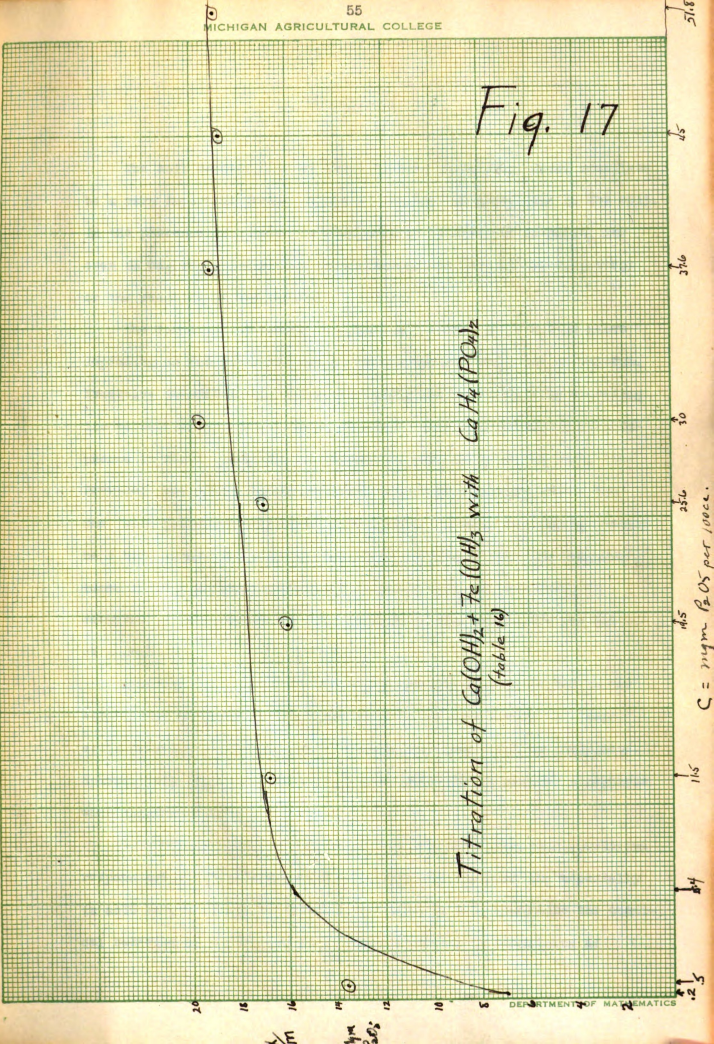

Fig. 17

Titration of $Ca(OH)_2 + Fe(OH)_3$ with $CaH_4(PO_4)_2$
(table 16)

Conclusions

The soil reaction, if no other factors prevailed, would doubtless be a very important factor in the solubility of phosphorus in the soil. In the presence of a base the $CaH_4(PO_4)_2$ is reverted to $CaHPO_4$ and even to $Ca_3(PO_4)_2$ depending on the amount and kind of bases present or the reaction of the medium.

The formation of $CaHPO_4$ is placed at about pH of 5.6 or above depending on the concentration of the phosphorus compounds of calcium. Excessive concentrations force the $CaHPO_4$ out of solution by exceeding its solubility product. In an alkaline soil this reversion of phosphorus is rapid (16)(39). However in terms of crop response, the reverted and precipitated phosphates are more available than the raw rock phosphate ([illegible]). These results tend to show that $CaHPO_4$ should be a more economical form of phosphorus fertilizer than the $CaH_4(PO_4)_2$ because of a probable lower cost of production, as less H_2SO_4 is required in its preparation from rock phosphate, and higher percent of phosphorus.

Lime and soil reaction can not be the determining factor in the solubility of phosphorus in soils as is shown by the work on acid soils in which there was marked retention of the applied phosphorus. Spurway (68) found some acid soils very retentive of applied phosphorus when applded as acid phosphate.

Compounds of iron (11) and aluminum (1[illegible]) have long been considered responsible for the insolubility of phosphorus in soils and especially in acid soils. Very little work has been done to determine the chemical behavior of these compounds toward compounds of phosphorus as relation to the solubility of the phosphorus. The conclusions that have been commonly advanced (42) have been based on crop response. In the titrations with $Fe(OH)_3$ and $Al(OH)_3$, the reaction changed, with the increase in $Fe(OH)_3$ or $Al(OH)_3$ present, and there was a rise in the pH and a decrease in the phosphorus in solution; in other words the applied phosphorus is more soluble in acid solutions when $Fe(OH)_3$ or $Al(OH)_3$ are present.

The adsorption curves secured in these experiments do not conform closely enough to the adsorption isotherm curve (72)(73) to warrant any positive conclusions. Since Chemical reactions are, without doubt, present in soils, and since their effect on adsorption is not known, but where there is a solid-liquid interface it is known that adsorption does take place to some extent, it is warranted to conclude that adsorption is one of the factors effecting the solubility of phosphorus in soils.

Factors affecting the solubility of phosphorus in soils are not few in number. Those studied in this paper are active and there are probably many others. Further studies of these factors and their behavior under varying conditions will undoubtedly add much to the meager and much, needed knowledge of the chemical constitution of soils.

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