REPLACEMENT OF THE NATURAL BASES OF THE EXCHANGE COMPLEXES OF SOIL WITH KNOWN CATIONS, AND THE EFFECT OF SUCH SOIL UPON THE SOLUBILITY OF PHOSPHATE FERTILIZERS IN THE PRESENCE OF VARYING AMOUNTS OF CALCIUM CARBONATE AND POTASSIUM CHLORIDE

by

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INTRODUCTION

This work was begun with the hope of answering certain questions which have arisen by observing interesting phenomena in connection with plants growing under natural conditions. It is known that even though phosphate fertilizer may be present in large amounts only a small amount of it is available to plants at any given time because of its sparing solubility; hence, it would be of interest to know which cations occurring naturally in the soil are responsible for rendering the phosphate ion insoluble, and whether the addition of dissimilar ions might increase the amount of phosphorus available to plants by causing more of it to enter solution.

Acid soils are often deficient in available phosphorus, and the common practice has been to add phosphate rock, or so-called super-phosphate, to supply this deficiency; however, the acidity must also be corrected, and as this is done by adding lime, or lime-stone, it seems likely that this might cause the phosphate to be less soluble than in the original acid soil. Experience shows that plants grow more rapidly if, with the limestone and super-phosphate, a comparatively small amount of potassium chloride is also added. At first one might conclude that the additional growth is due to the benefits of the extra potassium; however, soils not actually deficient in potassium show the same result, and the question arises may not the presence of the potassium chloride in some manner increase the availability of the phosphorus?

Thus, the problem resolves itself into two major divisions:

First-- To replace the natural bases of the exchange complexes (1) of the soil with known cations.

Second-- To use this soil and determine the solubility of phosphate fertilizer in the presence of varying amounts of $CaCO_3$ and KCl.

METHODS AND PROCEDURE

I. Replacement of the natural bases of soil with known cations.

An acid loam soil from Cherokee County, Kansas, was selected for use in the experiment. A large sample of the air-dried soil was carefully crushed, then screened through a 20-mesh sieve to remove the rocks and the coarse organic matter. After the soil was thoroughly mixed, approximately one-half of it was sealed up in fruit jars to serve as check samples and for subsequent moisture determinations; whereas, the remainder was distributed among eight 5-gallon bottles and treated as indicated below:

Bottle number	Weight of soil	Amount of reagent	Concentration of reagent	Nature of reagent
1	7750 grams	12 liters	N/20	HCl
2	6340 grams	12 liters	N/10	NH_4Cl
3	5963 grams	12 liters	N/10	KCl
4	6259 grams	12 liters	N/10	$CaCl_2$
5	6612 grams	12 liters	N/10	$MgCl_2$
6	6070 grams	12 liters	N/10	$NaCl$
7	6681 grams	12 liters	N/10	$FeCl_3$
8	7066 grams	12 liters	N/10	$AlCl_3$

After the addition of the reagent each bottle was vigorously shaken to insure intimate contact between the soil particles and those of the reagent and then set aside for the suspended material to settle. This was accomplished in each case at the end of about twenty hours; whereupon, the supernatant liquid was carefully siphoned off and replaced with the same reagent in the amounts given below:

Bottle No. 1	7.5 liters	N/20	HCl
Bottle No. 2	8.5 liters	N/10	NH_4Cl
Bottle No. 3	8.5 liters	N/10	KCl
Bottle No. 4	8.0 liters	N/10	$CaCl_2$
Bottle No. 5	8.0 liters	N/10	$MgCl_2$
Bottle No. 6	8.0 liters	N/10	$NaCl$
Bottle No. 7	8.0 liters	N/10	$FeCl_3$

Bottle No. 8 ________________ 8.0 liters N/10 $AlCl_3$

Again the bottle was vigorously shaken and set aside for another twenty-four hours.

It is obvious that this method depends solely upon the increased concentration of the known cation to effect its substitution in the exchange complex of the soil for the bases naturally occurring there. Gedroiz (2) has shown that equilibrium appears to be reached in a very short time, for almost as much calcium was displaced by a solution of sodium chloride in five seconds as in fourteen months, and as much calcium by a solution of ammonium chloride in three minutes as in three days. Moreover, the amount of calcium replaced before equilibrium is established is proportional to the concentration of the cation with which the soil is being treated; thus, it appears that the replacement reaction follows the mass action law.

Calcium has been shown by Gedroiz (1) to constitute the major percentage of replaceable bases of soil complexes in most soils; hence, when all of the calcium was displaced, we assumed that all other natural bases of the soil had likewise been displaced. In order to determine when all of the calcium had been removed a qualitative test was made upon the supernatant liquid each time after the suspended material had settled. Obviously this afforded no means of telling when the calcium solution had displaced all of the other bases, but since calcium is more active than magnesium, we concluded that when magnesium had replaced all of the bases from its soil that calcium had done likewise.

The number of treatments necessary to replace all of the calcium is summarized in Table I. It will be observed from the table that the trivalent elements, iron and aluminum, were most energetically absorbed; then the bivalent magnesium and lastly the monovalent elements or radicals, hydrogen, ammonium, potassium, and sodium. These results are entirely in accord with those described by Gedroiz (1).

The more concentrated normal solutions were substituted for the N/10 solutions of the chlorides of potassium, ammonium, sodium, magnesium, and calcium, in order to increase the rate of substitution and to check the action of molds and bacteria, which was imparting a bad odor to some of the solutions.

As soon as the natural bases had been displaced, the treated soils were washed to remove the soluble salts which were not combined with the soil. Ten liters of distilled water were added to the soil in the bottles; the bottles were shaken for a time and then set aside for the suspended material to settle. When this had occurred, the supernatant liquid was tested qualitatively for the presence of the chloride ion, then siphoned off and replaced with

Table I.

Summary of Soil Treatment

	Bottle No. 1		Bottle No. 2		Bottle No. 3		Bottle No. 4		Bottle No. 5		Bottle No. 6		Bottle No. 7		Bottle No. 8	
Grams of soil	7750		6340		5963		6259		6612		6070		6681		7066	
No. of treatments	Treated with N/20 HCl	Test for Ca	Treated with N/10 NH_4Cl	Test for Ca	Treated with N/10 KCl	Test for Ca	Treated with N/10 $CaCl_2$	Test for Ca	Treated with N/10 $MgCl_2$	Test for Ca	Treated with N/10 NaCl	Test for Ca	Treated with N/10 $FeCl_3$	Test for Ca	Treated with N/10 $AlCl_3$	Test for Ca
1.	12 l.		12 l.		12 l.		12 l.	+	12 l.		12 l.		12 l.		12 l.	
2.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+	8	+	8	+
3.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+	8	+	8	+
4.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+	8	+	8	+
5.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+	8	+	8	+
6.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+	8	+	8	+
7.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+		-	8	+
8.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+			8	+
9.	7.5	+	7.5	+	8.5	+	8	+	8	+	8	+			8	
											N NaCl					
10.	7.5	+	8.5	+	8.5	+	8	+	8	+	8	+				
			N NH_4Cl		N KCl		N $CaCl_2$		N $MgCl_2$							
11.	7.5	+	8.5	+	8.5	+	8	+	8	+	8	+				
12.	7.5	+	8.5	+	8.5	+	8	+	8	+	8	+				
13.	7.5	+	8.5	+	8.5	+	8	+		-	8	+				
14.	7.5	+	8.5	+	8.5	+					8	+				
15.	7.5	+	8.5	+	8.5	+					8	+				
16.	7.5	+	8.5	+	8.5	+					8	+				
17.	7.5	+	8.5	+	8.5	+					8	+				
18.	7.5	+	8.5	+	8.5	+					8	+				
19.		-		-		-						-				

fresh water. This process was repeated until the wash water no longer contained chloride ions. The scheme sounds very simple; however, a great deal of difficulty was encountered.

In the first place when the concentration of the electrolyte became low, the suspended material would not coagulate and settle except after a long period of waiting; and in the case of sodium and potassium not at all after the first washing. When this condition obtained, it became necessary to remove the wash water by filtering the soil through Büchner funnels. Very little difficulty was met in filtering the soils treated with $FeCl_3$, $AlCl_3$, $CaCl_2$, and HCl, but in the case of the others it often required as much as fifty hours of continual suction to filter from ten to twelve liters of water from the soil, even though seventeen funnels were used. It was so nearly impossible to remove water from the soils treated with NaCl and KCl that the last washings were made with 80% ethyl alcohol. Although these chlorides are but very little soluble in alcohol, the water present dissolved them, while the alcohol in some manner made filtering easier.

Another interesting phenomenon was the difference in the amounts of organic matter leached from the soils by the wash water. None was discernible in the water from the soils treated with $FeCl_3$, $AlCl_3$, $CaCl_2$, or HCl; however, it was colored a pronounced yellow with organic matter from the soils treated with $MgCl_2$, NaCl, KCl, and NH_4Cl. In some cases this color was dark enough to suggest the "black alkali" soils of some regions.

The number of times the soils were washed and filtered is summarized in Table II.

After the prepared soils were thoroughly washed, they were air-dried, crushed, screened through a 20-mesh sieve, and sealed in quart fruit jars. An analysis was made of each of the prepared soils and of the untreated soil (3).

The results of the analysis showing the comparative composition of each soil is given in Table III.

2. Determination of the solubility of the phosphate ion in the presence of varying amounts of calcium carbonate and potassium chloride.

The triangulation method was selected as the one best suited to the experiment. Each side of an equilateral triangle, arranged as shown below, was divided into seven equal portions; and when lines were drawn from the divisions, the intersections formed rows of points, some of which were selected for use. The letter R, bearing a subscript to indicate the row and a number following a dash to indicate the position in the row, was used to designate a given point.

Table II.

Summary of Soil Washings

	Bottle No. 1		Bottle No. 2		Bottle No. 3		Bottle No. 4		Bottle No. 5		Bottle No. 6		Bottle No. 7		Bottle No. 8	
No. of washings	Treated with N/20 HCl		Treated with N/10 NH_4Cl		Treated with N/10 KCl		Treated with N/10 $CaCl_2$		Treated with N/10 $MgCl_2$		Treated with N/10 NaCl		Treated with N/10 $FeCl_3$		Treated with N/10 $AlCl_3$	
	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl	Washed with	Test for Cl
1.	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+	10 l. distilled H_2O	+
2.	"	+	"	+	"	+	"	+	"	+	"	Filtered +	"	+	"	+
3.	"	+	"	+	"	Filtered +	"	+	"	+	"	Filtered +	"	+	"	+
4.	"	+	"	Filtered +	"	Filtered +	"	+	"	+	6 l. 80% alcohol	Filtered +	"	+	"	+
5.	"	+	"	Filtered +	7 l. 80% alcohol	Filtered +	"	+	"	+	"	Filtered +	"	+	"	+
6.	"	Filtered +	"	Filtered +	"	Filtered +	"	+	"	Filtered +	"	Filtered +	"	+	"	+
7.	"	Filtered +	"	Filtered -	"	Filtered -	"	+	"	Filtered +	"	Filtered -	"	+	"	+
8.	"	Filtered -					"	Filtered +	"	Filtered -			"	+	"	+
9.							"	Filtered +					"	+	"	+
10.							"	Filtered +					"	+	"	+
11.							"	Filtered -					"	Filtered +	"	+
12.													"	Filtered +	"	+
13.													"	Filtered -	"	+
14.															"	Filtered +
15.															"	Filtered -

Table III.

Results of Analysis

Soil treated with	% moisture	% SiO_2	% NH_4	% Fe_2O_3	% P_2O_5	% Al_2O_3	% CaO	% MgO	% K_2O	% Na_2O
$FeCl_3$	2.567	82.351	.028	3.805	.113	6.927	.206	.541	.678	2.708
$AlCl_3$	2.350	82.200	.029	2.617	.112	8.117	.229	.543	.682	2.720
$CaCl_2$	2.797	82.423	.030	2.628	.107	7.519	.576	.560	.702	2.596
$MgCl_2$	2.572	82.195	.031	2.936	.108	7.591	.195	.993	.698	2.686
NH_4Cl	2.060	82.123	.128	2.932	.102	7.342	.194	.552	.616	2.359
KCl	2.070	82.408	.027	2.847	.109	7.120	.205	.730	1.183	2.769
NaCl	2.505	82.324	.029	2.944	.113	7.220	.252	.602	.638	3.357
HCl	1.732	82.224	.026	2.841	.110	6.971	.250	.595	.718	2.739
Untreated	2.425	82.190	.025	3.075	.118	7.526	.447	.868	.730	2.802

R_1-1

R_2-1 R_2-1.5 R_2-2
$R_{2.5}$-2 $R_{2.5}$-3
R_3-1 R_3-2 R_3-3

R_4-1 R_4-2.5 R_4-4

R_5-1 R_5-3 R_5-5

R_6-1 R_6-3 R_6-4 R_6-6
$R_{6.5}$-1 $R_{6.5}$-6 $R_{6.5}$-7 $R_{6.5}$-12
R_7-1 R_7-4 R_7-7

Beginning at the top, row 1 received thirty tons of $CaCO_3$ per acre, row 2, twenty-five tons, etc., until row 7 received none. The first point in the left-hand corner represented 1200 pounds of KCl per acre, and each succeeding row one-sixth less, until the last received none; whereas, the first point in the right-hand corner represented 1200 pounds of $CaH_4(PO_4)_2$, and each succeeding row one-sixth less, causing the last row to receive none.

Assuming that an acre of surface soil weighs two million pounds, the amounts of the three compounds which each point represented in tons and pounds per acre as well as the comparative weight in grams per one hundred grams of soil are as follows:

	Wt. per acre			Wt. per 100 gms. of soil		
Point	Tons $CaCO_3$	Lbs. KCl	Lbs. $CaH_4(PO_4)_2$	Gms. $CaCO_3$	Gms. KCl	Gms. $CaH_4(PO_4)_2$
R_1-1	30.0	0.0	0.0	3.0	0.0	0.0
R_2-1	25.0	200.0	0.0	2.5	0.01	0.0
R_2-1.5	25.0	100.0	100.0	2.5	0.005	0.005
R_2-2	25.0	0.0	200.0	2.5	0.0	0.01
$R_{2.5}$-2	22.5	200.0	100.0	2.25	0.01	0.005
$R_{2.5}$-3	22.5	100.0	200.0	2.25	0.005	0.01
R_3-1	20.0	400.0	0.0	2.0	0.02	0.0
R_3-2	20.0	200.0	200.0	2.0	0.01	0.01
R_3-3	20.0	0.0	400.0	2.0	0.0	0.02
R_4-1	15.0	600.0	0.0	1.5	0.03	0.0
R_4-2.5	15.0	300.0	300.0	1.5	0.015	0.015
R_4-4	15.0	0.0	600.0	1.5	0.0	0.03
R_5-1	10.0	800.0	0.0	1.0	0.04	0.0
R_5-3	10.0	400.0	400.0	1.0	0.02	0.02
R_5-5	10.0	0.0	800.0	1.0	0.0	0.04
R_6-1	5.0	1000.0	0.0	0.5	0.05	0.0
R_6-3	5.0	600.0	400.0	0.5	0.03	0.02
R_6-4	5.0	400.0	600.0	0.5	0.02	0.03
R_6-6	5.0	0.0	1000.0	0.5	0.0	0.05
$R_{6.5}$-1	2.5	1100.0	0.0	0.25	0.055	0.0
$R_{6.5}$-6	2.5	600.0	500.0	0.25	0.03	0.025
$R_{6.5}$-7	2.5	500.0	600.0	0.25	0.025	0.03
$R_{6.5}$-12	2.5	0.0	1100.0	0.25	0.0	0.055
R_7-1	0.0	1200.0	0.0	0.0	0.06	0.0
R_7-4	0.0	600.0	600.0	0.0	0.03	0.03
R_7-7	0.0	0.0	1200.0	0.0	0.0	0.06

One hundred grams of soil and the proper amount of the three compounds for each point were carefully weighed and placed in a 400 c.c. centrifuge bottle. 250 c.c. of CO_2--free, distilled water were added; the bottles were placed upon a shaking machine and allowed to shake continuously for four hours, and then let stand over night. They were then centrifuged for five minutes, the liquid portions filtered through Pasteur filters, and the amount of inorganic phosphorus in the filtrates determined by the following method due to Atkins (4).

50 c.c. of the clear filtrate were placed in a 100 c.c. Erlenmeyer or other convenient flask. 1 c.c. of reagent A was added, and while the flask was being vigorously shaken three drops of reagent B were added to develop the blue color.

A series of standards containing .1, .2, .3, .4, and 1 p.p.m. were prepared by properly diluting the standard P_2O_5 solution, and the color was developed in them as directed above.

After both the standards and the unknowns had stood for five minutes, each unknown was compared with a standard of approximately the same color intensity in the colorimeter.

The necessary solutions were prepared by the following simple directions:

1. Reagent A-- Mix 100 c.c. of 10 per cent ammonium molybdate solution with 300 c.c. of a 50% (by volume) solution of H_2SO_4. The acid must be arsenic-free, and the reagent should be kept in the dark or in a brown bottle.

2. Reagent B-- To .5 gm. of powdered tin add five drops of a 4 per cent solution of $CuSO_4$ and 10 c.c. of HCl, arsenic-free. Warm to hasten the reaction and, when the tin is in solution, dilute to 50 c.c. This reagent must be

prepared fresh each day.

3. Standard P_2O_5 solution-- Dissolve 0.1917 gm. of KH_2PO_4 in distilled water, transfer quantitatively to a 1000 c.c. volumetric flask, add 5 c.c. of toluene, and dilute to the mark. This solution contains 100 parts of P_2O_5 per million. Take 10 c.c. of this solution and dilute to 1000 c.c. to obtain a standard containing 1 part of P_2O_5 per million. Other standards may be made from these solutions by the proper dilutions.

Considerable trouble was experienced because of the yellow color imparted to some of the filtrates by the dissolved organic matter. This, when mixed with the blue due to the phosphorus, gave a green which was very difficult to match against the clear blue of the standards. An attempt was made to correct this by adding Bismarck brown (4) to the standards before the phosphorus color was developed, until a yellow color was imparted of approximately the same intensity as that of the unknown. This made matching much easier and seemed to give good results.

The pH value of each filtrate was determined by the quinhydrone method (5).

RESULTS OF PHOSPHORUS SOLUBILITY TESTS AND pH VALUE DETERMINATIONS

The results in Table V give the solubility of the phosphorus in parts of P_2O_5 per million parts of the filtrate. For each soil the results are given first in table form followed by a triangle bearing the results for each point.

Table IV

Soil Treated with $FeCl_3$

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.255	7.190
R_2-1	0.052	7.155
R_2-1.5	0.058	7.155
R_2-2	0.058	7.335
$R_{2.5}$-2	0.114	7.250
$R_{2.5}$-3	0.461	7.220
R_3-1	0.096	7.245
R_3-2	0.214	7.275
R_3-3	0.083	7.325
R_4-1	0.071	7.350
R_4-2.5	0.392	7.350
R_4-4	0.252	7.380
R_5-1	0.108	7.280
R_5-3	0.101	7.385
R_5-5	0.080	7.480
R_6-1	0.142	7.120
R_6-3	0.096	7.155
R_6-4	0.066	7.155
R_6-6	0.092	7.250
$R_{6.5}$-1	0.094	5.475
$R_{6.5}$-6	0.093	6.270
$R_{6.5}$-7	0.275	6.465
$R_{6.5}$-12	0.099	6.660
R_7-1	0.078	4.320
R_7-4	0.104	4.495
R_7-7	0.344	4.640

Soil Treated with $FeCl_3$

0.255
7.190

0.052 0.058 0.058
7.155 7.155 7.335

0.114 0.461
7.250 7.220

0.096 0.214 0.083
7.245 7.275 7.325

0.071 0.392 0.252
7.350 7.350 7.380

0.108 0.101 0.080
7.280 7.385 7.480

0.142 0.096 0.066 0.092
7.120 7.155 7.155 7.250

0.094 0.093 0.275 0.099
5.475 6.270 6.465 6.660

0.078 0.104 0.344
4.320 4.495 4.640

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with $AlCl_3$

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.106	7.395
R_2-1	0.098	7.265
R_2-1.5	0.086	7.465
R_2-2	0.067	7.400
$R_{2.5}$-2	0.054	7.350
$R_{2.5}$-3	0.055	7.395
R_3-1	0.273	7.415
R_3-2	0.055	7.350
R_3-3	0.095	7.395
R_4-1	0.082	7.380
R_4-2.5	0.115	7.400
R_4-4	0.109	7.450
R_5-1	0.132	7.450
R_5-3	0.094	7.385
R_5-5	0.090	7.580
R_6-1	0.066	7.220
R_6-3	0.073	7.135
R_6-4	0.095	7.205
R_6-6	0.097	7.285
$R_{6.5}$-1	0.087	6.730
$R_{6.5}$-6	0.098	6.745
$R_{6.5}$-7	0.111	6.760
$R_{6.5}$-12	0.109	6.885
R_7-1	0.112	6.265
R_7-4	0.082	4.430
R_7-7	0.082	4.065

Soil Treated with $AlCl_3$

0.106
7.395

0.098 0.086 0.067
7.265 7.465 7.400

0.054 0.055
7.350 7.395

0.273 0.055 0.095
7.415 7.350 7.395

0.082 0.115 0.109
7.380 7.400 7.450

0.132 0.094 0.090
7.450 7.385 7.580

0.066 0.073 0.095 0.097
7.220 7.135 7.205 7.285

0.087 0.098 0.111 0.109
6.730 6.745 6.760 6.885

0.112 0.084 0.082
6.265 4.430 4.065

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Untreated Soil

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.090	7.690
R_2-1	0.098	7.700
R_2-1.5	0.087	7.835
R_2-2	0.099	7.795
$R_{2.5}$-2	0.091	7.710
$R_{2.5}$-3	0.080	7.842
R_3-1	0.079	7.610
R_3-2	0.095	7.775
R_3-3	0.082	7.805
R_4-1	0.075	7.710
R_4-2.5	0.107	7.690
R_4-4	0.113	7.625
R_5-1	0.107	7.690
R_5-3	0.248	7.610
R_5-5	0.305	7.560
R_6-1	0.126	7.640
R_6-3	0.130	7.495
R_6-4	0.305	7.670
R_6-6	0.800	7.690
$R_{6.5}$-1	0.132	7.450
$R_{6.5}$-6	0.139	7.470
$R_{6.5}$-7	0.134	7.535
$R_{6.5}$-12	0.661	7.510
R_7-1	0.194	6.860
R_7-4	0.381	6.565
R_7-7	3.174	6.470

Untreated Soil

0.090
7.690

0.098 0.087 0.099
7.700 7.835 7.795

0.091 0.080
7.710 7.842

0.079 0.095 0.082
7.610 7.775 7.805

0.075 0.107 0.113
7.710 7.690 7.625

0.107 0.248 0.305
7.690 7.610 7.560

0.126 0.130 0.305 0.800
7.640 7.495 7.670 7.690

0.132 0.139 0.134 0.661
7.450 7.470 7.535 7.510

0.194 0.381 3.174
6.860 6.565 6.470

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with $CaCl_2$

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.076	7.865
R_2-1	0.061	7.830
R_2-1.5	0.060	7.780
R_2-2	0.113	7.830
$R_{2.5}$-2	0.073	7.860
$R_{2.5}$-3	0.125	7.845
R_3-1	0.057	7.780
R_3-2	0.111	7.895
R_3-3	0.272	8.010
R_4-1	0.071	8.020
R_4-2.5	0.277	7.930
R_4-4	0.423	7.930
R_5-1	0.058	7.845
R_5-3	0.179	7.875
R_5-5	0.778	7.895
R_6-1	0.085	7.780
R_6-3	0.307	7.960
R_6-4	0.363	7.895
R_6-6	1.562	7.895
$R_{6.5}$-1	0.197	8.000
$R_{6.5}$-6	0.579	7.925
$R_{6.5}$-7	0.620	7.935
$R_{6.5}$-12	2.439	7.805
R_7-1	0.144	6.720
R_7-4	3.076	6.605
R_7-7	3.703	6.555

Soil Treated with $CaCl_2$

0.076
7.865

0.061 0.060 0.113
7.830 7.780 7.830

0.073 0.125
7.860 7.845

0.057 0.111 0.272
7.780 7.895 8.010

0.071 0.277 0.423
8.020 7.930 7.930

0.058 0.179 0.778
7.845 7.875 7.895

0.085 0.307 0.363 1.562
7.780 7.960 7.895 7.895

0.107 0.579 0.620 2.439
8.000 7.925 7.935 7.805

0.144 3.076 3.703
6.720 6.605 6.555

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with HCl

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.054	7.530
R_2-1	0.104	7.575
R_2-1.5	0.105	7.665
R_2-2	0.107	7.680
$R_{2.5}$-2	0.069	7.665
$R_{2.5}$-3	0.056	7.695
R_3-1	0.053	7.610
R_3-2	0.074	7.650
R_3-3	0.087	7.695
R_4-1	0.109	7.735
R_4-2.5	0.077	7.755
R_4-4	0.069	7.710
R_5-1	0.066	7.650
R_5-3	0.102	7.465
R_5-5	0.097	7.450
R_6-1	0.069	7.080
R_6-3	0.067	6.995
R_6-4	0.050	6.920
R_6-6	0.414	6.830
$R_{6.5}$-1	0.242	6.460
$R_{6.5}$-6	0.130	6.460
$R_{6.5}$-7	0.214	6.505
$R_{6.5}$-12	1.036	6.475
R_7-1	0.638	3.330
R_7-4	0.722	3.750
R_7-7	1.811	3.820

Soil Treated with HCl

0.054
7.530

0.104 0.105 0.107
7.575 7.665 7.680

0.069 0.056
7.665 7.695

0.053 0.074 0.087
7.610 7.650 7.695

0.109 0.077 0.069
7.735 7.755 7.710

0.066 0.102 0.097
7.650 7.465 7.450

0.069 0.067 0.050 0.414
7.080 6.995 6.920 6.830

0.242 0.130 0.214 1.036
6.460 6.460 6.505 6.475

0.638 0.722 1.811
3.330 3.750 3.820

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with $MgCl_2$

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.082	7.925
R_2-1	0.081	7.895
R_2-1.5	0.099	7.960
R_2-2	0.077	7.905
$R_{2.5}$-2	0.065	8.050
$R_{2.5}$-3	0.078	7.925
R_3-1	0.275	7.900
R_3-2	0.215	7.925
R_3-3	0.204	7.925
R_4-1	0.128	7.895
R_4-2.5	0.194	7.920
R_4-4	0.237	7.940
R_5-1	0.073	7.900
R_5-3	0.335	7.960
R_5-5	0.432	8.025
R_6-1	0.167	7.960
R_6-3	0.191	7.995
R_6-4	0.275	7.985
R_6-6	0.866	7.980
$R_{6.5}$-1	0.165	7.850
$R_{6.5}$-6	0.353	7.860
$R_{6.5}$-7	1.041	7.825
$R_{6.5}$-12	1.574	7.895
R_7-1	0.143	6.820
R_7-4	1.980	6.705
R_7-7	3.751	6.755

Soil Treated with $MgCl_2$

0.082
7.925

0.081 0.099 0.077
7.895 7.960 7.905

0.065 0.078
8.050 7.925

0.275 0.215 0.204
7.900 7.925 7.925

0.128 0.194 0.237
7.895 7.920 7.940

0.073 0.335 0.432
7.900 7.960 8.025

0.167 0.191 0.275 0.866
7.960 7.995 7.985 7.980

0.165 0.353 1.041 1.574
7.850 7.860 7.825 7.895

0.143 1.980 3.751
6.820 6.705 6.755

Parts P_2O_5 per Million

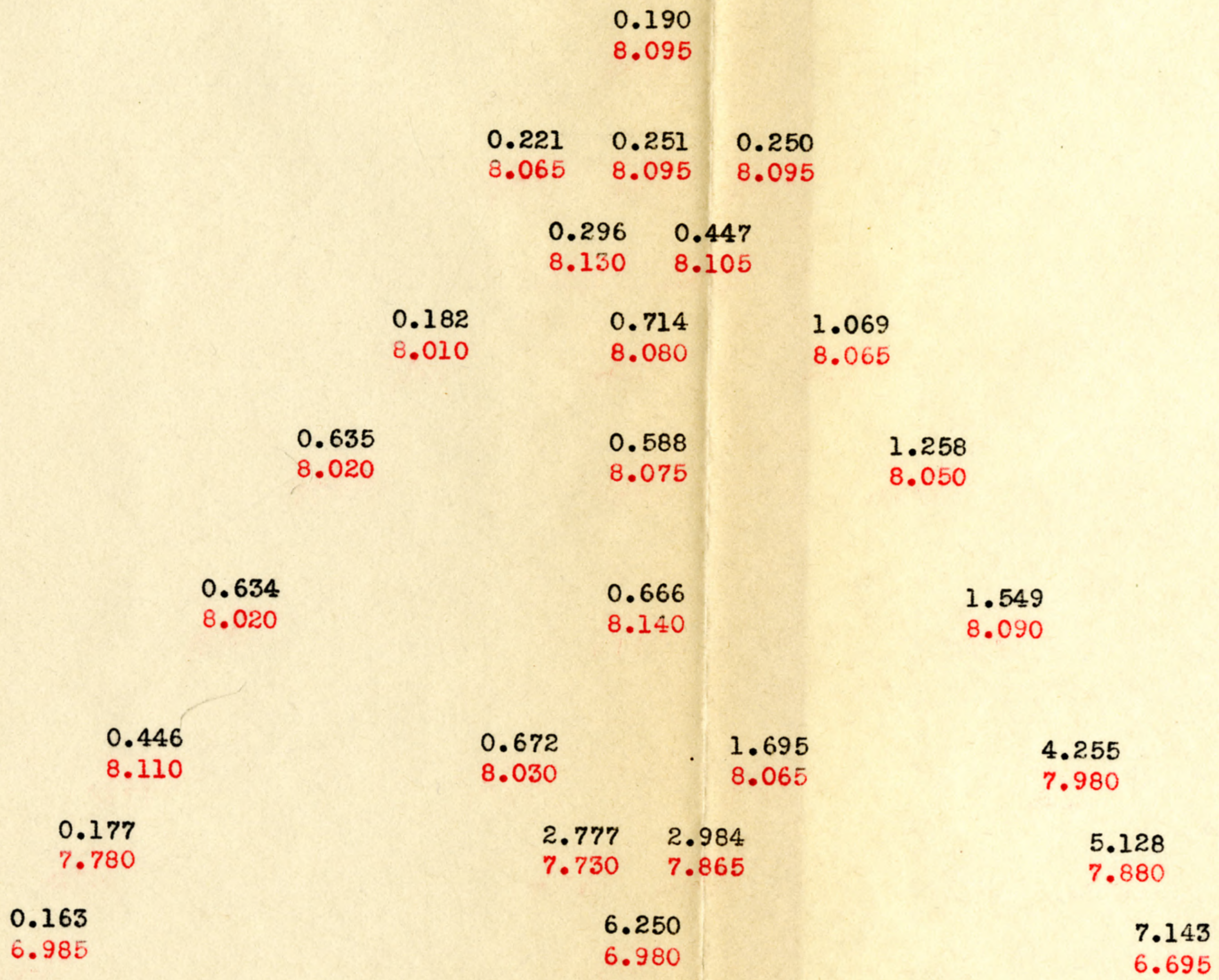
pH Values Given in Red

Table IV (continued)

Soil Treated with KCl

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.190	8.095
R_2-1	0.221	8.065
R_2-1.5	0.251	8.095
R_2-2	0.250	8.095
$R_{2.5}$-2	0.296	8.130
$R_{2.5}$-3	0.447	8.105
R_3-1	0.182	8.010
R_3-2	0.714	8.080
R_3-3	1.069	8.065
R_4-1	0.635	8.020
R_4-2.5	0.588	8.075
R_4-4	1.258	8.050
R_5-1	0.634	8.020
R_5-3	0.666	8.140
R_5-5	1.549	8.090
R_6-1	0.446	8.110
R_6-3	0.672	8.030
R_6-4	1.695	8.065
R_6-6	4.255	7.980
$R_{6.5}$-1	0.177	7.780
$R_{6.5}$-6	2.777	7.730
$R_{6.5}$-7	2.984	7.865
$R_{6.5}$-12	5.128	7.880
R_7-1	0.163	6.985
R_7-4	6.250	6.980
R_7-7	7.143	6.695

Soil Treated with KCl


0.190
8.095
0.221
8.065
0.251
8.095
0.250
8.095
0.296
8.130
0.447
8.105
0.182
8.010
0.714
8.080
1.069
8.065
0.635
8.020
0.588
8.075
1.258
8.050
0.634
8.020
0.666
8.140
1.549
8.090
0.446
8.110
0.672
8.030
1.695
8.065
4.255
7.980
0.177
7.780
2.777
7.730
2.984
7.865
5.128
7.880
0.163
6.985
6.250
6.980
7.143
6.695

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with NH_4Cl

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.342	7.960
R_2-1	0.250	7.985
R_2-1.5	0.592	8.000
R_2-2	0.402	8.020
$R_{2.5}$-2	0.259	7.995
$R_{2.5}$-3	0.620	8.055
R_3-1	0.495	8.055
R_3-2	0.394	8.035
R_3-3	0.748	8.055
R_4-1	0.352	7.995
R_4-2.5	0.491	7.995
R_4-4	1.005	8.010
R_5-1	0.350	8.025
R_5-3	1.197	7.970
R_5-5	1.307	8.035
R_6-1	0.862	7.940
R_6-3	0.553	7.855
R_6-4	0.816	8.030
R_6-6	1.694	8.020
$R_{6.5}$-1	1.111	7.885
$R_{6.5}$-6	1.360	7.910
$R_{6.5}$-7	1.923	7.865
$R_{6.5}$-12	4.000	7.815
R_7-1	0.833	6.975
R_7-4	5.128	7.060
R_7-7	6.060	7.120

Soil Treated with NH_4Cl

0.342
7.960

0.250 0.592 0.402
7.985 8.000 8.020

0.259 0.620
7.995 8.055

0.495 0.394 0.748
8.055 8.035 8.055

0.352 0.491 1.005
7.995 7.995 8.010

0.350 1.197 1.307
8.025 7.970 8.035

0.862 0.553 0.816 1.694
7.940 7.855 8.030 8.020

1.111 1.360 1.923 4.000
7.885 7.910 7.865 7.815

0.833 5.128 6.060
6.975 7.060 7.120

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Soil Treated with NaCl

Sample	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
R_1-1	0.224	8.310
R_2-1	1.438	8.580
R_2-1.5	1.025	8.430
R_2-2	0.625	8.540
$R_{2.5}$-2	0.357	8.595
$R_{2.5}$-3	0.483	8.460
R_3-1	0.377	8.460
R_3-2	0.888	8.540
R_3-3	1.321	8.495
R_4-1	0.368	8.610
R_4-2.5	0.413	8.495
R_4-4	1.550	8.435
R_5-1	0.285	8.635
R_5-3	1.408	8.455
R_5-5	3.571	8.310
R_6-1	0.298	8.520
R_6-3	1.351	8.420
R_6-4	1.818	8.480
R_6-6	3.381	8.540
$R_{6.5}$-1	0.447	8.060
$R_{6.5}$-6	2.985	8.450
$R_{6.5}$-7	3.571	8.235
$R_{6.5}$-12	5.720	8.425
R_7-1	0.533	7.350
R_7-4	6.250	7.865
R_7-7	8.333	7.270

Soil Treated with NaCl

0.224
8.310

1.438 1.025 0.625
8.580 8.430 8.540

0.357 0.483
8.595 8.460

0.377 0.888 1.321
8.460 8.540 8.495

0.368 0.413 1.550
8.610 8.495 8.435

0.285 1.408 3.571
8.635 8.455 8.310

0.298 1.351 1.818 3.381
8.520 8.420 8.480 8.540

0.447 2.985 3.571 5.720
8.060 8.450 8.235 8.425

0.533 6.250 8.333
7.350 7.865 7.270

Parts P_2O_5 per Million

pH Values Given in Red

Table IV (continued)

Water Extract of Soils

Soil treated with	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
$FeCl_3$	0.072	4.410
$AlCl_3$	0.073	6.300
$CaCl_2$	0.092	6.580
$MgCl_2$	0.119	6.650
NH_4Cl	0.723	7.020
KCl	0.307	7.035
NaCl	0.893	7.155
HCl	0.111	5.890
Untreated	0.088	6.565

REVIEW OF RELATED LITERATURE

The facts of absorption by soils have been known for years; in fact they seem to have been established by the early sixties of the past century. Soluble salts, such as potassium and ammonium sulphate, which one would expect to be easily washed out of the soil by rain water, are not, but seem to be held back in such a way that they slowly become available to plants. Apparently they are in some manner absorbed into the soil, and in the process of being absorbed they displace other cations. Later they can be replaced by other salts.

Thompson (6) appears to have made the first investigations of this phenomenon as early as 1850. Upon shaking dissolved ammonium sulphate with soil, he showed that the ammonium radical is fixed and calcium enters the solution. Way (7) took up the problem and proved that the quantities of ammonium absorbed and calcium displaced were chemically equivalent. As a result of his work Way summarized his conclusions as follows:

1. The salt was not absorbed as a whole, but only the base.
2. The filtered liquid contained the acid of the given salt united to lime.
3. The quantity of lime acquired by the solution cor-

responded exactly to that of the base removed from it-- the action was, therefore, a true chemical decomposition.

4. The combination between the soil and the base was rapid, if not instantaneous, suggesting therefore the nature of the ordinary union between an acid and an alkali.

A. Voelcker (8) and others showed that the same action takes place in the soil itself when ammonium sulphate is added in the ordinary way as manure. Potassium sulphate reacts in a similar way, the potassium being precipitated and an equivalent quantity of calcium being displaced. Potassium phosphate is completely precipitated since calcium phosphate is also insoluble. The precipitated potassium compound can be decomposed by sodium salts; hence, the addition of sodium sulphate to soil increases the amount of potassium in solution and thus acts like a dressing of potassium fertilizer. Calcium sulphate, however, does not appear to increase the amount of potassium available to plants.

During the early investigations of this subject a controversy arose concerning the mechanism of absorption. Way argued that it was a purely chemical phenomenon, and that the exchange between the ammonium and calcium was analogous to any double decomposition reaction. He then attempted to determine which constituent of the soil was responsible for the absorption, and proved that it was a part of the clay; moreover, he showed that the power of absorption was lost upon ignition. Not knowing of any simple silicates possessed of these properties, he prepared a number of double silicates which did. Although he could not prove their presence in the soil, he assumed their existence.

Way's views were generally accepted in England, but Liebig of Germany (9) contended that the phenomenon was not chemical but physical, comparable to absorption by charcoal.

Quoting Russell (9): "Knop combined both chemical and physical hypotheses. The absorption of acid radicles he attributed to precipitation by the iron and aluminum hydroxides supposed to be present in the soil: phosphoric acid, however, reacted first with the calcium compounds to form calcium phosphate and then with the iron compounds. With bases the action was rather more complex: the absorption in the first instance was due to a surface attraction, which was followed by a combination with silica or aluminum silicates: there was, however, invariably an equilibrium, the whole of the base never being removed, no matter how dilute the solution."

Russell (9) further states: "Van Bemmelen began by accepting Way's chemical hypothesis, and showed that soils with a high power of absorption usually contained a large quantity of easily decomposable silicates. Way's double silicates would presumably be of this nature. Further, absorption of bases always involved displacement of other bases from the soil, a strong indication of chemical change. Later on, however, he made extensive studies of absorption by simple gels: silica, alumina, ferric hydroxide, tin hydroxide, etc., and found it closely to resemble absorption by soils. Other studies of colloids were made, and in each case the similarity to soil phenomena was so close as to leave no doubt that soil was essentially a colloid and soil absorption simply a manifestation of the colloidal properties."

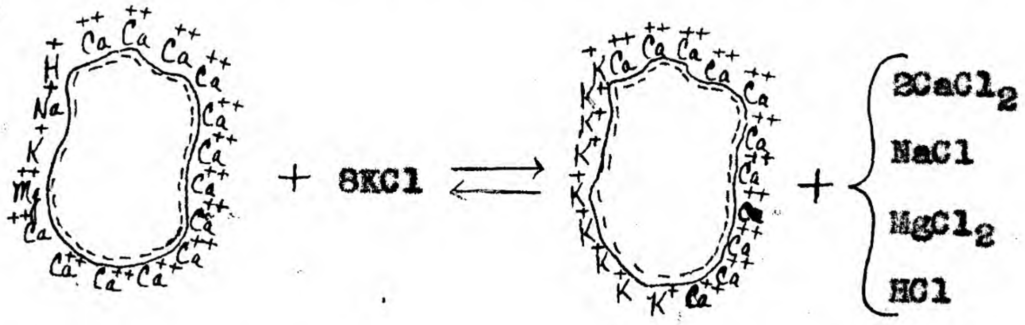
The term zeolite was applied for many years to Way's double silicates supposedly in the soil and is frequently used in earlier writings. In fact Gedroiz still uses the term very freely in his writings, but with the explanation that he merely uses it as a convenient designation of the inorganic exchange complex of soils. Judging from recent literature, however, it seems the direct evidence for the presence of zeolites is so slight that this view is now generally given up and the phenomenon of base exchange is considered to be essentially colloidal in nature.

Working upon this new idea, investigators have been able to explain many of the variations of absorption from true chemical phenomena. It is now known with certainty that there are organic as well as inorganic exchange complexes both of colloidal nature. Jones (10) states: "The colloids of the soil may be divided into two great classes: inorganic and organic. Silicic acid, silicates, aluminum hydroxide and its silicic acid and ferric hydroxide compounds belong to the farmer. Among the organic colloids are the humus compounds and the various species of micro-organisms, such as soil bacteria and fungi, as well as the mucous matter secreted by such micro-organisms."

Objections to the newer conception were made on the grounds that it did not explain the fact that absorbed bases displace an equivalent amount of some other bases from the soil, since this indicates a true chemical reaction. These objections have been met by assuming that the acid radical is not absorbed, but dissolves out other bases. As this is a purely chemical reaction, the amount of base brought out is equivalent to the acid set free, and hence in turn to the amount of base absorbed.

Thus it seems that the modern position is that the phenomonon is partly chemical and partly physical, or essentially the contention of Knop. Moreover, these phenomena have been connected up to many others either unknown during the earlier period or to which application had not been discovered. Among these is Hissink's (11) double-layer theory which he summarizes as follows: "The exchangeable bases are located on the surface of the soil particles; in other words, they occur in the adsorbed condition. The cause of this adsorption is to be sought in the chemical attraction between the bases and the clay and humus acids of the soil. When the soil is treated with water, a soil suspension is formed. A part of the surface molecules then become ionized, forming around the surface of the adsorbing clay and humus particles an electrical double layer. In the inner part of this double layer are found the anions of soil acids, in the outer part the cations: $\overset{+}{H}$, $\overset{++}{Mg}$, $\overset{++}{Ca}$, $\overset{+}{K}$ and $\overset{+}{Na}$."

Comber (12) has diagrammatically represented a soil particle as a salt, and by making use of this diagram the equation typifying base exchange might be pictured as follows:



As already stated, Way suggested that the exchange appeared to be rapid if not instantaneous, and Gedroiz showed that the establishment of equilibrium was a matter of seconds, but it varied for different cations. Repeated treatments with the same cation will finally replace all of the bases from the soil complex, but some will effect the replacement more quickly. Combining my own observations with those given by Comber, the cations arranged in descending order of their replacing power would be:

$$\overset{+++}{Fe} > \overset{+++}{Al} > \overset{++}{Mg} > \overset{+}{H} > \overset{+}{K} > \overset{+}{NH_4} > \overset{+}{Na} > \overset{+}{Li}$$

Bradfield (13) insists that there is a wide difference between the behavior of artificial permutites such as Way prepared and the natural exchange complexes of soil in the percentage of bases which are replaceable. The exchangeable fraction ordinarily constitutes from but 10-30% in clays in comparison with 95-100% in permutites. With such existing variations he insists "the only way to learn about clays is to study clays," and not some substance more unlike than like them.

According to Comber (12): "When the whole of the adsorptive power of the soil is satisfied with metallic cations, the soil is said to be saturated. When hydrogen ions are among the cations, the soil is unsaturated."

Needless to say, a subject as old, important, and far-reaching as base exchange has stimulated a vast amount of productive research. Dutch scientists (12) have found that sodium can be washed from newly reclaimed "polders" by first replacing the sodium from the saturated complexes with calcium from $CaSO_4$ and then flooding with river water. The same principle has been made use of in reclaiming alkali soils by irrigation (23). More recently attempts have been made to correlate the degree of unsaturation with lime requirement. Valuable contributions have been made by soil workers from Russia, England, France, Germany, America, Japan, and in fact from nearly every agricultural nation of the world. Obviously the briefest of reviews of all related literature is impossible, and as the chief interest of my problem lies in the fixation of anions, the phosphate ion in particular, attention will now be turned to this phenomenon.

Upon this point Comber (12) makes the concise statement: "The removal of certain anions such as phosphate ions from solution is a consequence of the exchange of bases between the soil and the solution. Whenever the cations passing from the soil into solution form insoluble salts with the anion present, that salt is, of course, precipitated with the consequent removal of the anion from the solution. When cations, going into solution, do not form insoluble salts with the anion present, that anion is never removed."

This explanation makes clear what actually takes place in the removal of phosphate ions from solution, but tells nothing of the cations responsible. Much work has been devoted to the determination of these cations and other factors which influence solubility of phosphates. As a result of such efforts it seems to be quite generally conceded that phosphate ions are rendered insoluble by combination with $\overset{+++}{Fe}$, $\overset{+++}{Al}$, or $\overset{++}{Ca}$ ions, and that after fixation, the $\overset{+}{H}$ ion concentration is a significant factor in subsequent availability.

According to Wityn (14), in neutral and slightly alkaline soils the phosphorus is present chiefly as $Ca_3(PO_4)_2$; whereas in acid soils it occurs in combination with organic materials and with Fe and Al hydroxides. With a change in reaction of the soil there is a transition of these compounds. He concludes that carbonic acid and other weak acids decrease the solubility of $FePO_4$ and $AlPO_4$, while alkaline materials increase the solubility of these phosphates. Liming acid soils, therefore, increases the solubility of the phosphates by changing them into calcium phosphates, which in turn appear to be somewhat susceptible to the solvent action of carbonic acid. Thus acid soils usually contain larger amounts of P_2O_5 than neutral or productive soils, because the P_2O_5 is less available.

Spurway (15) partially saturated with calcium, magnesium, and potassium, by a neutral salt extraction method, each of four sandy loams of different reaction and containing different amounts of active bases. Upon determining the effect of each upon the retention of phosphorus applied as $CaH_4(PO_4)_2$, he found that the KCl treatment increased the solubility over the check in all cases and the $MgCl_2$

in all but three cases; whereas, the $CaCl_2$ treatments decreased the solubility of phosphorus in the neutral and alkaline soils and increased it in the acid soil except in three cases of very heavy application.

Ingham (16) observed that the availability of phosphorus is generally low on acid soils and high on non-acid soils. He found it to be closely related to the contents of Fe, Al, and organic matter. Fe and Al phosphates precipitated by super-phosphate were readily soluble in 1% citric acid; hence, it is suggested that low availability may be due to the adsorptive power of organic and inorganic colloids, especially those of iron and aluminum. Acid soils have a high adsorptive capacity for P_2O_5 as well as for CaO; however, it appears probable that flocculation of the inorganic colloids would reduce their excessive adsorption capacity. This conception was substantiated when the removal of the $CaCO_3$ from a soil containing a large amount of iron and aluminum doubled the absorption capacity, but reduced the citric acid solubility to one-half. It appeared also that excessive adsorption by organic colloids might be prevented by creating conditions favorable to decomposition of humus as by liming. For these experiments it was assumed that the solubility in 1% citric acid was a fair measure of availability of phosphorus, but it is likely that the use of a solution of H_2CO_3 would be more in accordance with conditions actually present in the soil.

That the solubility of phosphates is greatly affected by the nature of the acid used and the presence of other compounds has been shown by Kappen and Bolfenbeck (17). A solution of humic acid was shown to dissolve $Ca_3(PO_4)_2$. More phosphate is dissolved in soil of the same pH value when the acidity is due to neutral salt decomposition than when due to hydrolytic dissociation and less when due to base exchange. The presence of K_2SO_4 or colloidal SiO_2 increases the solubility in each case, but artificial permutites do not. It seems that SiO_2, in some manner, facilitates the transportation of H_3PO_4 into the plant body.

Breazeale and Burgess (18) make an interesting explanation of the role played by CO_2 in rendering phosphorus available in acid and alkaline soils. The presence of CO_2 in solution increases the solubility and availability of both $Ca_3(PO_4)_2$ and $CaHPO_4$. In western soils that contain black alkali there is no free CO_2; hence, the solvent action of H_2CO_3 upon insoluble phosphorus is eliminated. Iron and aluminum hydroxides react slowly with calcium phosphate to form insoluble iron and aluminum phosphates. This action is accelerated by the presence of carbonic acid alone, but retarded by carbonic acid plus $CaCO_3$.

Teakle (19) asserts that $FePO_4$ is least soluble under acid conditions corresponding to pH 3. Under less acid conditions $Fe(OH)_3$ is precipitated at the expense of $FePO_4$, and some PO_4 ions are liberated. Mn and Al phosphates are least soluble under slightly acid conditions; whereas calcium phosphate is insoluble under alkaline conditions. Excess Ca ions in the presence of OH ions appear to be the main factors in the depression of the solubility of calcium phosphate. OH ions alone probably cause the formation of a basic phosphate with the liberation of some PO_4 ions. Comparison of the solubility of the various phosphate ions in pure solutions with the concentrations found in soil solutions suggests that the chemical properties of the compounds account for the behavior of soil phosphates. Adsorption of PO_4 ion appears to be unimportant if it occurs at all in soils. Calcium is the base most important in controlling the PO_4-ion concentrations in neutral soils. Organic forms of phosphorus may constitute an important part of the total phosphorus in solutions from certain soils, but not from all.

Miller (20) determined the extent to which the PO_4 ion is carried down by precipitated $Al(OH)_3$ at different H-ion concentrations in solutions which he believed to be at least partially applicable to hydrated Al_2O_3 and Fe_2O_3 of soil colloids. From the pH value at which precipitation begins up to a pH value of 4.5 the mol ratio of Al_2O_3 to P_2O_5 was 1:1; that is, the precipitate had the composition $AlPO_4$. At higher pH values the PO_4 content of the precipitate rapidly decreased. The H-ion concentration at which the PO_4 content of the precipitate became zero was not realized, since the precipitates formed at the higher pH values were extremely colloidal and difficult to study; however, the indications were that at pH values above 8.5 the PO_4 content was very small.

Ungerer (21) showed that the amount of H_3PO_4 extracted from phosphates of magnesium, calcium, aluminum, and iron is affected by the reaction of the extracting solutions and the presence in it of electrolytes and univalent permutites. Neutral salts decrease the solubility of $FePO_4$ and $AlPO_4$ and increase the pH value of the solution. Clay and potassium and ammonium permutites absorb Ca and Mg ions from the above phosphates, and an equivalent amount of phosphate appears in solution. In soils $FePO_4$ and $AlPO_4$ in the presence of neutral salts are involved in base exchange activities, and titratable $Al(OH)_3$ is found in solution. The value of these phosphates as plant nutrients depends on the water and chalk content and on the reaction of the soil. When the soil moisture rises to 90% of the maximum capacity, $AlPO_4$ has a greater nutrient value than $CaHPO_4$. Soil reactions more acid than pH 5 decrease the nutrient values of Fe and Al phosphates.

Gaarder (22) studied the solubilities of the phosphates of Fe, Al, Ca, and Mg in dilute solutions of varying reaction and base content. In solutions containing equivalent quantities of P_2O_5 and base the solubility of $FePO_4$ reached a minimum at a pH of about 2.2 and then increased gradually up to a pH of 8.0; whereas, above pH 8 and below 2.2 the solubility increased rapidly. The solubility of $AlPO_4$ reached a minimum at a pH of about 3.7. For the solubility of $Ca_3(PO_4)_3$ the minimum was reached at a pH of approximately 6.5 and then remained fairly constant at least up to pH 11. In the case of magnesium phosphate the P_2O_5 has a minimum solubility at pH 10, the solubility being greater at lower and higher pH values. In the presence of an excess of the base the solubility of P_2O_5 is at a minimum over a wider range of pH values than when the P_2O_5 and the base are present in equivalent quantities. The variable effects of soil treatments on the solubility of phosphates are attributed to differences in the quantity and nature of the base present, either in the adsorbed or soluble condition. Within the pH of normal soils the phosphate of Fe and Al are of prime importance in controlling phosphate solubility. In soils rich in "active" sesquioxides, within the pH range of 4.0-7.5, the phosphate is largely insoluble, and liming does not always effect an improvement. In humid and semi-humid soils containing humus the solubility of the phosphates depends mainly on the relative proportions of "active" sesquioxides and humus present, the former tending to decrease and the latter to increase the solubilities. From such soils having only a moderate sesquioxide content and pH values of 4.5-6.5, P in organic combination may be leached sufficiently rapidly to bring about a phosphate deficiency. Where lime did not increase the solubility of the P_2O_5 in soils rich in sesquioxides, treatment with sodium silicate proved effective, presumably by the precipitation or "deactivation" of sesquioxides.

Reports of much valuable work pertaining less specifically to this problem are available, but because of limited space will not be mentioned here. Instead of a further perusal of literature attention will now be turned to a discussion of the results obtained.

DISCUSSION OF RESULTS AND CONCLUSIONS

Although the major interest of the problem lies in the results of the phosphate solubility tests, the effect of electrolytes upon the soil suspensions deserves at least passing notice. It was plainly obvious that the electrolytes differ greatly in flocculating power. $FeCl_3$, $AlCl_3$, $CaCl_2$, and $MgCl_2$ appeared to flocculate and precipitate the suspended material in much lower concentrations than the HCl, NH_4Cl, KCl, and NaCl. In fact low concentrations of NaCl, KCl, and NH_4Cl seemed actually to deflocculate or disperse the suspensions. Only the qualitative effect was observed, and no attempt was made to determine the lowest concentration which would produce complete precipitation; however, this has been done by Gedroiz (24) for a large number of acids, bases, and salts under what he terms "electrolytic limits."

The concentration and nature of the dissolved electrolytes explain why water in streams and ponds from a limestone "water-shed" is perfectly clear a few hours after a rain, while in others it is often turbid with suspended material for weeks and even months. Deltas are deposited at the mouth of rivers largely because of the coagulating and precipitating influences of the electrolytes present in the ocean water. Moreover, it seems highly probable that the damage to soils by erosion is very materially influenced by their inorganic constituents, a fact not generally recognized by farmers of my acquaintance.

It was also interesting to notice the contrast in the physical properties of the soil due to saturation with different cations. When wet, the samples treated with $FeCl_3$, $AlCl_3$, and $CaCl_2$ filtered readily, packed only moderately, and were quite pervious to water. When dry, they crumbled freely and were quite easily reduced to powder. On the other hand, those samples treated with KCl and NaCl when wet were sticky, gummy masses, highly impervious to water, packed so tightly in the beakers and bottles as to be almost impossible to dislodge and were very difficult to filter. When dry they formed hard lumps that were almost impossible to powder. The properties of the samples saturated with magnesium, ammonium, and hydrogen were between these two extremes. Thus it is certain that the physical condition of soils is profoundly affected by the bases with which they are saturated.

A careful examination of the results of the chemical analysis of the differently treated soils reveals several interesting facts. The high SiO_2 content at first strikes one as being unusual, but appears quite ordinary when compared with the average given by Hilgard (25) for soils from many states.

Likewise the much greater percentage of magnesium than calcium might cause one to doubt the accuracy of the analysis; however, again referring to Hilgard (25) this is a common occurrence among soils badly in need of lime. Tables are given showing much wider differences than those reported here. In fact, he states: "It will be observed that the general average for magnesia in the soils of the Atlantic Slope is about double that of lime; Florida and

Rhode Island being the only states in which the average is lower for magnesia than for lime. In the arid region, on the contrary, magnesia on the general average is nearly the same as lime; in the average by states somewhat less; .... This also is so decisive a showing that no accident could bring it about." When one stops to consider the high calcium content of drainage water this is exactly what he would expect for soils subjected to considerable rainfall.

The amount of Fe_2O_3, Al_2O_3, P_2O_5, NH_4, and K_2O is so ordinary as to escape notice; however, a startling variation appears in the case of Na_2O. It seems almost impossible that this amount of sodium could be so firmly held as to resist removal by from 7-19 extractions with salt solutions and from 7-15 washings. Yet such seems to be the case, for a recheck on about half of the soils showed very satisfactory agreement, and a very careful recheck on two more gave similar results. Two tables given by Hilgard (25) show more Na_2O than K_2O in soils from North Dakota and Nevada; however, this seems to be rare except in cases of alkali soils. The most plausible explanation seems to be that the soil contains some stable sodium feldspar or other insoluble aggregate which remained unaffected by the treatments.

The results show that the soil contained replaceable

Ca, Mg, K, and Na, all of which are ordinarily accepted as occurring in the replaceable condition in certain soil types; however, replaceable Fe and Al (the results from the $MgCl_2$ treated soil is an exception, probably an error in the determination) are also indicated. This is more unusual, but is not unheard of. Smolik (26) reports that exchangeable Al was found in all layers of a large number of soils of the podsol type, forest as well as tilled, ranging from 21.1 to 229 mg. per 100 gms. of dry soil. Kelley and Brown (27) found the acid soils which they examined were characterized by a low total quantity of replaceable bases, and by the presence in replaceable form of Al, Fe, or Mn.

On the other hand this Al and Fe may not occur in the replaceable form, but may enter the solution slowly and gradually under the influence of the acids formed from neutral salt decomposition. Either phenomenon would decrease the total of Al and Fe in the extracted soils and be in accord with the results obtained.

A careful examination of the results of the phosphorus solubility tests show essentially what would be expected in spite of many apparent exceptions. Listing the results from R_5-3, a central point of the triangle, which received 10 tons of $CaCO_3$, 400 lbs. of KCl, and 400 lbs. of $CaH_4(PO_4)_2$ per acre, a comparison of the effect upon the solubility of the phosphate ion is obtained.

Soil treated with	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
$AlCl_3$	0.094	7.385
$FeCl_3$	0.101	7.385
HCl	0.102	7.465
$CaCl_2$	0.179	7.875
Untreated	0.248	7.610
$MgCl_2$	0.335	7.960
KCl	0.666	8.140
NH_4Cl	1.197	7.970
NaCl	1.408	8.455

Since all factors except the base absorbed by the soil were constant these results should serve to show the effect upon phosphate solubility of saturating the soil complexes with different cations.

Considering the two extremes Al-soil and Na-soil one might imagine the reactions accounting for these results to be:

$$\text{Al-soil} \rightleftharpoons \overset{+++}{\text{Al}} + \overset{---}{\text{soil}}$$

$$\text{CaH}_4(\text{PO}_4)_2 \rightleftharpoons \overset{++}{\text{Ca}} + \overset{--}{\text{H}_4(\text{PO}_4)_2}$$

$$2\overset{---}{\text{soil}} + 3\overset{++}{\text{Ca}} \rightleftharpoons \text{Ca}_3(\text{soil})_2$$

$$2\overset{+++}{\text{Al}} + 3\text{H}_4(\text{PO}_4)_2 \rightleftharpoons \text{Al}_2(\text{H}_4(\text{PO}_4)_2)_3$$

$$\text{Al}_2(\text{H}_4(\text{PO}_4)_2)_3 + 6\text{CaCO}_3 \rightleftharpoons \underset{\downarrow}{\underline{2\text{AlPO}_4}} + \underline{2\text{Ca}_3(\text{PO}_4)_2}\downarrow + 6\text{H}_2\text{CO}_3$$

But the $AlPO_4$ and Ca_3PO_4 are both highly insoluble, and the phosphorus is precipitated; whereas, in the case of the sodium treated soil:

$$\text{Na-soil} \rightleftharpoons \overset{+}{\text{Na}} + \overset{-}{\text{soil}}$$

$$CaH_4(PO_4)_2 \rightleftarrows \overset{++}{Ca} + H_4(\overset{--}{PO_4})_2$$

$$2\overset{+}{Na} + H_4(PO_4)_2 \rightleftarrows Na_2H_4(PO_4)_2$$

$$3Na_2H_4(PO_4)_2 + 6CaCO_3 \rightleftarrows \underline{2Ca_3(PO_4)_2}\downarrow + 2Na_3PO_4 + 6H_2CO_3$$

Although $Ca_3(PO_4)_2$ appears again, the Na_3PO_4 is soluble, thus accounting for the greatly increased phosphorus solubility.

Similar equations for the other saturated soils would serve to explain their effect upon the soluble phosphorus. The Fe-soil would ionize and insoluble $FePO_4$ would be formed, Ca-soil would tend to form $Ca_3(PO_4)_3$, the Mg-soil $Mg_3(PO_4)_2$, etc. The fact that the untreated soil contained a small amount of replaceable K and Na would account for greater phosphate solubility than in the case of Al-soil, Fe-soil, and Ca-soil; moreover, the replaceable Ca and Mg and possibly Al and Fe would hold this solubility below that for the K-soil, NH_4-soil, and Na-soil. The solubility of $Mg_3(PO_4)_2$ in water is approximately ten times as great as that of $Ca_3(PO_4)_2$, hence the greater solubility in the case of the Mg-soil. At first one might wonder why the H-soil did not render the phosphorus highly soluble since H_3PO_4 would be formed; however, this in turn would likely react with the $CaCO_3$ to form $Ca_3(PO_4)_2$ or to bring Fe or Al ions into solution and be precipitated out by interaction with them. Evidence for the latter hypothesis is found in the fact that the water extract from the H-soil to which no $CaCO_3$ had been added contained but little more phosphorus than the filtrate from R_5-3. Since $(NH_4)_3PO_4$ and K_3PO_4 are both soluble, the increased phosphate solubility in the case of the K-soil and NH_4-soil can be accounted for in the same way as that of the Na-soil.

Nor is the one point selected above the only point in the tables which shows a marked effect upon the phosphate solubilities; in fact, it is quite typical of the general trend of the results. Considering $R_{6.5}$-12, which received only 2.5 tons of lime, no KCl, and 1100 lbs. of $CaH_4(PO_4)_2$ per acre, a marked variation is apparent:

Soil treated with	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
$FeCl_3$	0.099	6.660
$AlCl_3$	0.109	6.885
Untreated	0.661	7.510
HCl	1.036	6.475
$CaCl_2$	1.562	7.805
$MgCl_2$	1.574	7.895
NH_4Cl	4.000	7.815
KCl	5.128	7.880
NaCl	5.720	8.425

Although the sequence of increasing solubilities is changed, it is very obvious that Fe-soil, Al-soil, and U-soil precipitated much more of the added phosphorus than did the H-soil, Ca-soil, and Mg-soil, which in turn precipitated much more than did the NH_4-soil, K-soil, and Na-soil; results which harmonize well with those cited before.

R_4-1 received 15 tons of lime, 600 lbs. of KCl, and no $CaH_4(PO_4)_2$ per acre; hence, the phosphorus in the filtrate came entirely from the soil, yet the results show the same typical variation:

Soil treated with	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
$FeCl_3$	0.071	7.350
$CaCl_3$	0.071	8.020
Untreated	0.075	7.710
$AlCl_3$	0.082	7.380
HCl	0.109	7.735
$MgCl_2$	0.128	7.895
NH_4Cl	0.352	7.995
NaCl	0.368	8.610
KCl	0.635	8.020

Again the six rendering the phosphate least soluble were the Fe-soil, Ca-soil, U-soil, Al-soil, H-soil, and Mg-soil. Comparing these now with the phosphorus in the water extract at least comparable results are obtained:

Soil treated with	Parts P_2O_5 per million parts of filtrate	pH value of the filtrate
$FeCl_3$	.072	4.410
$AlCl_3$	.073	6.300
Untreated	.088	6.565
$CaCl_2$	.092	6.580
HCl	.111	5.890
$MgCl_2$	.119	6.650
KCl	.307	7.035
NH_4Cl	.723	7.020
NaCl	.893	7.155

Thus, the results show quite conclusively that the nature of the cation with which the soil is saturated profoundly affects the solubility of inorganic phosphorus;

moreover, it appears that the cations responsible for its precipitation are $\overset{+++}{Fe}$, $\overset{+++}{Al}$, $\overset{++}{Ca}$, and $\overset{++}{Mg}$; the first three apparently rendering it more insoluble than the $\overset{++}{Mg}$. This then is the answer to one of the questions which were raised in the beginning: namely, that the formation of iron, aluminum, calcium, and magnesium compounds precipitate the phosphorus into the soil and cause it to be only sparingly available to plants. However, such a naturally occurring condition should not be considered unfortunate, but on the contrary one of the wise provisions of nature. Without such a provision all of the phosphorus would be quickly removed from the soil, either by plants or by leaching, and the soil would become sterile. Also a too concentrated solution of phosphorus would quite likely be harmful to plants instead of being beneficial. Parker (28), working upon the phosphorus needs of corn plants, found a very dilute solution of inorganic phosphorus was sufficient for optimum growth, if constantly maintained; whereas, a 1% solution of potassium and phosphorus compounds was shown by Avattaneo (29) to be actually toxic.

The effect of KCl upon the solubility of the phosphate ion can best be observed by comparing the results of the water extract with the results for the points $R_{6.5}$-1 and R_7-1. $R_{6.5}$-1 received 2.5 tons of $CaCO_3$, no $CaH_4(PO_4)_2$, and 100 lbs. of KCl per acre; while R_7-1 received no $CaCO_3$, no

$CaH_4(PO_4)_2$, and 1200 lbs. of KCl per acre:

Soil treated with	Parts P_2O_5 per million parts of filtrate		
	Water extract	$R_{6.5}$-1	R_7-1
$FeCl_3$	.072	.094	.078
$AlCl_3$	.073	.087	.112
Untreated	.088	.132	.194
$CaCl_2$	.092	.197	.144
HCl	.111	.242	.638
$MgCl_2$	.119	.165	.143
KCl	.307	.177	.163
NH_4Cl	.723	1.111	.833
NaCl	.893	.447	.533

An increase in phosphorus solubility over that in the water extract is observed for both points in the case of the Fe-soil, Al-soil, U-soil, Ca-soil, H-soil, Mg-soil, and NH_4-soil; whereas, a decrease is shown in the case of the Na-soil and K-soil. That such would be the case seems altogether probable considering the usual effect of dissimilar ions upon the solubility of compounds. The mechanism of the reaction accountable for increased solubility might be typified by $Ca_3(PO_4)_2$:

$$Ca_3(PO_4)_2 \rightleftharpoons 3\overset{++}{Ca} + 2\overset{--}{PO_4}$$

$$KCl \rightleftharpoons \overset{+}{K} + Cl$$

$$3\overset{+}{K} + PO_4 \rightleftharpoons K_3PO_4$$

The K_3PO_4 being readily soluble would tend to increase the phosphate solubility. Lower solubilities in the case of the K-soil are possibly due to the common ion effect; however, the Na-soil is plainly an exception.

It is true that applications of 1100 and 1200 lbs. of

KCl per acre are much heavier than could profitably be used, but it is probable that the lighter applications produced proportionate increases, which were too slight to be perceptible by the methods used, yet enough to materially benefit plants.

An attempt to correlate phosphorus solubility and pH values from the results discloses so many variations that specific differentiation is impossible, and only broad tendencies can be cited. In general it appears that soils with a high pH value render the phosphorus more soluble than do those with a low pH value; and so far as $AlPO_4$ and $FePO_4$ are concerned a higher pH value would tend to cause more phosphorus to enter solution because of hydrolysis. Thus,

$$AlPO_4 + 3HOH \rightleftarrows Al(OH)_3 + H_3PO_4$$

Since the $Al(OH)_3$ is insoluble this would cause the equilibrium to shift to the right, and more soluble phosphorus would be formed. With $Ca_3(PO_4)_2$, however, it appears that the reverse would be true.

$$Ca_3(PO_4)_2 + 6HOH \rightleftarrows 2H_3PO_4 + 3Ca(OH)_2$$

Increasing the $\overline{OH}$ ion concentration here would shift the equilibrium to the left, and phosphorus would be precipitated. Hence, the true cause for the differences in the phosphate solubilities more likely lies in the nature of the cation with which the soil is saturated, and the high pH value is merely incidental instead of being the causative agent.

Low pH values would result from the hydrolysis of Fe-soil and Al-soil, because $Fe(OH)_3$ and $Al(OH)_3$ would be precipitated, and the H ions would combine with the soil particles; whereas, hydrolysis of K-soil, Na-soil, NH_4-soil, Ca-soil, and Mg-soil would cause a rise in pH values due to the formation of strongly ionized bases.

The reactions of the filtrates from Na-soil and NH_4-soil were well above the neutral point without the addition of any $CaCO_3$. Two and a half tons of $CaCO_3$ per acre brought the pH values of the K-soil, U-soil, Mg-soil, and Ca-soil filtrates above the neutral point, while five tons of $CaCO_3$ per acre produced neutrality in the filtrates from Fe-soil and Al-soil and approximate neutrality in the filtrate from the H-soil.

SUMMARY OF CONCLUSIONS

1. Electrolytes differ markedly in their power to flocculate soil suspensions. Thus, the inorganic constituents of soils have an important bearing upon the content of drainage water, the amount of organic matter leached from the soil, and the damage due to erosion.

2. The cations with which soils are saturated greatly affect their physical texture, porosity, tendency to puddle when wet, and friability when dry. Iron, aluminum, and cal-

cium produced favorable qualities, potassium and sodium very undesirable qualities; whereas, magnesium, ammonium, and hydrogen produced qualities ranging between the two extremes.

3. Analyses of the soils show quite ordinary percentages of the constituents determined, except Na_2O, which is extraordinarily high.

4. Fe-soil, Al-soil, U-soil, Ca-soil, H-soil, and Mg-soil rendered phosphorus much more insoluble than did K-soil, NH_4-soil, and Na-soil. It appears that $\overset{+++}{Fe}$, $\overset{+++}{Al}$, $\overset{++}{Ca}$, and $\overset{++}{Mg}$ are the cations responsible for precipitating phosphorus into the soil. The $\overset{+}{H}$ ion of the H-soil apparently causes the phosphate ion to be precipitated by bringing $\overset{+++}{Fe}$, $\overset{+++}{Al}$, or $\overset{++}{Ca}$ ions into solution.

5. Heavy applications of KCl, alone or accompanying light applications of $CaCO_3$, appeared to increase phosphate solubility above that in the water extract of the differently treated soils, except in the filtrates from the K-soil and Na-soil. It seems probable that lighter applications of KCl would produce proportionate increases in phosphate solubility, too small to be detected by the methods used, yet large enough to benefit plants.

6. The results show no close correlation between pH value and phosphorus solubility, the pH values probably being incidental to the cations with which the soils were saturated rather than the cause of the variations in solu-

bilities.

7. The low pH values in the filtrates from the Al-soil and Fe-soil are likely due to hydrolytic dissociation, which results in the precipitation of $Al(OH)_3$ and $Fe(OH)_3$ and increased concentration of $\overset{+}{H}$ ions.

8. That five tons of $CaCO_3$ produced a favorable reaction in the filtrate from even the most acid soils is a point of practical interest.

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