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POTASSIUM IN CALCAREOUS SOILS

PART I—SOLUBILITY AND AVAILABILITY

PART II—SOME PROPERTIES OF REPLACEABLE
POTASSIUM

By W. T. McGEORGE

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POTASSIUM IN CALCAREOUS SOILS

BY W. T. McGEORGE

PART I.—SOLUBILITY AND AVAILABILITY

INTRODUCTION

The Westward shifting of crop acreages in the United States is a migration which has been in operation for more than a century. Within the last 25 years Eastern and Southern farmers have become large consumers of commercial fertilizer. This practice has been found to be necessary to maintain profitable crop yields and to recoup lost fertility. Thus, for the past 15 years, at least, the migration toward the West is from fertilizer using to non-fertilizer using lands. Most virgin lands possess an ample supply of plant food, a so-called natural fertility, which has been stored up in their confines during the process of soil formation. It is inevitable that this supply will sometime be exhausted or that disintegration and solution of the soil minerals will reach a point where it will not be sufficiently rapid to meet the immediate needs of crops. With limited areas of desirable lands now available in the West, the experiences of Eastern and Southern farmers suggest that it is not amiss for the students of Western soils to "take inventory" and to guide the farmers, in so far as is possible, in attempting to conserve the plant food reserves of our Western soils.

In the great arid Southwest nitrogen is, of course, the most deficient plant food. This is clearly manifested in the large number and variety of leguminous plants which make up the natural flora. The plants which have survived, other than cacti, are largely those which have been able to obtain their nitrogen from the air. Phosphorus is abundant in Arizona soils, but due to factors which depress the availability and solubility (4), as well as its absorption by crops, phosphate fertilization is often necessary and is a steadily growing practice. On the basis of consumption, potassium is usually classified as the third most important plant food in fertilizer because it is usually the last to be exhausted from soils. While it must be admitted that the requirement of most soils and crops for potassium is less urgent than for nitrogen or phosphorus, nevertheless soils are frequently found in which it is a major limiting factor in crop production, both as to amount and quality of the crop.

So far as we have been able to learn there is no definite information regarding the need, or rather the status, of potassium in Southwestern arid soils. This applies especially to the influences which the existing environmental conditions exert on the solubility and absorption of potassium by crops. The present investigation is therefore in the nature of a preliminary study of soil potassium as it relates to Southwestern agriculture.

In the problem of potassium fertilization there are four important things to consider, namely (a) the amount of potassium in the soil; (b) its availability or solubility; (c) factors affecting potassium absorption by crops; and (d) the cropping program, that is, whether single cropping or rotation is practiced.

The average soil contains 30,000 to 60,000 pounds potassium per acre-foot of soil. This is much higher than is true for nitrogen or phosphorus. Most of the potassium is, however, present in a form which is not only insoluble in water but also insoluble in many acids. The feldspars (orthoclase and microcline) and the micas (biotite and muscovite) carry the major portion of soil potassium. In fact McCaughey and Fry (18) found these four to be the only potassium minerals present in soils. The rate of solution of potassium from these minerals, under soil conditions, is almost negligible in so far as the immediate need of the crop is concerned. Thus, one cannot be guided by the amount of total potassium present in soils. Often soils containing large reserves will return a profit from potassium fertilization.

The soil potassium which is of immediate value to crops consists of the forms present in the soil solution or those in loose combination with the soil colloids. These include the chloride, sulphate, and nitrate of potassium and the replaceable or adsorbed potassium. They represent only a small percentage of the total amount of potassium present in the soil. Where soils are intensively cropped this supply may be largely exhausted in a comparatively short time, especially in a single-cropping system where the entire crop is removed from the field. Thus, potassium fertilization is found to be most extensively practiced on the older agricultural lands, such as those of Europe and southern or eastern United States.

Exchangeable potassium is largely held in the clay fraction of the soil and for this reason sandy soils, which are often lacking in clay and thus in fixing power, are often deficient. The capacity of the soil to adsorb or fix potassium is indeed a fortunate property but it is extremely variable. It is subject to loss or exchange when soil comes in contact with water containing salts (ions) in solution. That is, if a soil is leached with water containing the salts of sodium, calcium, or magnesium, as irrigation water usu-

ally does in arid regions, potassium will be set free from the clay, its place will be taken by the predominant base of the leaching solution, and potassium will either be lost or reabsorbed farther down by the subsoil. Fortunately clay has a greater affinity for potassium than for sodium and it therefore strongly resists replacement by this base which is the most common in our irrigation waters.

Peat soils, acid soils, and soils subject to heavy rainfall and leaching are usually deficient in potassium. Under these conditions, potassium may be displaced by hydrogen to form acid soils, the hydrogen being formed by the slight ionization of water and of carbonic acid produced by biological respiration. Hydrogen is much more active than other bases in displacing potassium which explains why acid soils are so often in need of potassium fertilization. In arid soils where just the opposite conditions prevail, namely little rainfall and no excessive leaching, soils should require less potassium fertilization and retain their natural supply of potassium for longer periods against cropping.

The system of cropping in part determines the limit of time a soil will be able to supply potassium from its own reserves. That is to say, while large amounts of nitrogen and phosphorus are stored in the seed and other marketable parts of the crop, potassium is largely present in the leaves and stems or other vegetative parts. Hence, if the leaves or straw of grain crops, to cite an example, are allowed to remain on the field a large part of the potassium used during the life of the crop will be returned to the soil. The potassium held in plant tissues is almost completely soluble in water and so, very soon after the residual plant material becomes dry, the potassium is washed back into the soil.

During investigations on phosphorus availability and its absorption by plants from arid soils, which have been conducted in this laboratory (4), it was found that the soil environs may exert a very great influence upon the assimilation of phosphorus by plants, regardless of its solubility in the soil solution. Whether potassium assimilation is likewise affected is not known, but this will be made a part of our future investigations.

EXPERIMENTAL

SOIL SAMPLES

As we had a set of Arizona soils on hand (19) which had been used in our phosphate work, these were selected for a preliminary study of potassium determinations by a number of methods. They represent Yuma sands (Superstition Series) from the Yuma Mesa, clay soils from the Yuma Valley and Santa Clara Valley,

and a wide variety of soils from the Salt River Valley. Except to state that all were calcareous soils, pH varying from 7.5 to 9.0, a description of the soils will be omitted for brevity.

METHODS OF ANALYSIS

Total potassium.—The total amount of potassium in these soils was determined by evaporating 1 gram soil in a platinum dish, on the steam bath, with hydrofluoric and nitric acids, followed by addition of sulphuric acid, and then gently heating over a Bunsen flame. Silicates were easily decomposed by this method and all silica completely removed by volatilization as silicon tetrafluoride. The residue was taken up in HCl and potassium determined by the regular method as potassium chlorplatinate after removing the interfering elements.

Water-soluble potassium.—Water-soluble potassium was determined by shaking one part soil with five parts water for 5 hours in an end-over-end shaking machine. Filtration was made through paper and potassium determined colorimetrically in the filtrate by the cobaltinitrite method (5).

Carbonic-acid-soluble potassium.—The solubility of potassium in carbonic acid was determined by passing CO₂ through a mixture of one part soil and five parts water for 15 minutes and then shaking the whole for 5 hours. Potassium was determined colorimetrically in the solution after filtration.

Replaceable potassium.—Replaceable potassium was determined by three methods: leaching with 0.1 N solutions of ammonium chloride or acetate; leaching with a saturated solution of gypsum; and leaching with 0.1 N calcium-chloride solution. By means of a preliminary study of the replacement activity it was found that by leaching 25 grams of soil with 250 cc. of 0.1 N solutions of ammonium salts a complete replacement of potassium could be accomplished. Hence all of the data presented in this bulletin were determined using this proportion of soil to displacing solution.

COMPOSITION OF SOILS

The results obtained in the analyses of soils by the above methods are given in Table 1.

These data show that the total amount of potassium present in Arizona soils is above the average, varying in these samples from a minimum of 1.37 to a maximum of 3.01 percent. This is equivalent to 41,100 and 90,300 pounds potassium per acre-foot using 3,000,000 pounds as the weight of one acre-foot of soil. The replaceable potassium, that is, the supply which should be readily available for crops, varies from 0.017 to 0.173 percent or 510 pounds to 5,190 pounds per acre-foot. Water-soluble potassium,

TABLE 1.—POTASSIUM IN A REPRESENTATIVE SET OF ARIZONA SOILS—PERCENT K.

Soil No.	Rep. K by NH ₄ Cl	Rep. K by NH ₄ C ₂ H ₃ O ₂	Water-sol. K	Carbonic acid-sol. K	Rep. K by CaSO ₄	Total K	District
1	.072	.067	.0083	.020	.049	2.31	Litchfield
2	.056	.053	.0067	.015	.040	1.95	Litchfield
3	.062	.055	.0069	.021	.027	2.32	Litchfield
4	.103	.092	.0074	.021	.058	2.38	Litchfield
5	.026	.024	.0037	.008	.015	2.40	Litchfield
6	.030	.037	.0031	.007	.018	2.15	Marinette
7	.017	.017	.0041	.003	.013	1.67	Marinette
8	.056	.058	.0069	.020	.046	1.68	Laveen
9	.027	.026	.0075	.007	.023	2.64	Laveen
10	.083	.087	.0056	.020	.047	2.76	Kyrene
11	.170	.173	.0134	.044	.090	3.01	Kyrene
12	.127	.129	.0097	.032	.061	2.55	Kyrene
13	.160	.138	.0093	.034	.067	2.50	Kyrene
14	.082	.091	.0064	.032	.043	2.59	Tempe
15	.078	.082	.0078	.024	.041	2.34	Tempe
16	.116	.114	.0118	.028	.044	2.47	Tempe
17	.146	.131	.0069	.031	.042	2.18	Tempe
18	.044	.043	.0044	.013	.023	2.30	Peoria
19	.023	.032	.0048	.011	.019	2.44	Peoria
20	.020	.023	.0028	.008	.017	2.25	Scottsdale
21	.034	.024	.0071	.016	.012	2.00	Yuma Valley
22	.095	.090	.0096	.051	.043	2.36	Sacaton
23	.109	.111	.0321	.067	.076	1.77	Bard, Calif.
24	.032	.029	.0040	.011	.022	1.70	Yuma Mesa
25	.031	.029	.0058	.010	.025	1.59	Yuma Mesa
26	.023	.026	.0026	.004	.013	1.83	Tal-Wi-Wi
27	.014	.017	.0009	.002	.004	2.68	Tal-Wi-Wi
28	.029	.028	.0027	.007	.021	2.32	Tal-Wi-Wi
29	.017	.018	.0009	.003	.006	2.26	Tal-Wi-Wi
30	.026	.033	.0032	.008	.021	2.73	Tal-Wi-Wi
31	.022	.023	.0014	.005	.012	1.37	Tal-Wi-Wi
32	.022	.023	.0035	.008	.016	1.78	Camel Back
33	.027	.026	.0045	.012	.021	2.58	Camel Back
34	.027	.035	.0041	.012	.026	2.01	Camel Back
35	.042	.040	.0035	.015	.027	2.91	Camel Back
36	.070	.068	.0048	.012	.040	2.55	Tucson
37	.090	.091	.0060	.013	.028	1.92	Mesa

which closely approximates the amount actually present in the soil solution, varies from 0.0009 to 0.0321 percent or 27 pounds to 963 pounds per acre-foot. These figures should be compared with 50 to 100 pounds per acre, which represent slightly better than average applications of water-soluble potassium as fertilizer.

In view of the fact that plants are aided in the absorption of food by the secretion of carbonic acid from their roots, the solubility of potassium in this acid was determined. The data show

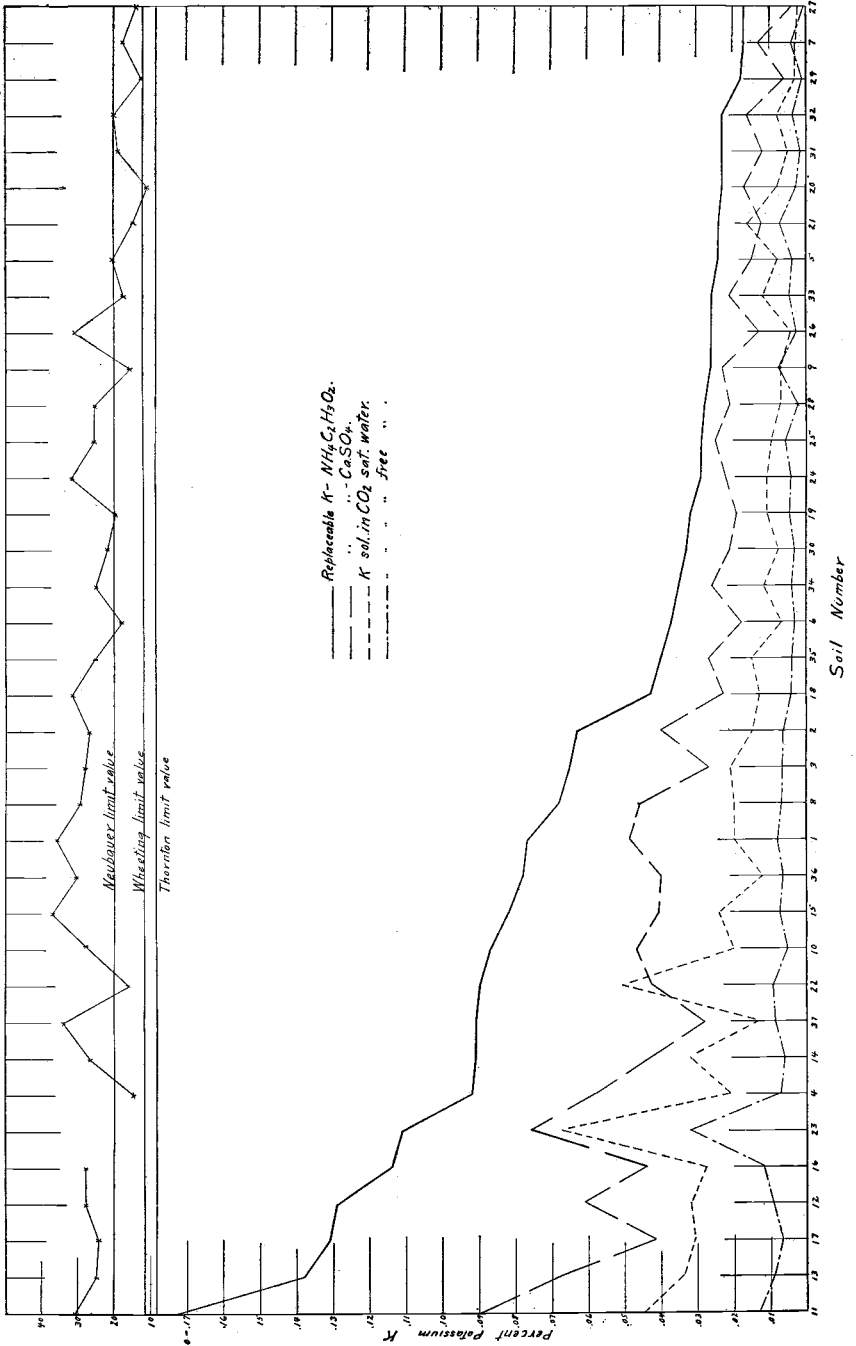


Fig. 1.—Showing Neubauer values, percent replaceable potassium by 0.1 N ammonium acetate and saturated solution of calcium sulphate and solubility of potassium in carbon dioxide free and carbon dioxide saturated water.

that the solubility in water is greatly increased if carbonic acid is present in the water and that the secretion of this by the plant roots should greatly aid the plant in obtaining potassium from calcareous soils. Water-solubility is increased by the presence of carbonic acid to a minimum solubility of 60 pounds potassium per acre-foot and a maximum solubility of 2,010 pounds per acre-foot.

In Figure 1 the soils have been arranged in order, from left to right, according to the amount of replaceable potassium which they contain, thus enabling one to visualize the relation between replaceable potassium and its solubility in carbon-dioxide-free and carbon-dioxide-saturated water. In no case does the replacing power of calcium sulphate equal that of ammonium chloride or acetate, the difference being greater when a larger amount of replaceable potassium is present in the soil. It is of interest to note that the solubility of potassium in water is greatly increased by the presence of carbon dioxide in the water and that the increase is greatest in the soils containing the most water-soluble potassium. In two cases the solubility in carbon-dioxide-saturated water is greater than the replaceability by calcium-sulphate solution and in both of these cases the soils are high in alkali. Soil No. 23 is the highest in alkali salt content and contains the largest amount of water-soluble potassium. The effect of carbon dioxide on solubility of potassium is of especial interest in view of the fact that we have previously shown the major part which it plays in the availability of phosphate in these same calcareous soils (4).

In view of the importance of solubility of potassium in water, and especially the manner in which soil potassium responds to carbonic-acid treatment in calcareous soils, the relation between replaceable potassium and its solubility in carbon-dioxide-free and carbon-dioxide-saturated water is presented graphically in Figure 2. In this figure replaceable-potassium determinations in 37 soils are used as ordinates and their solubilities as abscissas. All values are on the basis of percentage potassium in soils. The ratios show practically linear relationships, at least as close as one could expect in such a complex material as soil where so many factors, which influence solubility, are present. The relative solubility, or rather importance of carbonic acid to potassium availability in calcareous soils, is best measured by the angle which the two lines make with the ordinate or Y axis. On account of the low solubility in water the units selected along the X axis were taken as double those along the Y axis in order to avoid confusion of points. The angle is shown to be 9° for water-soluble potassium and 27° for solubility in carbon-dioxide-satur-

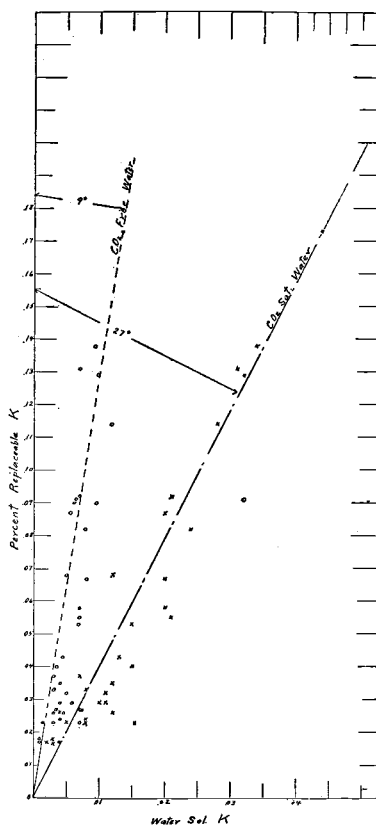


Fig. 2.—Relation between replaceable potassium and its solubility in carbon dioxide free and carbon dioxide saturated water.

ated water. Using equal units the angles are 4.5° and 13.5° and the equations for the two lines may be represented by

$$Y = 12.70X \text{ (Tan. } 85^\circ 30' \text{ being } 12.70)$$

for solubility in water, and by

$$Y = 4.16X \text{ (Tan. } 76^\circ 30' \text{ being } 4.16)$$

for solubility in carbon-dioxide-saturated water. While there are some wide variations from these equations, they are confined largely to the soils highest in alkali content. The equations and curves are not submitted as being infallibly suited to calculation of available potassium, but rather to illustrate the approximate relation between replaceable potassium and the influence of carbon dioxide upon its solubility.

NEUBAUER TEST

On the basis of the chemical data presented in Table 1 the conclusion seems justified that this group of soils is amply supplied

with potassium and that there is no immediate need for potash fertilization. The only possible exceptions are those at the lower end of the curve in Figure 1. In the absence of field experiments with which these data may be compared, we resorted to the Neubauer test as the best means of comparing the chemical data with availability as measured by plants. Detailed descriptions of this test may be found elsewhere (25, 27) so will not be repeated here. Suffice it to say that Thornton (25) and Wheeting (27) have clearly shown its value as a measure of potassium availability in American soils. Briefly the test involves the planting of 100 selected rye seeds in 100 grams of soil which has been mixed with 300 grams of silica sand and at the end of 18 days carefully washing the soil from the plants and determining, by analysis of the plants, the amount of potassium which they have removed from the soil. The amount of potassium present in an equal number of plants grown in sand alone is determined as a check and subtracted from that found in those grown in 100 grams of soil. The difference represents relative potassium availability. The data obtained from the application of this test to Arizona soils are given in Table 2.

TABLE 2.—NEUBAUER VALUES FOR SOILS ANALYSES OF WHICH ARE GIVEN IN TABLE 1.

Soil No.	Neubauer mgs. K	Soil No.	Neubauer mgs. K	Soil No.	Neubauer mgs. K	Soil No.	Neubauer mgs. K
1	35.8	11	30.8	21	14.7	31	18.8
2	26.8	12	37.8	22	15.9	32	20.0
3	27.8	13	24.8	23	no growth	33	17.3
4	14.5	14	26.8	24	31.5	34	25.0
5	20.1	15	37.1	25	25.2	35	25.0
6	17.8	16	27.7	26	30.5	36	30.0
7	17.8	17	24.0	27	13.4	37	34.0
8	29.3	18	31.3	28	25.2		
9	15.4	19	19.8	29	12.2		
10	26.8	20	10.8	30	21.5		

The data are also shown graphically at the top of Figure 1 in order that they can be more easily studied in comparison with the chemical data on these soils.

In interpreting Neubauer values of soils it is necessary to establish a limit value below which a deficiency of potassium is indicated. Neubauer himself, established a limit value of 24 mgs. K_2O or 19.9 mgs. K. For American soils, Thornton (25) found that a much lower limit value is necessary. His work indicates a limit value of 8.3 mgs. K as the value below which a deficiency

of potassium is shown. Wheeting (27), also working with American soils, found good correlation between the Neubauer test and field performance where 11.6 mgs. K was used as the limit value. In Germany higher values are used because of the more intensive cultural methods employed by German farmers. Of course there is a great deal of variation in the feeding power and potash requirement of different crops so that the limit values must represent average soils and average crops, and in the case of such plants as tobacco, which possess a high potassium requirement, allowances must be accorded.

Comparing the data in Table 2 with the above values it will be noted that 24 soils out of 32 show values higher than the Neubauer limit for German soils (five subsoils are not included in the average), all except 1 out of 37, including the subsoils, are above the limit value used by Wheeting, and all are above the value established by Thornton. The Neubauer test therefore reveals a high availability for potassium in our calcareous soils and thereby confirms the conclusion reached in the chemical studies.

On the whole, there is a gradient trend to the Neubauer curve in Figure 1 showing a decrease in Neubauer value with decrease in replaceable and soluble potassium, but nevertheless there are a number of wide breaks or variations in values. This indicates that some factor or factors must be present which influence the assimilation of potassium by the plants.

In soil No. 23, the highest in alkali content, there was no germination and therefore no value could be obtained. With the exception of soil No. 22 it will be noted that there is a distinct "hump" in the curve between the points represented by soil 14 and soil 18. This indicates that the factor depressing the assimilation of potassium is present in the group of soils to the left of soil 14 on the curve, namely those highest in replaceable and soluble potassium. On examining the alkali content of these soils it was found that the soils on the curve between Nos. 14 and 18 are lower in saline material than those to the left which showed lower Neubauer values in spite of higher replaceable and soluble potassium. The data therefore indicate a depressive effect of salines upon potassium assimilation. On the other hand, it cannot be overlooked, in view of the large amounts of potassium taken up by the rye plants from these soils, that excessive amounts of potassium may have presented an unbalanced nutrient to the plant in soils 11, 13, 17, 12, and 16 which depressed assimilation of potassium. While many plants can and do exercise a luxury consumption of potassium this element may easily become toxic when in great excess.

DISTRIBUTION OF POTASSIUM BETWEEN SOIL AND SUBSOIL

In the case of deep-rooted crops, the potassium content of the subsoil is of considerable importance. In view of this, a study of the distribution of potassium in several depths of soil was made. Eighteen soils were included in this study* and the first, second, and third feet sampled separately. Replaceable potassium and water-soluble potassium were determined. The data are given in Table 3, and shown graphically in figures 3 and 4.

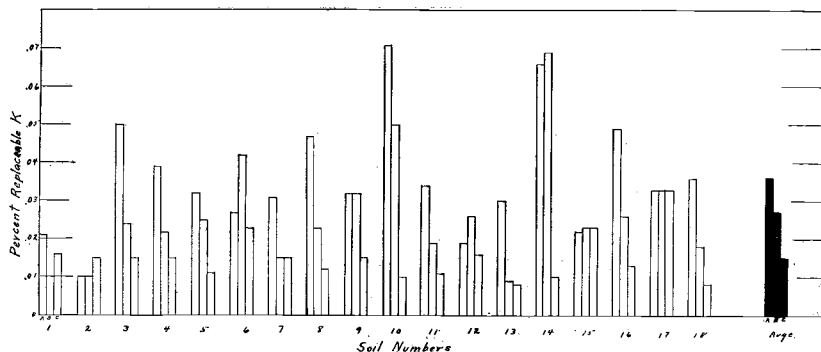


Fig. 3.—Showing percent replaceable potassium in first, second, and third foot depths of calcareous soils. A column represents surface soil, B column second foot, and C column third foot with the average represented by shaded columns.

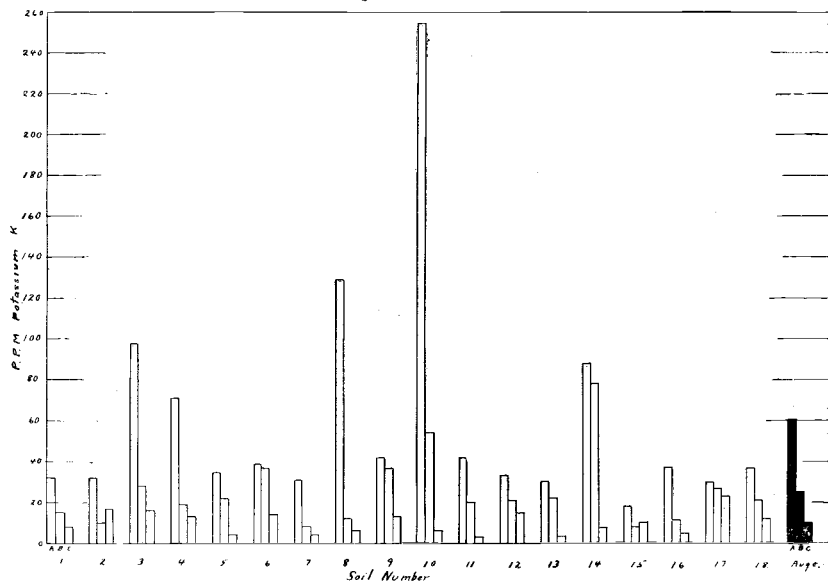


Fig. 4.—Showing parts per million water soluble potassium in first (A), second (B) and third (C) foot depths of calcareous soils with the average represented by shaded columns.

* These soil samples were collected by D. W. Albert, Associate Horticulturist.

In several cases total potassium was determined and the results obtained showed little or no difference in the amounts present in the three soil depths. The amounts were in close accord with the total potassium shown in Table 1 so they are not presented.

TABLE 3.—REPLACEABLE POTASSIUM IN FIRST, SECOND, AND THIRD FOOT OF SOIL AS PERCENT K, AND WATER-SOLUBLE POTASSIUM AS PARTS PER MILLION K.

Soil No.	Percent replaceable potassium			P.p.m. water-soluble potassium		
	1st ft.	2nd ft.	3rd ft.	1st ft.	2nd ft.	3rd ft.
1	.021	.010	.016	32	15	8
2	.010	.010	.015	32	10	17
3	.050	.024	.015	98	28	16
4	.039	.022	.015	71	19	13
5	.032	.025	.011	35	22	4
6	.027	.042	.023	39	37	14
7	.031	.015	.015	31	8	4
8	.047	.023	.012	129	12	6
9	.032	.032	.015	42	37	13
10	.071	.050	.010	255	54	6
11	.034	.019	.011	42	20	3
12	.019	.026	.016	33	21	15
13	.030	.009	.008	30	22	3
14	.066	.069	.010	88	78	7
15	.022	.023	.023	18	8	10
16	.049	.026	.013	37	11	5
17	.033	.033	.033	30	27	23
18	.036	.018	.008	37	21	12
Av.	.036	.027	.015	60	25	10

These data present a rather clear picture of the potassium problem as applied to Arizona soils, but are perhaps made clearer by the following summary.

	Max.	Min.	Av.
Pounds water-soluble K in acre-foot top soil (1-12)	765	64	180
Pounds water-soluble K in acre-foot subsoil (12-24)	234	24	75
Pounds water-soluble K in acre-foot subsoil (24-36)	69	9	30
Pounds replaceable K in acre-foot top soil (1-12)	2130	300	1080
Pounds replaceable K in acre-foot subsoil (12-24)	2070	270	810
Pounds replaceable K in acre-foot subsoil (24-36)	990	240	450

The data obtained from this set of soils present some interesting information dealing with the relative amount of replaceable potassium at the several soil depths and its solubility in water. In five out of the eighteen soils the replaceable potassium is higher in the second foot than the surface foot, and in two cases it is even higher in the third foot. In two cases the replaceable potassium in the third foot is higher than in the second. On the other hand, in most samples the replaceable potassium gradient is quite consistent with depth.

An examination of the water-soluble potassium does not show such irregularity for in every case solubility is greatest in the surface soil regardless of the amount of replaceable potassium present. These data show a lower solubility of potassium in the subsoil which is even less in the third foot than in the second foot of soil.

EFFECT OF SUBSOIL ON NEUBAUER VALUE

In order to determine the effect of subsoil on assimilation of potassium by plants the Neubauer test was made upon 16 of these soils in which equal parts of the three depths of soil were mixed. That is, the 100 grams of soil was made up of 33 1-3 grams each from the first, second, and third foot. The Neubauer values obtained are given in Table 4.

TABLE 4.—NEUBAUER VALUES OF SOIL—SUBSOIL MIXTURES.

Soil No.	Neubauer value mgs. K	Soil No.	Neubauer value mgs. K
1	15.0	10	12.3
2	14.8	11	11.3
3	20.3	12	20.0
5	13.8	13	15.0
6	15.9	14	18.6
7	14.5	15	15.3
8	17.3	16	22.4
9	11.4	18	12.9

It is evident from a comparison of these data with those given in Table 2 that the absorption of potassium by the plants is greatly reduced by the presence of the subsoil. Further evidence of this is given by the data which are assembled in Table 5.

TABLE 5.—COMPARING NEUBAUER VALUES FOR SOIL AND SUBSOIL.

Soil No.	Total potassium percent K	Replaceable potassium percent K	Water-sol. potassium percent K	Carbon-dioxide sol. potassium percent K	Neubauer value mgs. K
1a	1.83	.026	.0026	.004	30.5
1b	2.68	.017	.0009	.002	13.4
2a	2.32	.028	.0027	.007	25.2
2b	2.26	.018	.0009	.003	12.2
3a	2.73	.033	.0032	.008	21.5
3b	1.37	.023	.0014	.005	18.8
4a	1.78	.023	.0035	.008	20.0
4b	2.58	.026	.0045	.012	17.3
5a	2.01	.035	.0041	.012	25.5
5b	2.91	.040	.0035	.015	25.0

(a) represents soil and (b) the respective subsoil.

These soils, with the respective subsoils, are admirably suited to yielding the information which was sought. Numbers 1, 2, and 3 are from a district north of Litchfield which has been in cultivation for only a short period of years; 1, representing virgin soil; 2, a citrus orchard; and 3, a grape vineyard. Numbers 4 and 5 represent a citrus orchard and grape vineyard respectively in the Camel Back district of the Salt River Valley which have been under cultivation for a much longer period than soils 2 or 3. In the first three subsoils there is a notable drop for the replaceable potassium, its solubility in water and carbon-dioxide-saturated water, and the Neubauer value, as compared to the surface soils. There is some indication that the replaceable potassium in the second foot is increasing with cultivation.

Turning now to similar data for the soils which have been under cultivation for a longer time, it is noted in both cases that the replaceable potassium is higher in the second foot of soil than in the first, while the same is true for the solubility in carbon-dioxide-saturated water. The close agreement between the Neubauer values of soil and subsoil is also significant. In one case they are practically equal.

These data show conclusively that potassium availability is much lower in the subsoil than in the surface soil, but after continued cultivation, and the leaching effect of irrigation water, both soluble and available potassium will be increased steadily after the soil is put under culture. It is clearly revealed that the environment within the virgin subsoil is conducive to poor availability. On the other hand, it is shown that the subsoil is possessed of a strong fixing power which is instrumental in retaining the potassium leached out of the surface soil and that this reabsorbed potassium retains a ready availability.

In Figure 5 the ratio of water-soluble potassium to replaceable potassium in the first, second, and third foot of soil is illustrated in such a manner as to reveal more clearly the gradient relation of depth of soil to potassium solubility. As already mentioned and shown in Figure 2, the solubility of potassium in water is closely a linear function of replaceable potassium, and if the line is drawn through the intersection of the horizontal and vertical axes the angle which the line makes, or the equation for the line, reveals the ratio.

Since the function is linear it will conform to the simple equation $y = mx$ and the slope of the line, a constant, will be equal to y/x . By calculating this constant for the solubility of potassium for each soil given in Table 3 and taking an average of these calculations the slopes denoted by the broken lines in Figure 5

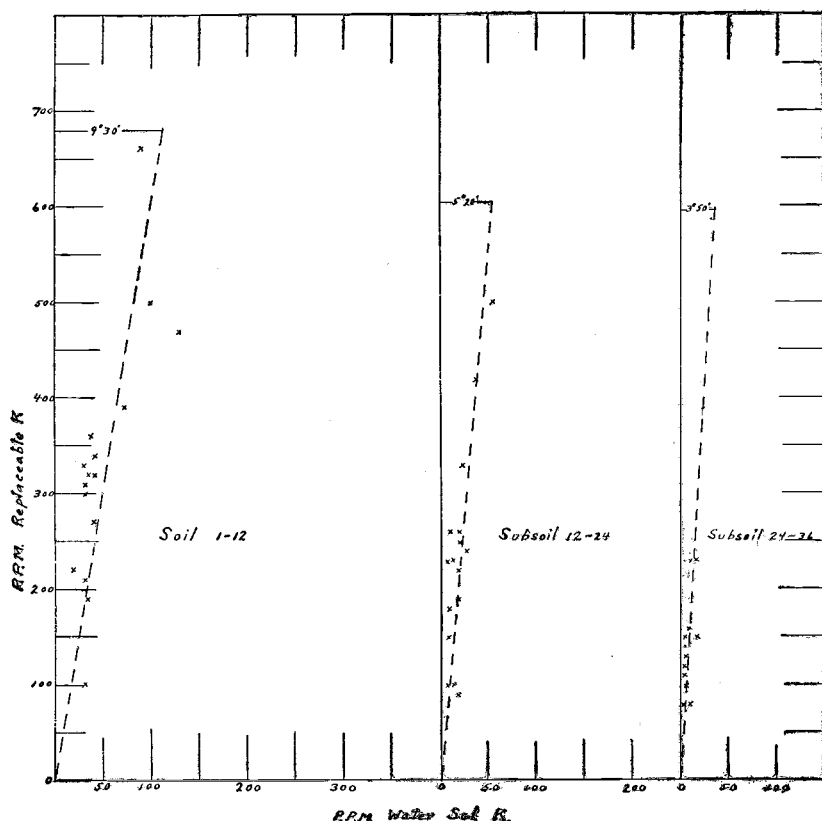


Fig. 5.—A graphic illustration of comparative solubility of replaceable potassium in first, second, and third foot depths of soil.

were obtained while the crosses in Figure 5 represent the actual ratios obtained and therefore the variation from the constant. In the surface soil there appear to be many factors which influence the solubility of potassium and variations from the average, represented here by the constant, are wide. This is true to a much less extent in the subsoil. In view of this, the data are presented in the form shown in Figure 5 primarily to illustrate the variation of potassium solubility in soil and subsoil.

For the surface soil the slope of the line is 6, the line making an angle of $9^{\circ} 30'$ with the Y axis, and therefore may be represented by the equation $y = 6x$. For the second foot of soil the slope of the line is 10.8, the line making an angle of $5^{\circ} 20'$ with the Y axis, and may be represented by the equation $y = 10.8x$. For the third foot of soil the slope of the line is 15.0, the line making an angle of $3^{\circ} 50'$ with the Y axis, and may be represented by the equation $y = 15x$.

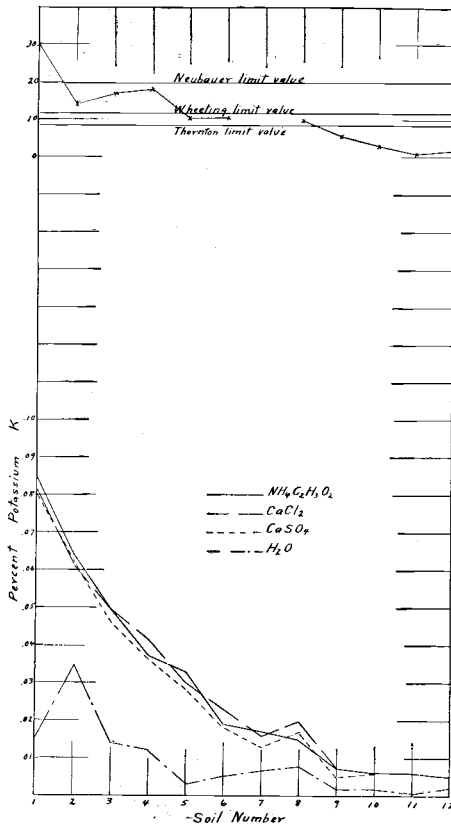


Fig. 6.—A comparison of the Neubauer values, percent replaceable potassium by 0.1 N ammonium acetate, 0.1 N calcium chloride and saturated solution of calcium sulphate and solubility of potassium in carbon dioxide free and carbon dioxide saturated water for non-calcareous soils.

NON-CALCAREOUS SOILS

As already mentioned, most of the soils of the irrigated valleys of this State are calcareous and all those given in Table 1 are of this type. In view of this a number of non-calcareous soils were assembled and subjected to the same tests as the group of calcareous soils. The chemical analyses are given in Table 6 and Figure 6.

Numbers 1 and 4 are forest types from northern Arizona, 2 and 3 are laterite types from Hawaii, 5 is a Carrington loam from Iowa, 6 is a granitic silt loam from California, 7 is a black alkali soil from Fresno, California, 8 is a Sassafras loam from New Jersey, and 9, 10, 11, and 12 are soils from Indiana which are known to be very deficient in potassium. The Neubauer values of this same set of soils are also given in Table 6 and Figure 6.

TABLE 6.—REPLACEABLE AND SOLUBLE POTASSIUM IN NON-CALCAREOUS SOILS—PERCENT K.

Soil No.	Rep. K by NH ₄ Cl	Rep. K by CaCl ₂	Rep. K by CaSO ₄	K sol. in CO ₂ -sat. water	K sol. in water	Neubauer value
1	.085	.081	.080	.015	.0153	29.9
2	.064	.061	.062	.035	.0285	14.4
3	.049	.049	.046	.014	.0146	17.1
4	.037	.042	.036	.012	.0118	18.4
5	.035	.030	.028	.003	.0024	10.3
6	.019	.023	.018	.005	.0039	10.8
7	.017	.016	.013	.007	.0076	—*
8	.015	.020	.018	.008	.0062	10.0
9†	.007	.007	.005	.002	.0007	5.8
10	.006	.006	.006	.002	.0010	3.2
11	.006	.006	.006	.001	.0009	1.2
12	.005	.005	.008	.002	.0008	2.0

When these data are compared with the data in Tables 1 and 2, we are confronted with an entirely different picture revealing the fact that the potassium problems of calcareous and non-calcareous soils are not so closely related as one might anticipate. The correlation between chemical data and Neubauer values, for the non-calcareous soils is quite good, where wide variations (breaks in the Neubauer curve) were obtained for the calcareous soils. This indicates that factors influencing potassium absorption by plants are more prevalent in our arid, calcareous soils. The identification of these factors may probably be found in the chemical data. Replaceable potassium as determined by 0.1 N ammonium salts and saturated-calcium-sulphate solution agrees within experimental error for non-calcareous soils, while for the calcareous soils saturated-calcium-sulphate solution is far less effective as a replacing salt. It is further significant that solubility in carbon-dioxide-free and carbon-dioxide-saturated water are the same for the non-calcareous soils, while for the calcareous soils, potassium solubility is greatly increased by the presence of carbon dioxide in the water. While definite conclusions cannot be drawn from such a small number of non-calcareous soils, the data strongly emphasize the difference between the potassium nutrition of plants in the two types of soil under study. It is definitely shown that potassium solubility in calcareous soils reacts more easily to the presence of carbon dioxide in the soil solution, and that potassium is more readily absorbed from calcareous soils by plants. If the Neubauer values for all soil samples given in tables 1 and 3 containing between 0.02 per-

* Soil too alkaline, no germination.

† The author is indebted to Dr. G. N. Hoffer, N. V. Potash Export MY. for the four potassium deficient soils, 9, 10, 11, and 12.

cent and 0.06 percent replaceable potassium are averaged, it is found to be 22 for the calcareous and 12.5 for the non-calcareous soils. According to these figures potassium is practically twice as available per unit of replaceable potassium in calcareous soils as in non-calcareous soils.

DISCUSSION OF POTASSIUM AVAILABILITY

Dr. Hilgard, one of the earliest students of arid soils, is credited with the statement, "One of the most important practical conclusions flowing from the comparison of potassium in humid and arid soils is that while in the former potash is usually among the first substances to be supplied by fertilization, in the arid regions it will come last." This statement, made probably 30 years ago, is entirely borne out by this preliminary investigation of potassium and its availability in the arid soils of Arizona.

The function of potassium in plant nutrition is indeed an important one. It is associated with the efficiency of the leaf and the synthetic processes taking place therein. It is credited with a vital function in the synthesis of sugars and their translocation and to the reduction of nitrate which is the first step in the synthesis of protein. Naturally, then, it is found most abundant in the young vegetative parts of the plant. Having such an important part to play in organic synthesis, plants draw most heavily upon potassium during the early stages of growth. In fact, the absorption of potassium is so great during this initial period that it is possible for plants to take up sufficient potassium for their entire growth period. In cases of potassium deficiency, the plant can translocate potassium from older leaves to the younger leaves, which are the vital points of activity.

Potassium is very freely absorbed from the soil by plants, probably being one of the most readily absorbed elements. Therefore plants often absorb more potassium than is needed, so-called luxury consumption, and this may seriously lower the amounts of calcium or even phosphate absorbed.

This investigation of potassium in calcareous soils shows that there is an excellent store of readily available potassium present in Arizona soils and, judging from the high Neubauer values, it is very easily assimilated by rye plants during the early stages of growth. In fact there is some evidence that considerable luxury consumption will take place in plants grown on some of our calcareous soils.

There are several theories which explain this apparent discrepancy of high Neubauer value and low water-solubility in alkaline

calcareous soils. The Helmholtz double-layer theory as suggested by Starkey and Gordon (24) is especially applicable. The potassium ion being a positively charged ion, would naturally be most readily adsorbed by negatively charged soil colloids. In calcareous soils, such as exist in the arid regions, amphoteric colloids, being closely associated with hydroxyl ions as the inner layer of Helmholtz, offer an attractive wall for the adsorption of the cation potassium. It has been shown that small changes in pH near the neutral point produce marked changes in the adsorption of potassium by the soil. There is some question in our minds as to whether this adsorbed potassium should be considered in the same light as so-called zeolite potassium or is analogous to our present conception of exchangeable potassium, and this will be taken up in greater detail in Part II of this bulletin. The adsorbed potassium of alkaline soils is given up more readily by slight changes in pH than is that of neutral or acid soils, and this is clearly revealed by both the Neubauer values and the chemical data showing effect of carbonic acid on potassium solubility in calcareous and non-calcareous soils.

MacIntire's (14) investigations also throw some light upon the apparent discrepancy which we have observed between Neubauer values and water solubility. He has demonstrated that hydroxides of calcium and magnesium depress the solubility of soil potassium even in the presence of neutral salts of these bases. It is apparent from his investigations that in the presence of hydroxyl ions there will be a re-adsorption of potassium by the negatively charged colloids if any replacement takes place following the contact of the potassium zeolite with the neutral salts of calcium or magnesium. On this basis, then, an apparent decrease in water solubility will exist.

The investigations presented and literature cited clearly reveal why acid soils are usually deficient in potassium and alkaline soils rarely deficient. The fixing power of alkaline soils for potassium is many times greater than acid soils. Amphoteric colloids have the same electric charge in acid soils as the potassium ions, while in alkaline soils the charges are opposite thereby imparting a property to repel in the former and to attract in the latter. Alkaline calcareous soils will then, as Hilgard has stated, be the last to require potassium fertilization and if one is allowed to assume that the re-adsorbed potassium of the negatively charged, amphoteric soil colloids is of greater availability than so-called zeolite adsorbed potassium, availability will also remain higher in alkaline calcareous soils.

PART II—SOME PROPERTIES OF REPLACEABLE POTASSIUM

INTRODUCTION

In Part I of this bulletin, a survey is presented of the potassium content of a group of soils from the more extensively cultivated valleys of Arizona, together with some of the properties of this soil potassium, notably its solubility and availability. During the course of this work some outstanding differences between calcareous and non-calcareous soils were observed.

The influence of calcium upon soil potassium, both in the form of basic liming materials and neutral calcium salts, is a subject which has received a great deal of attention from students of soil fertility. On the other hand, little of this work has dealt with natural calcareous types. The literature covering investigations on the effect of lime on soil potassium is so extensive that no attempt will be made here to cover it thoroughly. Sufficient review will however be submitted to reveal the widely conflicting conclusions which have been drawn. This conflict is in the main due to the narrow range of soil types covered by the different investigations, in many cases only single types being studied. All conclusions reached in our investigations are presented as applicable largely to calcareous soils, especially the types which are widely scattered throughout the Southwest.

REVIEW OF LITERATURE

Bizzell and Lyon (1) found no increase of potassium in drainage water from the Cornell lysimeter experiments when lime was added to the soil. In fact potassium was somewhat less in the drainage from the limed lysimeters. Tressler (26) found that gypsum increased the solubility of soil potassium to a greater extent in clay soils than in sandy soils, but was less active where the potassium mineral was mica. He also found calcium bicarbonate and sodium chloride to be quite active in dissolving potassium. Bradley (3) found that gypsum released potassium from Oregon soils while the effect of lime was variable. Curry and Smith (9) found calcium carbonate and oxide had practically no effect on the solubility of potassium in granitic New Hampshire soils. Briggs and Breazeale (6) found no liberation of potassium from a California soil either by calcium oxide or calcium sulphate. This work was later confirmed by Lipman and Gericke (13) working on the same soil, but they obtained just the opposite results using a soil from northern California, namely liberation of potassium by both calcium sulphate and oxide.

Their observations led them to caution soil workers against drawing wide conclusions from a limited number of soils. Erdman (10) found that excessive amounts of gypsum increased the solubility of potassium in Iowa soils in all cases, but small applications only in part of them. After 15 years, experimental plots at the New Jersey Experiment Station (2) show that potassium has been reduced in the limed plots. Plummer (23) found that micaceous soils respond less to lime than feldspathic soils. In comparing the chemical composition of water from streams in Kentucky, McHargue (20) found that those from limestone districts contained little or no potassium while those from sandstone and shale districts were rich in potassium. This is quite illustrative of the natural effect of limestone on potassium solubility.

The contributions of MacIntire (14, 15) and his co-workers to the problem of the calcium-potassium relationship are outstanding, and many of the conclusions which they have reached are true under the natural environment of calcareous soils. Their investigations demonstrate quite conclusively that lime represses potassium solubility but some liberation will follow the application of calcium sulphate. It is shown that, when pH values indicate an excess of hydrogen ions, potash liberation is effected by neutral calcium salts but the reverse, potassium fixation, is brought about when the hydrogen ion concentration is greatly reduced or superseded by hydroxyl ion concentration, if the hydroxyl ion is not sufficiently concentrated to induce hydrolysis of the native zeolitic potassium. Light applications of lime will conserve soil potassium while excessive applications will set it free.

These few references, presenting a fair cross section of the literature, will suffice to illustrate the variation in calcium-potassium relationships in different soil types. They indicate that soil reaction, amounts of lime, and forms of calcium hold the answer to the conflict of conclusions drawn by different investigators.

EXPERIMENTAL

REPLACEABLE POTASSIUM IN CALCAREOUS SOILS

The portion of soil potassium subject to replacement, when the soil is brought in contact with salt solutions containing another base or hydrogen, is by far the most important from the standpoint of plant nutrition. It is considered to be practically 100 percent available. On the other hand, its solubility is largely dependent upon the composition of the soil solution, to a lesser extent upon solid phases of less soluble soil constituents, and finally upon the electric charge of the soil colloids. It is thus

inevitable that replaceable potassium will exhibit different properties in alkaline calcareous soils than in non-calcareous, acid or neutral soil types.

For a study of the potash problem in arid calcareous soils a group of nearly 50 soils was assembled. There were included among these 12 non-calcareous soils from widely separated parts of the United States, some of which were very deficient in potassium and must be heavily fertilized for good crop production, while for others no potash fertilization is required.

As an initial step the replaceable potassium was determined with ammonium acetate, ammonium chloride, and calcium-sulphate solutions. The analytical procedure was to weigh 25 grams of soil into a glass cylinder and leach with 250 cc. of 0.1 N solutions of the ammonium salts and the same volume of a saturated solution of calcium sulphate, potassium being determined in the leachates. As stated in Part I, it has been found in this laboratory that replacement of potassium is quantitatively complete when 250 cc. of 0.1 N ammonium salt solutions are leached through 25 grams of soil. The analytical data have already been presented in tables 1 and 6 so will not be repeated here, but they are shown graphically in Figure 7. Calcareous soils and non-calcareous soils are shown as separate curves.

The replacing activities of ammonium salts and calcium salts are strikingly revealed in this figure by the amounts of potassium replaced by 250 cc. of their solutions. In the calcareous soils the amounts of potassium set free by calcium sulphate solution is far less than the actual amount of replaceable potassium present and revealed by the replacement with ammonium salts. The replacement by ammonium chloride and ammonium acetate agreed as well as duplicate determinations, hence only the one set of determinations is presented for the two salts. Turning now to the comparison of the amount of potassium replaced from non-calcareous soils by ammonium salts and saturated-calcium-sulphate solutions it will be noted that the curves practically coincide. Calcium sulphate is then capable of quantitatively replacing potassium from non-calcareous soils. While a saturated solution of calcium sulphate falls far short of 0.1 normal, containing only approximately 600 parts per million Ca, the results obtained with the non-calcareous soils indicate that the difference in the case of calcareous soils is not a question of concentration of base in the replacing solution. Calcium ions are known to be more strongly attracted by soil colloids than potassium ions so, in view of this, the results suggested a further comparison of the replacing activity of solutions of these two bases for calcareous soils.

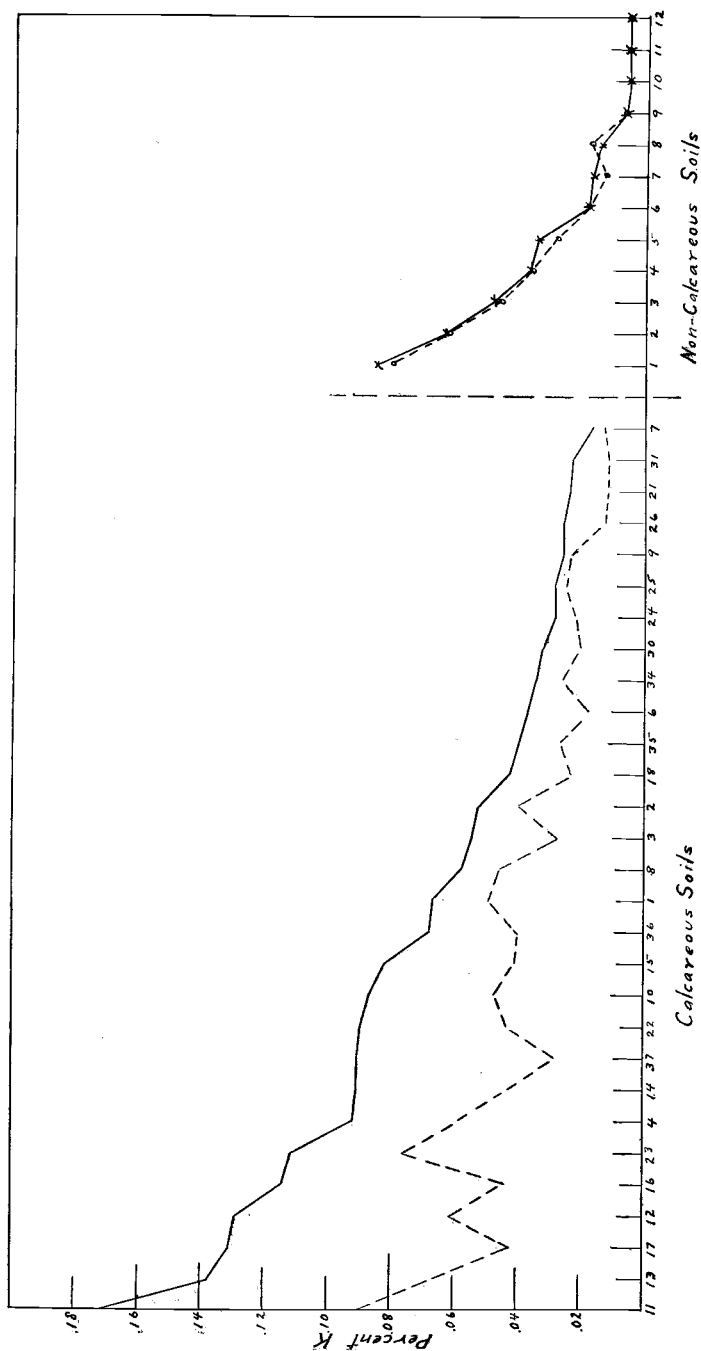


Fig. 7.—Replaceable potassium in calcareous and non-calcareous soils by 0.1 N ammonium acetate and saturated gypsum solution.

COMPARISON OF CALCIUM CHLORIDE AND AMMONIUM
CHLORIDE AS REPLACING AGENTS

If any difference exists between the replacing action of calcium salts and ammonium salts it should be more in evidence when equinormal or equimolar solutions are compared. Chlorides of the two bases, therefore, were selected. Eight soils which contained a wide variation in replaceable potassium content were chosen for the experiment. Twenty-five grams each were weighed into leaching cylinders, in quadruplicate. Each was leached with two separate portions of 0.1 N and 0.1 M solutions of ammonium chloride and calcium chloride respectively. These were then analyzed for replaced potassium. The amount of potassium replaced by 0.1 N and 0.1 M solutions of each individual salt agreed as closely as the duplicate determinations showing no difference between normal and molar solutions, so these data are omitted. On the other hand there was a very great difference between the amount of potassium replaced by both equinormal and equimolar solutions of the different bases and these data for 0.1 N solutions are given in Table 7.

TABLE 7.—MILLIGRAMS K REPLACED BY 0.1 NORMAL SOLUTIONS
OF AMMONIUM CHLORIDE AND CALCIUM CHLORIDE.

	First 250 cc.		Second 250 cc.	
	CaCl ₂ mgs. K	NH ₄ Cl mgs. K	CaCl ₂ mgs. K	NH ₄ Cl mgs. K
1	25	33	4.8	1.6
2	20	26	2.5	0.9
3	24	34	3.8	1.0
4	22	32	5.1	2.1
5	23	37	5.4	2.3
6	10	9	1.6	Trace
7	7	7	1.8	Trace
8	3	3	1.8	Trace

The results show that in the soils low in replaceable potassium the amount replaced by the first 250 cc. is equal but that where the soils are high in replaceable potassium the calcium chloride is much less active in the replacement of potassium. The relative activity of the two salt solutions is quite constant, the ammonium salt being closely 1.4 times as active for the first 250 cc. of leachate. This experiment demonstrates that the difference between the amount of potassium replaced by 250 cc. of saturated calcium sulphate solution and 0.1 N ammonium acetate solution is not a result of difference in concentration but rather a difference in replacing activity of calcium and ammonium ions in *calcareous soils*.

In view of the fact that there was agreement in the soils which contained the smallest amounts of replaceable potassium, the above experiment was repeated in a slightly different manner. Three 25-gram portions each of three different soils were leached with 0.1 N solutions of ammonium chloride and calcium chloride and with water. Each successive 100-cc. portion of the leachates was collected separately and analyzed for potassium. The data obtained in this experiment are given in Table 8.

TABLE 8.—RATE OF POTASSIUM REPLACEMENT BY CONTINUOUS LEACHING WITH 0.1 N, NH₄Cl, CaCl₂, and H₂O—MILLIGRAMS K PER 100 cc.

Soil No.	Displacing solution	1st 100 cc.	2nd 100 cc.	3rd 100 cc.	4th 100 cc.	5th 100 cc.	6th 100 cc.	7th 100 cc.	8th 100 cc.
1	(NH ₄ Cl	29.1	3.9	.7	.37	.19	.15	.14	—
	(CaCl ₂	23.5	4.5	2.2	2.00	1.32	1.32	1.08	1.05
	(Water	Soil	too	pud-	dled	to	leach	with	water
2	(NH ₄ Cl	7.2	.7	.3	.09	.06	.02	.04	.05
	(CaCl ₂	4.8	1.2	.5	.57	.43	.40	.33	.32
	(Water	.7	.6	.4	.42	.33	.34	.26	.08
3	(NH ₄ Cl	3.7	.2	.12	.08	.05	.06	.04	.04
	(CaCl ₂	1.7	.6	.28	.34	.30	.24	.21	.25
	(Water	.3	—	.31	.10	.10	.10	.10	.08

By determining the potassium in each successive 100 cc. of leachate, it is shown that there are no exceptions to the observation that solutions of calcium salts are not able to exercise their full replacing power in calcareous soils. It is also evident that solutions of calcium salts should not be used here for determining the replaceable potassium unless very large volumes of leaching solution are employed.

The differences which have been brought out in the preceding suggest the conclusion that potassium is more soluble but relatively less available in non-calcareous soils. This suggestion arises from the fact that the hydrolysis of potassium zeolite apparently is repressed in alkaline calcareous soils, especially where soluble calcium salts are present along with the carbonate.

EFFECT OF LIME ON SOLUBILITY OF POTASSIUM IN CALCAREOUS SOILS

Exchangeable soil potassium hydrolyzes in presence of water to form potassium hydroxide and the amount of hydrolysis, and therefore the amount of potassium in the soil solution, is a function of dilution. Concentration of potassium in solution is, thus, subject to modification depending upon factors which repress or enhance hydrolysis.

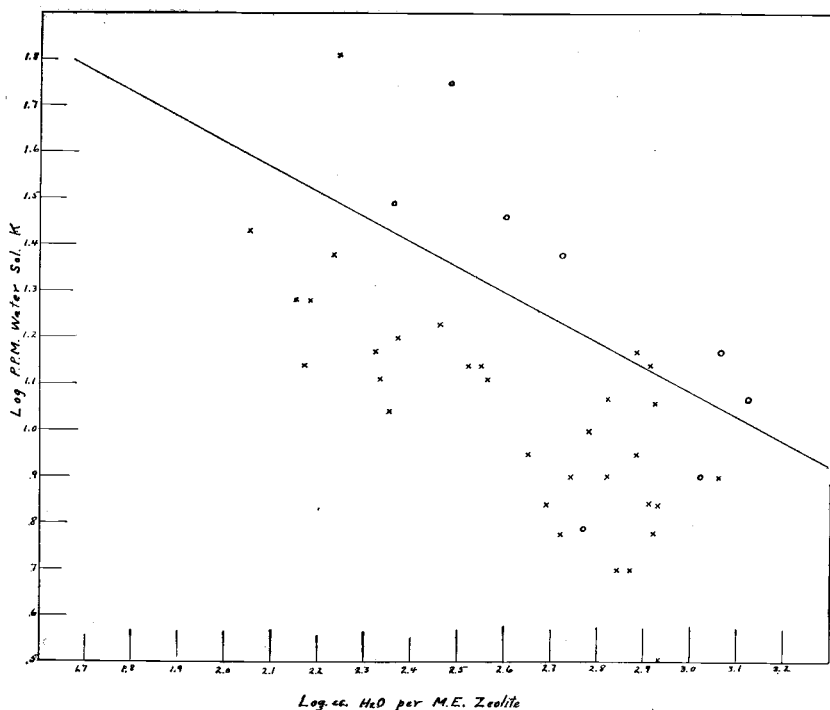


Fig. 8.—Influence of calcareous soils on the solubility of replaceable potassium according to Magistad's formula.

Magistad (16) has derived an equation from which solubility of potassium in parts per million may be calculated at all ratios of water to replaceable potassium. In plotting these calculations graphically he shows that the logarithm of p.p.m. potassium in solution is a linear function of the logarithm of the number of cc. water per milliequivalent of zeolitic potassium. The equation developed by Magistad is as follows:

$$\text{Log } U = 2.70 - 0.537 \log Y$$

or

$$U = 501.2 Y^{0.537}$$

In this equation Y represents cc. water per M. E. replaceable potassium and U represents p.p.m. potassium in solution.

In view of the large amount of data on hand showing the replaceable potassium content of the soil and its solubility in 1:5 water extract, it appeared of interest to note just how closely the solubilities conformed with or deviated from the linear function observed by Magistad. It seems fair to assume that any deviation can be interpreted as an indication of the presence of factors enhancing or depressing the solubility of replaceable

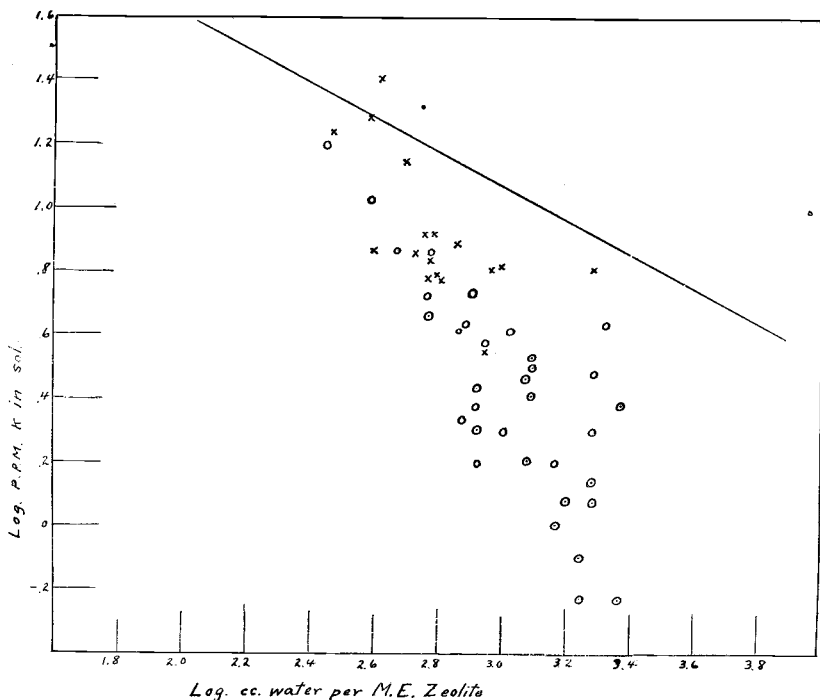


Fig. 9.—Deviation of soil and subsoils from Magistad's formula.

potassium. The logarithms of cc. water per M. E. replaceable potassium, and p.p.m. potassium in solution were obtained from logarithm tables for data in tables 1 and 6, and the ratios found are plotted in Figure 8.

In this figure the line drawn is that of Magistad, which represents the ratio between log M. E. replaceable potassium and log p.p.m. potassium soluble in water, for synthetic zeolites. The points marked with X represent actual values found for calcareous soils (Table 1), and those marked O represent the actual points found for non-calcareous soils (Table 6), when log p.p.m. potassium in solution is plotted against log cc. water per M. E. replaceable potassium. With three exceptions the calcareous soils fall below the line of theoretical solubility, while the non-calcareous soils, with two exceptions, fall above this line. This is interpreted as further evidence of the repressive effect of calcareous material upon the solubility of potassium in soils.

Having another set of data (Table 3), in which replaceable potassium and water-soluble potassium in soil and subsoil were determined, these were also plotted graphically and are shown in Figure 9. The effect of calcium carbonate on potassium solubility is more strongly emphasized in this figure than in Figure 8.

The first foot of soil is represented by X, the second foot by O and the third foot by ©. The trend of deviation from theoretical increases with depth which is similar to the trend exhibited by relative amounts and activity of calcareous matter in our arid soils.

There is further evidence in these graphs that potassium is less soluble in calcareous soils than in non-calcareous soils, that hydrolysis of replaceable potassium is less, and that zeolitic potassium is more difficultly replaced. Following this, the logical question then is, what of the absorption of potassium from calcareous soils by plants, and does it correlate with the solubility relations revealed by the chemical studies?

NEUBAUER VALUES

Since there were no data available on the field performance or response to potash fertilization for the soils under study, we resorted to the Neubauer test in order to secure data on assimilation of potassium by plants from these soils. These data are shown graphically in Figure 10 along with the percent replaceable and water-soluble potassium for 16 calcareous soils and 8 non-calcareous soils. These soils were especially selected from tables 1 and 6 because their content of replaceable potassium ranged between the same limits, namely 0.087 percent to 0.015 percent and, as replaceable potassium is considered to be completely available to plants, Neubauer values should be closely similar unless some factor or factors are repressing solubility or assimilation. On comparing the water solubility of potassium in these soils it will be noted that there is a definite trend toward greater solubility in the non-calcareous soils than in calcareous soils of equivalent replaceable potassium content. However, on surveying the curve of Neubauer values an entirely different picture is presented. Neubauer values are distinctly lower for non-calcareous soils than for calcareous soils of equivalent replaceable potassium content. We thus are confronted with the fact that while the solubility of potassium and hydrolysis of potassium zeolite are lower in calcareous soils, its availability, as measured by rye plants in the Neubauer test, is greater. If one is familiar with the work of Parker (21), Starkey and Gordon (24), and MacIntire *et al* (14 and 15), a brief discussion of which is presented in Part I, the reason for this discrepancy will be apparent.

As early as 1913 Parker suggested that the exchange by which potassium is liberated in soils is due to the adsorption of the base by the soil and the formation of free acid from the anion of the

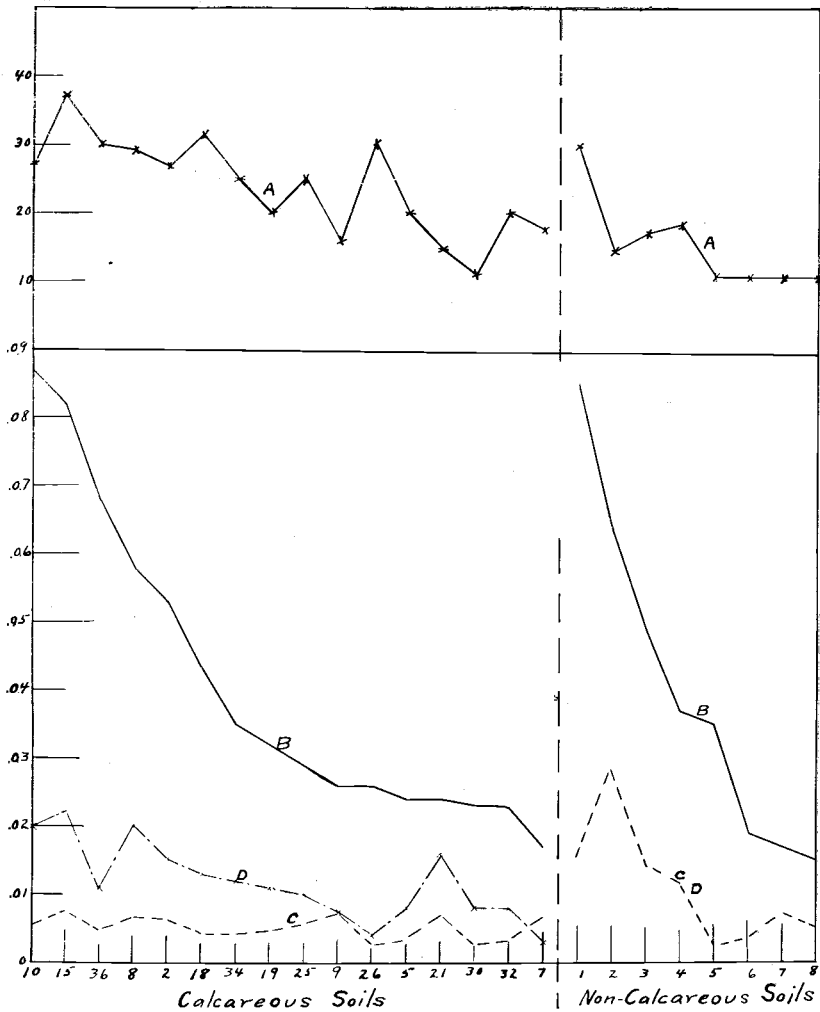


Fig. 10.—Relation of replaceable potassium, solubility in carbon dioxide free and carbon dioxide saturated water and Neubauer values.

salt. The resulting acid exercises a solvent effect on soil potassium. If the acid is neutralized by carbonates or hydroxides, as in alkaline soils, no potassium will be set free whether the anion be chlorine, sulphate, or bicarbonate. Hence potassium is readily set free in acid soils but with extreme difficulty in alkaline soils and, therefore, acid soils are very often deficient and calcaireous soils rarely deficient. The investigations of Starkey and Gordon dealt largely with the effect of soil reaction upon the adsorption

of potassium. The greatest adsorption of potassium takes place at alkaline reactions, potassium being positively charged and the amphoteric soil colloids being negatively charged in alkaline soils. A small change in pH of a soil near the neutral point will produce a marked change in the adsorption of potassium, solubility of potassium increasing with drop in pH. They suggest that potassium held by negatively charged colloids in alkaline soils is attracted by hydroxyl ions which are associated with the colloid in accordance with the double-layer theory of Helmholtz. MacIntire *et al* have clearly demonstrated the depressive effects of the hydroxides and carbonates of calcium and magnesium on the solubility of potassium even in the presence of an abundance of the neutral salts of these two bases. Lime not only reduces the solubility of potassium but will aid in its conservation. It not only depresses the solubility but, through its alkalinity, enhances the tendency of alkaline soils to reabsorb potassium which is set free by exchange. The results obtained by the experiments recorded in this bulletin are therefore supported by theory and by the experiments of others.

EFFECT OF CaCO_3 AND CaSO_4 ON THE LOSS OF POTASSIUM BY LEACHING

The investigations reviewed in the literature presented in the previous pages have been conducted on non-calcareous soils. In order to determine what results follow the addition of calcium salts to natural calcareous soils, which contain both zeolite exchangeable potassium and that adsorbed in accordance with the Helmholtz double-layer theory, some leaching experiments were conducted.

Five-hundred-gram portions of soil were weighed into each of 6 glass percolators according to the following program.

1. Control—nothing added to soil.
2. 5 grams CaCO_3 worked into the surface of the soil.
3. 5 grams CaCO_3 and 5 grams CaSO_4 worked into surface of the soil.
4. Control—nothing added to the soil.
5. 5 grams CaSO_4 worked into surface of the soil.
6. 5 grams CaO worked into surface of the soil.

These percolators were then leached with eleven 500-cc. portions of water and the leachings analyzed for phenolphthalein alkalinity, bicarbonate, calcium, and potassium. The results obtained are given in Table 9.

The control (untreated soil) yielded 23.6 mgs. potassium to 4,500 cc. of water. Where CaCO_3 was added this was reduced to 22.3 mgs., indicating that additional CaCO_3 did not appreciably

TABLE 9.—SHOWING EFFECT OF CaCO₃ AND CaSO₄ ON LOSS OF POTASSIUM FROM CALCAREOUS SOILS.
Milligrams in leachate

Soil No.	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	Total	10th*	11th*	Total
<i>Potassium</i>													
Control	3.9	2.3	3.0	2.1	2.8	2.5	2.9	2.2	2.0	23.6	6.9	6.2	13.1
CaCO ₃	3.2	2.4	2.2	2.1	2.6	2.5	2.9	2.2	2.2	22.3	4.6	6.5	11.1
CaCO ₃ -													
CaSO ₄	11.0	11.1	10.2	8.3	5.9	5.1	3.9	1.8	2.4	59.7	3.8	3.3	7.1
Control	3.5	2.6	3.7	2.3	2.3	2.1	2.3	3.2	2.5	24.5	4.5	4.3	8.8
Soil-CaSO ₄	10.2	11.1	12.4	7.3	5.4	4.5	3.2	3.2	1.7	59.0	2.8	2.9	5.7
Burnt lime	3.6	3.2	3.3	3.5	3.3	2.9	2.9	2.8	2.3	27.9	2.8	3.3	6.1
<i>Calcium</i>													
Control	2.6	7	9	8	8	9	11	10	12	100	37	33	70
CaCO ₃	3.7	4	10	11	6	10	13	16	11	118	33	33	66
CaCO ₃ -													
CaSO ₄	17.6	221	195	135	170	108	45	11	10	1071	40	45	85
Control	3.0	4	4	5	6	9	12	12	9	70	30	37	67
Soil-CaSO ₄	15.7	217	180	153	120	86	135	25	15	1088	37	37	74
Burnt lime	2.6	15	45	34	32	30	3	40	19	244	4	30	34
<i>Bicarbonates</i>													
Control	3.0	2.5	1.9	1.4	1.5	1.7	1.3	1.4	1.7	16.4	6.6	8.3	14.9
CaCO ₃	3.3	2.3	1.8	1.6	1.4	1.7	1.4	2.2	1.7	17.4	6.3	7.6	13.9
CaCO ₃ -													
CaSO ₄	1.7	1.3	1.3	1.4	1.5	1.9	1.7	0.7	1.3	12.8	6.0	7.1	13.1
Control	3.0	2.4	2.1	1.8	1.6	1.6	1.4	2.3	1.7	17.9	5.7	5.4	11.1
Soil-CaSO ₄	1.5	1.1	1.2	1.6	1.6	1.8	1.8	2.3	1.7	14.6	4.8	6.8	11.6
Burnt lime	2.5	1.2	0.3	0.6	0.4	0.5	0.3	0.6	0.6	7.0	0.4	4.8	5.2

* Water saturated with CO₂ before leaching.

reduce potassium solubility below that resulting from the CaCO_3 naturally present in the soil. On including CaSO_4 in the treatment the initial increase in potassium present in the leachate was very evident, but this was rapidly reduced to a figure in close agreement with the untreated soil. In view of the fact that in studies on non-calcareous soils (14, 15) the repressive effect of CaCO_3 held, even in the presence of solutions of the neutral salts of calcium, we are led to suggest that the early initial high concentration of potassium in the leachate from the gypsum treatments of our calcareous soils was being displaced from the adsorbed potassium of the Helmholtz double layer rather than the zeolite exchange compound. Five hundred grams of this soil contained 160 mgs. replaceable potassium by ammonium acetate and 95 mgs. replaceable potassium by CaSO_4 , yet after a removal of 32.3 mgs. in the first 1,500 cc. the potassium set free rapidly dropped to a near constant. Where burned lime, CaO , was added there was a slight increase in the amount of potassium set free by the high concentration of hydroxyl ions in the leaching solution. It will be noted that calcium ions are present in greatest concentration in the leachings which had the largest amount of potassium. The amount of bicarbonate apparently shows no relation to the liberation of potassium.

For the 10th and 11th leachings the water was saturated with carbon dioxide before adding to the percolators. Following this change in the leaching water there was an increase in amount of potassium set free which is greatest in the untreated controls and the soil receiving CaCO_3 . In view of the ready release of the potassium adsorbed in the Helmholtz double layer to carbonic-acid treatment, it is suggested that this is the source of the potassium set free, since it had already been largely exhausted in those to which gypsum was added during the first leachings.

EFFECT OF SOIL PUDDLING ON REPLACEABLE POTASSIUM

Experiments conducted on the effect of puddling on the solubility of phosphate (19) showed that the solubility and availability is much depressed by poor aeration. A group of five soils was selected to determine the effect of puddling on replaceable potassium. The soils were carefully puddled in 500-gram lots and kept in this condition for 6 months, being kept supersaturated with water throughout this time. At the end of this period the soils were dried in the air, ground to break up hard lumps, and replaceable potassium determined. The results showed no change in percent replaceable potassium.

EFFECT OF LEACHING ON CONTENT OF REPLACEABLE POTASSIUM

The rate at which potassium may be leached from soils is a matter of great importance to their fertility. A group of eight soils was selected and 300 grams of each leached with 3,500 cc. of distilled water. The replaceable potassium was determined before and after leaching with the following results:

TABLE 10.—PERCENT REPLACEABLE POTASSIUM IN SOILS BEFORE AND AFTER LEACHING.

Soil No.	Before	After
1	.018	.018
2	.061	.049
3	.076	.075
4	.061	.051
5	.023	.023
6	.023	.021
7	.044	.037
8	.053	.049

These data show that potassium is held very strongly by the calcareous soils of the Southwest. There was little or no potassium lost during the time the above experiment was conducted.

EFFECT OF HEAT ON SOLUBILITY AND REPLACEABILITY OF SOIL POTASSIUM

Many investigations have been conducted upon the effect of heat on the solubility of the inorganic constituents of soils, notably phosphorus and potassium. It has recently been shown that differentiation can be made by means of heat between inorganic and organic exchange compounds. Organic exchange compounds are destroyed at 350° C., while higher temperatures are necessary for the destruction of the inorganic exchange compounds.

In order to determine the effect of heat upon potassium solubility in calcareous soils, two representative samples were selected, one a sandy loam from the Salt River Valley and the other a silty loam (alluvial soil) from Sacaton. Fifty-gram portions were heated for 8-hour periods in an electric oven for the two lowest temperatures and an electric muffle for the highest temperatures. After heating, the soils were analyzed for replaceable potassium, using 0.1 N ammonium chloride, and for water-soluble potassium by shaking one part of soil with five parts of water. The results are given in Table 11, in which the percent replaceable potassium has been corrected by subtracting the water-soluble potassium. Weight lost by the soils is also given.

TABLE 11.—EFFECT OF HEAT ON REPLACEABLE AND WATER-SOLUBLE POTASSIUM.

	Sandy-loam soil			Silty-loam soil		
	Loss in wt. grams	Percent Rep. K	P.p.m. water-sol. K	Loss in wt. grams	Percent Rep. K	P.p.m. water-sol. K
Control, air dried, not heated	—	.028	45	—	.104	112
Heated to 110° C.	1.1	.033	45	0.6	.102	126
Heated to 170° C.	1.3	.034	58	1.2	.095	158
Heated to 350° C.	1.4	.041	80	1.3	.092	231
Heated to 530° C.	1.9	.070	118	2.3	.098	165
Heated to 750° C.	2.3	.092	59	3.2	.083	100
Heated to 1050° C.	2.6	.007	25	3.9	.007	51

The sandy-loam soil shows a steady increase in replaceable potassium with increase in temperature up to and including 750° C., while water-soluble potassium increases up to 530° C., beyond which volatilization of potassium exceeds liberation from insoluble forms. It is evident that in this soil there is a steady increase in amount of surface exposed to the displacing solution with increases in temperature to which the soil is exposed. In the Sacaton soil, a finer grained alluvial soil, the replaceable potassium remains practically constant with a slight tendency to decrease with increase in temperature. The increase in water-soluble potassium with increase in temperature is considerable. This gradient change both in replaceable and water-soluble potassium in this soil is due in part to dehydration or destruction of colloids and in part to destruction of the organic exchange complex. Loss in weight of soil due to heat is greater in this soil than in the sandy-loam soil as it contained more organic matter.

EFFECT OF GRINDING ON REPLACEABLE POTASSIUM

Kelley (12) and his co-workers have shown that the base-exchange capacity of bentonites and the clay fraction of soils can be greatly increased by grinding the clay to particles of smaller dimensions. The effect of fineness of division upon the amount of potassium which can be replaced from calcareous soils was therefore determined. For this work four soils were selected, three of them being calcareous and one a peat. The latter was included in order to determine effect of grinding upon the exchange properties of the organic exchange complex. These soils were each ground in a ball mill for 72 hours. The entire soil was ground, only large stones being removed. The replaceable potas-

sium was then determined by leaching with 0.1 N ammonium chloride, and water-soluble potassium by shaking one part of soil with five parts of water. The results are given in Table 12.

TABLE 12.—EFFECT OF GRINDING ON REPLACEABLE POTASSIUM.

Soil No.	Percent replaceable K		P.p.m. water-soluble K	
	Unground	Ground	Unground	Ground
5	.026	.079	98	232
29	.028	.060	117	218
30	.018	.057	44	154
16	.065	.072	257	258

These data show a notable increase in replaceable potassium from grinding calcareous soils. Even if the water-soluble potassium is subtracted from the replaceable potassium, the proportionate increase is practically the same. The peat soil shows practically no alteration in replaceable potassium on grinding and in a later test was shown not to have altered in exchange capacity. Apparently this is a characteristic difference between organic and inorganic exchange compounds.

DISCUSSION OF REPLACEABLE POTASSIUM

The colloidal compounds in our soils, *i.e.*, that fraction which functions in base adsorption and exchange, are largely hydrated oxides of silicon, iron, and aluminum. They usually exist as gels coating the larger soil particles. Their composition and properties are greatly influenced by moisture, temperature, and soil reaction, and hence should be distinctly different in arid alkaline calcareous soils when compared with soils from other more humid parts of the country. Colloidal behavior also varies with composition, and adsorption of bases is manifested in varying degrees according to this composition and, in the case of amphoteric colloids, to soil reaction. Arid soils contain so little organic matter that we are not greatly concerned with organic colloids in this discussion.

Soil colloids are divided electrokinetically into positive and negative forms. Silica and humus are usually classified as negative in calcareous soils, and are therefore sometimes referred to as acidoids. The iron and aluminum oxides or hydrated oxides are amphoteric colloids and are positively charged in acid soils and negatively charged in alkaline soils.

Soil reaction is the most important single factor influencing the adsorption of potassium. Being positively charged, potassium will naturally be most readily attracted and held by negatively

charged colloids. In acid soils where colloids are largely positively charged, potassium is loosely held. Thus we find acid soils are usually deficient in potassium, as it is leached away with comparative readiness. In alkaline soils negatively charged colloids predominate, potassium ions are strongly adsorbed and potassium is rarely deficient in arid soils because of this ability to resist loss by leaching.

In the case of the montmorillonite-type clays it is conceivable, as pointed out by Brown and Byers (7), that exchange capacity and possibly degrees of adsorption are subject to variation depending upon the nature of the products of disintegration, according to the amounts of orthoclase, montmorillonite, halloysite, or kaolinite which make up the larger part of the clay fraction. It has been definitely shown that a high silica-sesquioxide ratio is accompanied by high exchange capacity and *vice versa*. It is further conceivable, as pointed out by Kelley, Dore, and Brown (12), that, since the exchange colloid is of crystalline structure, exchangeable potassium, or rather immediately available potassium, will exist in different degrees of replaceability according to the size of the crystal.

Our own investigations, along with those which have been cited, lead to the suggestion that we must consider soil potassium as existing in soils in several degrees of availability. As just mentioned, there is positive evidence of this in crystalline materials where potassium attached to the outside of the crystal is more readily available than that inside the crystal lattice, yet both must be recognized as replaceable forms.

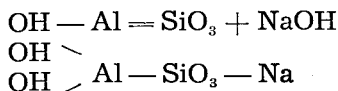
At this point it is well to review some of the observations made in our study of calcareous soils, using chemical and Neubauer tests. Replaceable potassium in equivalent amounts is more available to plants in alkaline calcareous soils than in neutral or acid non-calcareous types. There is evidence that water-solubility of potassium in calcareous soils is lower than in non-calcareous soils, except in soils containing a large excess of OH^- ions. Solubility of potassium is greatly increased by carbonic acid in calcareous soils but in non-calcareous soils there is much less effect, and in many cases no increase in solubility at all. This latter observation explains the greater availability in calcareous soils, namely that the adsorbed potassium in such soils responds more readily to the solvent action of carbonic acid given off by the roots. In other words, in summarizing, water-solubility of potassium is less, but assimilation of potassium by plants is greater, in calcareous soils.

Since the solubility of exchange potassium in water is a linear function it is difficult to reconcile these experimental data with

the recognition of only two exchangeable forms, namely the potassium inside the crystal not immediately available and the potassium adsorbed on the surface of the crystal, except that the solubility of the latter may be dependent upon the factors which alter the micellar atmosphere. If we assume that all potassium replaceable by solutions of ammonium salts is adsorbed on the surface of the crystals of colloidal dimensions, then why the greater solubility in non-calcareous soils and the greater absorption by plants in calcareous soils? This question can be answered only by assuming that immediately available potassium exists in adsorbed forms other than that attached to the exchange compounds of crystalline structure.

There are a number of theories which can be employed in confirming and explaining our contention. The Helmholtz double-layer theory has already been mentioned and there is little question but that the OH^- ions, as the inner layer of Helmholtz, act as an attractive wall for the adsorption of cations. Alkaline calcareous soils possess a greater fixing power for potassium than neutral or acid non-calcareous soils, and furthermore in the presence of such a negatively charged colloid there is the additional advantage of a property to re-adsorb any potassium which may be liberated from the zeolite exchange complex. It has been demonstrated that potassium adsorbed in accordance with the Helmholtz double-layer responds more readily to carbonic acid than zeolite potassium and is therefore more available to plants. The increase in potassium availability which often follows liming is probably due to the potassium which has been set free from the zeolite complex and re-adsorbed on the surface of the clay fraction in accordance with the Helmholtz double-layer theory. Depression of potassium availability also often follows liming, but it is believed that this is due to the addition of lime in amounts just sufficient to depress the hydrolysis of soil zeolites. It is of interest to mention the investigations of Peck (22) showing that lime salts freed potassium from acid soils but not from alkaline soils.

Mattson (17) states that hydroxyl ions can partially displace the silicate ions from their union with iron and aluminum, giving rise to a number of free acidoid valences. The replaceable bases thus formed are more soluble in 0.05 N HCl than the untreated colloid, pointing to an unlocking of the colloid bonds according to the following scheme.



Increased exchange capacity in the presence of alkali then, according to Mattson, is due to liberation of silicate valences by hydroxyl ions.

Jenny (11) mentions one phase of colloidal adsorption which also may help to explain potassium availability in alkaline soils. Reference is made to the properties of oxygen and hydroxyl ions. The phases of attraction in colloidal particles are the negative O^{--} and OH^- ions. Their sizes are almost alike but on account of the double electric charge, the O^{--} is a more powerful adsorbent than OH^- with its single charge. According to this, potassium will be held in a more available form where OH^- ion predominates. Also, the potassium ion can approach the crystal or nucleus more closely in the case of O^{--} than if OH^- were in excess in the micellar atmosphere.

It is not improbable that the Donnan equilibrium, which involves an unequal distribution of ions on opposite sides of a colloidal film, is associated with the differences manifested by alkaline calcareous soils and other types, for in alkaline soils the micellar atmosphere will consist of cations, in this case potassium, attached to the outer surface of the electronegative colloid surrounding the soil particles.

Some years ago, in a publication (8) from this laboratory, it was shown that the exchange capacity of soils can be increased by treatment with alkali. It was suggested at that time that this increase was due to a synthesis of exchange colloids within the soil confines by a combination of sodium aluminate and sodium silicate somewhat in the same manner employed in the preparation of artificial zeolites or permutits. In view of the fact that the exchange capacity of these synthetic colloids is not increased by grinding, and Kelley, Dore, and Brown (12) have shown that synthetic zeolites do not show crystalline structure by X-ray examination, it appears reasonable to assume that such soil colloids will attract and hold potassium in a greater degree of availability than crystalline zeolites. It is immaterial whether we refer to them as synthetic colloids, the term used by us, or simply as isoelectric precipitates as Mattson prefers to call them. It has been estimated that at least one-third of the exchangeable potassium of soils is locked up within the crystal and our results confirm this in that on grinding calcareous soils replaceable potassium was increased approximately threefold. It is inevitable that potassium adsorbed by non-crystalline colloids which show 95-100 percent replaceability will present a more effective source of adsorbed potassium than a crystalline compound of 33 percent replaceability, as the number of potassium ions in the micellar atmosphere will be present in approximately these proportions.

The colloidal complex of soils is a dynamic thing and the exchange capacity, especially in the case of amphoteric colloids, cannot be considered a constant quantity but must depend upon the manner in which the valences are linked and whether of crystalline or non-crystalline nature. Fundamentally they are in large part similar substances, being hydrated aluminum silicates, but there are numerous factors which influence the thickness and properties of the atmosphere of cations which surround the colloidal particle, and potassium availability is greatly influenced by these factors.

SUMMARY

PART I

1. Arizona soils contain high reserves of potassium.
2. There is a wide variation in the amount of replaceable or less firmly held potassium, but even in the poorest soils there is no evidence of an immediate need for potassium.
3. The solubility in water is very low in the case of some soils but the adsorbed potassium responds so readily to the solvent action of carbon dioxide that low solubility in water does not handicap the absorption by the crop provided root respiration is normal.
4. The Neubauer test shows that plants will absorb large amounts of potassium from these soils during the early stages of growth. In fact, the indications are that luxury consumption will take place in many.
5. In most of our soils available potassium decreases with soil depth as does also the solubility of potassium in water.
6. The subsoils have a strong fixing power for potassium and thus, by fixation of potassium leached from the surface soil, the supply of available potassium in the subsoil increases with cultivation.

PART II

7. The calcareous soils of Arizona are well supplied with replaceable potassium.
8. Exchange potassium is readily replaced from calcareous soils by 0.1 N solutions of ammonium salts but not by calcium salts, while in non-calcareous soils the two salts are equally effective.
9. Calcium salts depress the hydrolysis of potassium zeolite and increase fixation of potassium in calcareous soils, but not in non-calcareous soils.

10. Calcareous material in soils depresses the solubility of soil potassium below the theoretical value found by Magistad.
11. Calcareous soils in Arizona show high Neubauer values for potassium.
12. Neubauer values for calcareous and non-calcareous soils containing equivalent amounts of replaceable potassium are higher for the former.
13. Solubility of replaceable potassium in calcareous and non-calcareous soils of equivalent replaceable potassium content are higher in the latter.
14. Neutral calcium salts will show an active initial liberation of potassium from calcareous soils.
15. Holding calcareous soils for an extended period in a puddled condition does not change the replaceability of potassium.
16. Loss of replaceable potassium by leaching with pure water is small for calcareous soils.
17. Heating calcareous soils increased replaceable potassium up to 750° C. in a sandy loam, while there was little change in a silty-clay loam.
18. Grinding calcareous soils in a ball mill increased the replaceability of potassium practically threefold.
19. Grinding a peat soil had no effect on replaceability of potassium.
20. Grinding increases the exchange capacity of the inorganic exchange complex, but does not alter the exchange capacity of organic colloids.
21. Theories are presented which explain the greater availability of potassium in calcareous soils and support the postulation that they contain a large part of their potassium adsorbed by non-crystalline colloids, either in the form of synthetic zeolite-like compounds or iso-electric precipitates.

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