

A STUDY OF AVAILABLE POTASSIUM
IN SOME OKLAHOMA SOILS

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INTRODUCTION

The behaviour of potassium ions in soil is in many cases somewhat complicated and confusing, and many scientific investigations have been conducted to obtain information which will help to solve this problem. Several theories have been suggested and proved to be true under certain conditions, but as to a general understanding of the problem still more information seems to be needed.

From a practical point of view one of the most important problems has been to find a method of determining the need of potassium in maintaining or creating a highly productive soil.

After it was found that the total amount of potassium in soil had little or no relation to the need for potash fertilization, the concept of "available potassium" (water soluble potassium plus exchangeable potassium) was readily accepted and has been useful in explaining the relative availability of soil potassium for plant growth. Although the quantity of available soil potassium in relation to total potassium in soil is rather limited and may be used up by crops within a short time, it has been found from practical experiences and experiments that in most cases the available potassium serves as a good measure of potassium supply for plant growth.

After various investigators learned that available soil potassium is the main source of potassium for plants, it became an interesting problem to find the relation between this form and other forms of potassium in the soil. Since it was found that some of the potassium applied to soils in a soluble form, is readily changed to less soluble compounds, it is evident that the processes of fixation and release of potassium may have an important influence on the economical use of potash fertilizers and on plant growth under varying soil and climatic conditions.

The experiments performed and presented in this thesis are intended as a general contribution to the problem of fixation and releasing of potassium in soils under different conditions and treatments.

Soils from different parts of Oklahoma were used to determine if any differences occur in the behaviour of those soils as compared to general theories found true for soils from other regions.

REVIEW OF LITERATURE

Suggested definitions and groupings of different forms of potassium in soils are legion and in many cases the same expressions are used for different purposes. A rather common and widely accepted grouping of potassium compounds in soil was given by Wood and DeTurk (39) as follows:

1. Primary mineral potassium (acid insoluble).
2. Fixed potassium (acid soluble).
3. Exchangeable potassium.
4. Water soluble potassium.

Group 3 and 4 are commonly referred to as available potassium, but sometimes this expression is used as a synonym for group 3. DeTurk and coworkers (9) used the term "Nonreplaceable" or colloidal held potassium for group 2 (fixed potassium). They found this group to represent about 18% of the total potassium in a fertile soil.

Attoe and Truog (2) estimated that the quantity of readily and moderately available potassium in a fertile loam soil is approximately 3% of the total, and classified the different forms of soil potassium into 3 groups which are as follows:

Readily available)	
Exchangeable potassium)	
Potassium in organic matter)	About 1% of total
Water soluble salts)	
Moderately available)	
Fixed potassium)	About 2% of total
Biotite potassium)	
Difficulty available)	
Feldspar potassium)	97-98% of total
Muscovite potassium)	

The influence of drying and wetting of soils on fixing and releasing of potassium and the rate of those processes under different moisture conditions has been the subject of much research. Attoe (3) found that fixation of potassium occurred on drying of potassium fertilized soils, but an increase in available potassium was observed in unfertilized soils low in available potassium. Nine out of ten unfertilized soils containing less than 100 ppm. of available potassium showed an increase in exchangeable potassium on drying, ranging from 4% to 90% of that present in the moist soils. Eight of ten fertilized soils showed a decrease of exchangeable potassium after 2 months storage under moist conditions and a decrease of 11% to 52% of the amount added, after drying at room temperature. Alternating drying and wetting facilitated the reactions in both cases. He also found the relative humidity at which the drying took place to be of considerable importance.

In a later paper (4) Attoe reported that most of the potassium added to a soil was recovered by seven crops. Fertilizer applications ranged from 0 to 1350 pounds per acre. Although up to 56% of the potassium in the 50 and 150 pound per acre rates was fixed in nonexchangeable form, the recovery ranged from 92 to 98% of the amount applied. Drying of the soil (Miami silt loam) between each of the crops caused a considerable increase in the liberation of potassium.

Ayres et al. (6) found that 3400 to 4200 pounds of potassium was liberated per acre during a four year period under field conditions in a Hawaiian soil cropped with Napier grass. More than one and one-half times the initial amount of available potassium was removed by electrodialysis for one month.

Blume and Purvis (7) found a great variation in the fixation of potassium from month to month. Under controlled conditions the quantity of replaceable potassium remained constant over a five month period while the fixed portion varied greatly, with the variation reflected in the water soluble fraction. A monthly removal of the water soluble potassium by leaching greatly reduced the replaceable and fixed fractions of potassium in all soils studied.

Bray and DeTurk (8) found a ready release of potassium from nonreplaceable forms from some Illinois soils during moist storage, upon removal of all or a part of the original replaceable potassium. Without removal of any potassium under the same conditions the release was very small or negligible. Increasing the fraction of replaceable potassium by adding a potassium salt resulted in a part of the replaceable potassium being changed over to a nonreplaceable form.

Heating to 200°C resulted in a release or fixation in the same way depending on the conditions at the beginning of the heat treatment.

Gholstone and Hoover (14) pointed out the importance of nonreplaceable potassium as a source of potassium for plants. In all soils tested, more than 50% of the potassium removed by 8 crops during 545 days was released by the soils from nonexchangeable forms. The ability of liberation varied widely between different soils.

Joffe and Kolodny (21) found a maximum fixation of potassium at 200°C, and above that temperature also a release of potassium. At 550°C they found a complete destruction of the soils capacity to fix potassium.

Leatz and Winters (34) stated that the release or fixation of potassium depends on the amount added to the soil. At an application rate of 200 pounds per acre 100% was recovered. When the rate was 800 pounds per acre only 70% was recovered under field conditions.

Stanford and Pierre (36) have noted a fixation of potassium under moist conditions in some soils. Joffe and Kolodny (20) found no fixation occurred without drying.

The effect of freezing and thawing is likely to be the same as that of drying and wetting, since freezing causes a concentration of the mineral matter in the remaining soil solution and obviously has the same effect as drying. This effect has been suggested by Attoe (3) and also by Fine et al. (13).

The influence of other ions in soil upon the behaviour of potassium ions has been a subject of considerable interest. Special attention has been paid to the effect of Ca and H

ions (in practice the influence of liming). Leatz and Winters (34) found a higher percentage recovery from a normal potassium application when Ca ions were predominating over H ions, than vice versa. On the contrary Allaway and Pierre (1) found a fixation of potassium under moist conditions in calcareous soils, but not in acid soils. This was confirmed by Attoe (3), who found an increase in potassium fixation by liming potassium fertilized Spencer silt loam under moist conditions, as well as dry. He suggested two types of fixation. One type, which proceeds in moist soils, is increased by liming, and fixes potassium in a form fairly soluble in .5 normal HCl. A second type occurs only on drying, and is quite independent of soil pH, fixing potassium in a form fairly resistant to extraction with .5 normal HCl.

According to Hoover et al. (18) more potassium was released in a Grenada silt loam at pH 6.6 to 7.2 than at a pH of 5.7 to 6.2. Shaw and MacIntire (35) obtained a complete recovery of applied potassium in a typical acid red clay subsoil while considerable fixation occurred in a calcareous top soil (Black loam derived from Chickamauga limestone).

Jenny and Shade (19) suggested that the retention of potassium by a limed soil might be attributed to activation of the soil flora and assimilation of potassium by the microorganisms. In general, however, liming increases the amount of available potassium. Marshall and coworkers (25, 26) studied seven different clay materials and found that the

chemical activities of the potassium ions are higher in a Ca-K-system than in a H-K-system. They also found a marked increase in the activities of Ca and K with increased clay concentration.

Wiklander (44) offered an explanation of the different opinions concerning the influence of liming. He pointed out that the order of replacing power between different ions changes under different conditions. The hydrogen ion has less replacing power than the calcium ion in the presence of montmorillonite, while in other materials the opposite conditions hold true.

Stanford (37) pointed out that while in extremely acid soils the difficultly exchangeable ions H, Al and Fe must be replaced before K can become fixed, causing a slow, if any, fixation in these soils under moist conditions; Mg, Ca, and Na in calcareous soils are replaced quite readily by K, thus accounting for a rapid fixation of K in these soils under moist conditions. Between these extremes the rate and extent of fixation may be expected to vary with the amounts of secondary micaceous minerals, the extent of weathering, pH and other factors.

The relations between potassium fixation, soil structure and base exchange capacity have been studied. Hoover et al. (18) studied the influence of different stages of weathering by cropping the top soil and the subsoil from a virgin Ruston sandy loam separate in a green house for 547 days. The non-exchangeable potassium in the virgin top soil was more readily and quickly available to millet than was that in the less weathered subsoil.

The base exchange capacity of feldspars, micas and soil colloids is greatly raised by grinding below a size of 1 μ as shown by Kelly and Jenny (24). DeTurk et al. (10) divided the soil fraction below 1 μ in several underfractions and showed that all of them fixed potassium.

A decrease in the exchange capacity of bentonite equal to the quantity of potassium (found by Kolodny) could not be duplicated in soil experiments performed by Joffe and Kolodny (21).

The behaviour of different soils concerning potassium fixation seems to be closely connected to the kind of minerals from which the soils originate. Rancy and Hoover (32) made an application of potassium to one montmorillonitic and one kaolinitic soil. Following moist storage, the soils were leached to determine the quantity of K in available form. The montmorillonitic soil fixed large amounts of the applied K while the kaolinitic soil did not have any significant K-fixation. Hoover and coworkers (18) also found a close relation between mineral type and potassium fixation.

According to Stanford (37) illite is capable of fixing potassium under moist conditions while minerals of an expanding lattice type do not fix potassium except when drying occurs. Illite fixes additional potassium when dried. Stanford's comparative studies on montmorillonitic and illitic clays indicate that some of the seemingly discordant results which appear in the literature on potassium fixation in soils are reconcilable.

Joffe and Kolodny (21) concluded that only the crystalline clay colloids having definite lattice structure, can fix potassium. They found no fixation by synthetic amorphous aluminosilicates with very high exchange capacity.

Many suggestions have been made to explain the mechanisms of potassium fixation, and experimental results are presented as support for different theories. Phosphorus was one of the first elements connected with potassium fixation. Joffe and Kolodny (20) found a considerable fixation of potassium by iron and aluminum phosphates on alternating drying and wetting, which increased with an increase in acidoid basoid ratio. They suggest that a complex iron-potassium-phosphate compound is, at least partly responsible for potassium fixation.

Eriksson (11, 12) made extensive investigations on the relation between potassium and phosphorus in soils. He showed that a considerable mutual influence exists concerning the availability of those two elements.

Shaw and MacIntire (35) finding the fixation of potassium to occur especially in calcareous soils, suggested the formation of a calcium complex. Volk (41) pointed out that several different processes appear to be involved in the fixation procedure.

Blume and Furvis (7) proposed the possibility of microbiological fixation, which theory is supported by the close relation found between changes in water soluble and fixed potassium. Martin et al. (27) on the other hand, did not find any connection between organic matter and potassium

fixation. That the liberation of potassium can be associated with organic matter was shown by Tam and Magistad (38). They reported an increase of available potassium from 121 to 401 ppm. in a soil under field conditions during a period of 35 weeks, evidently caused by the decomposition of organic matter.

While some investigators, like Blume and Purvis (7), did not find any tendency toward establishment of equilibrium between different forms of potassium, most research workers consider the processes reversible and that they will sooner or later reach an equilibrium. Stanford and Pierre (36) found equilibrium established within 48 hours in some soils under moist conditions while DeTurk et al. (10) found 25 weeks necessary to reach equilibrium in some other soils under similar conditions. Wood and DeTurk (40) found a slowly shifting equilibrium established after 16 weeks to one year, depending on the kind of soil and amount of potassium added. They found the reactions likely to obey the law of mass action.

Some authors believe that the formation of a mineral is the explanation of potassium fixation. Volk (42) after making chemical, mineralogical, and X-ray studies of Hagerstown silt loam, concluded that the formation of muscovite could account for the fixation of potassium. After experiments with serecite had been conducted, Joffe and Levine (22, 23) suggest that potassium is fixed as a part of the mineral structure. Potassium was released by means of electro dialysis and the same amount was afterwards fixed again by alternate drying and wetting.

Bray and DeTurk (8) did not find the theories involving the formation of a resistant mineral or an insoluble compound very likely. They suggested that secondary minerals formed during weathering have the property of holding potassium and probably other bases in a form usually considered as "fixed," but which could be designated as very difficultly replaceable. That means they were suggesting a double buffer system involving two types of base exchange reactions, which nature has provided for the preservation of potassium against leaching and luxury consumption.

Martin and coworkers (27) suggested that certain cations, when present in the exchange complex of some soils, can pass from a loosely held state to a very strongly held state. They found that some soils lost their potassium fixing power when treated with hydrogen ions and concluded that those ions have the same ability to be fixed as have the potassium ions, in that way taking up "the space for fixation."

Page and Brown (31) proposed a mechanism to explain the fixation of the potassium caused by drying, in which the size of the ions and the spaces in the variable lattice of the montmorillonitic clay minerals are shown to be the important contributing factor. They suggested that large cations when present between the sheets of the minerals can prevent the sheets from coming together which traps the potassium ions. Univalent and divalent cations were tested and it was found that the ionic size close to the size of certain free spaces within the lattice were highly correlated with the degree of fixation.

METHOD OF ANALYSES

Available Potassium in Soil.*

The method for determining available soil potassium was similar to the procedure used in the soils laboratory of the Oklahoma A & M College (16) and was as follows: Five grams of soil was weighed into a 2.5 X 150 mm Pyrex test tube. Ten ml of neutral molar ammonium acetate was added, the tube agitated vigorously, and placed in a water bath at 70°C. After about one minute the tube was plugged with a rubber stopper to prevent evaporation. (If the tubes were plugged before heating either the tube was broken or the stopper was expelled by the pressure generated from the expansion of the enclosed air.) The temperature was maintained at 70°C for one hour and the sample was agitated an additional five times. After one hour the suspension was filtered and the potassium content in the filtrate was determined with a flame photometer.

All analyses were made in duplicate or triplicate and the amount of potassium was calculated on the basis of the oven dry soil. When analyses were made on moist soils, a moisture determination was also made and the water content of the sample was added to the volume of the extracting solution before the available potassium was calculated. A slight error might be introduced by the lowering of the concentration of the extracting solution, but it is of minor importance and has not been considered.

*Available potassium in this study includes the water soluble and the exchangeable potassium.

Moisture content.

The moisture content was determined in a conventional way by drying the samples to constant weight in an oven at 110°C.

Ignition loss.

The ignition loss was determined by heating the soil for three hours in an electric furnace at 550°C.

Base exchange capacity.

The base exchange capacity was determined by the following method: Ten grams of soil was weighed into an Erlenmeyer flask and 100 ml of normal ammonium acetate at pH 6.8 was added. The flask was placed on a steamplate for one hour and agitated vigorously four times. The suspension was filtered under vacuum and the soil on the filter leached with six portions of normal ammonium acetate (25ml) to saturate the sample completely with ammonium ions. The soil was washed with methanol until the filtrate gave no test for ammonium salts by means of Nessler's reagent. This usually required four 30 ml portions of alcohol. The soil and filter paper was transferred to a Kjeldahl flask, magnesium oxide added and ammonia distilled in the usual way, being absorbed in an excess of standard hydrochloric acid and the excess acid determined by titration with standard alkali (.074 normal NaOH). The exchange capacities were calculated on the basis of oven dry soils.

SOILS USED IN THE EXPERIMENTS

The type, location and stage of cultivation of the soils used in the following experiments are given in Table I. When the soils were collected the moisture content varied widely for different samples, from 2.4 to 14.7%. The moisture content was determined and distilled water added to bring each sample to 20% of the dry soil.

After moistening, the samples were stored in air tight glass jars at laboratory temperature (about 25°C) for three days, and then in a refrigerator at plus 5°C for seven weeks, so that the moisture would reach an equilibrium with the mineral matter in the soil.

After this time each sample was divided into three parts. One part, which will be referred to in the following paragraphs as Series A, was kept in glass jars and stored in the refrigerator at a temperature of plus 5°C. The second part, Series B, was stored in open paper bags at the laboratory temperature (about 25°C). The third part, Series C, was transferred to beakers and placed in an oven at a temperature of 110°C.

The moisture content at the time of dividing each sample was determined, and also the base exchange capacity and the ignition loss. The results of these determinations are given in Table II.

TABLE I DESCRIPTION AND LOCATION OF OKLAHOMA SOILS
USED IN THE POTASSIUM EXPERIMENTS

No	Soil Type	Location	Cultivated or Virgin
1	Norge very fine sandy loam	Payne County	Cultivated
2	" " " " "	" "	Virgin
3	St. Paul very fine sandy loam	Woodward County	Cultivated
4	" " " " "		Virgin
5	Kirkland silt loam	Noble County	Cultivated
6	" " "	" "	Virgin
7	Albion silt loam	" "	Cultivated
8	" " "	" "	Virgin
9	Parsons silt loam	Mayes County	Cultivated
10	" " "	" "	Virgin
11	Bates very fine sandy loam	" "	Cultivated
12	" " " " "	" "	Virgin
13	Durant clay loam	Carter County	Cultivated
14	" " "	" "	Virgin
15	Durant loam	" "	Virgin

Samples 1, 2, 5, 6, 7, 8, are from north central Oklahoma;
3 and 4 from western; 9, 10, 11, 12, from eastern; and 13, 14,
and 15, from southern Oklahoma.

TABLE II
 MOISTURE CONTENT, IGNITION LOSS,
 AND BASE EXCHANGE CAPACITY OF SOILS
 USED IN THE POTASSIUM EXPERIMENTS.

Soil No.	Moisture content % of moist soil (Series A)	Ignition loss % of dry soil	Base exchange capacity m.e./100 g. soil
1	16.2	2.74	10.7
2	15.9	5.08	14.6
3	14.8	1.99	12.2
4	15.5	3.39	14.5
5	15.7	2.86	15.0
6	17.2	4.59	17.0
7	15.3	5.03	10.3
8	17.3	4.83	12.9
9	15.6	2.46	10.5
10	16.4	5.91	19.0
11	16.0	3.21	9.2
12	18.5	5.84	14.7
13	15.4	3.51	15.0
14	18.2	4.48	21.2
15	16.5	4.27	14.0

As indicated in Table II, relatively uniform moisture conditions were obtained in the soil samples with the moisture content slightly varying around the calculated value of 16.7%. The material lost from the soils by ignition consists mainly of organic matter and chemically bound water, the latter part increasing with decreasing particle size of the mineral matter. In all soils except Albion silt loam (No. 7 and 8), the

ignition loss is considerably higher in the virgin samples than in the cultivated samples which might be taken as an indication of decreasing organic matter content in the cultivated soils although variations in the amount of chemically bound water due to differences in the structure of the mineral matter might be responsible for a part of the differences.

In all cases the base exchange capacity was higher in the virgin soil than in the cultivated soil of the same type.

CHANGES IN THE AVAILABLE POTASSIUM CONTENT THROUGH IGNITION.

Available potassium was determined in the soils after ignition for three hours at a temperature of 550°C.

Ignition of the soils caused a considerable increase in the amounts of available potassium in all soils as seen in Table III, with the effect varying from an increase of 19% in the virgin Albion silt loam (No. 8) to 531% in the virgin Parson silt loam (No. 10). In soils No. 3 to 8, all containing more than 200 ppm. of available potassium, the increase in available potassium was larger in the cultivated sample than in the virgin sample from the same soil while in the other soils, all containing less than 200 ppm. of available potassium, the increase was larger in the virgin samples.

TABLE III

AVAILABLE POTASSIUM IN SOILS
BEFORE AND AFTER IGNITION.

Soil No.	Available potassium, ppm. of dry soil		
	Before ignition	After ignition	% increase
1	195	370	90
2	183	384	110
3	236	532	125
4	288	548	90
5	201	641	219
6	230	548	138
7	231	397	72
8	323	383	19
9	70	212	203
10	88	556	531
11	75	178	137
12	63	213	238
13	122	398	226
14	153	573	274
15	188	381	103

CHANGES IN THE CONTENT OF AVAILABLE POTASSIUM
UNDER DIFFERENT STORAGE CONDITIONS.

The soil samples stored as previously described in series A, B, and C were analyzed at periodic intervals to determine to what extent any change might occur in available potassium content.

The samples also were analyzed immediately after collection and before bringing them to a uniform moisture content.

TABLE IV AVAILABLE POTASSIUM IN MOIST SOILS AT
VARYING INTERVALS WHEN STORED AT A
TEMPERATURE OF 5°C.

Soil No.	Available potassium in dry soil				
	At collec- tion, ppm.	After 7 weeks, ppm.	After 8 weeks, ppm.	After 15 weeks, ppm.	After 18 weeks, ppm.
1	177	195	195	205	204
2	166	183	181	198	200
3	169	236	235	262	258
4	269	288	286	321	330
5	195	201	204	229	238
6	226	230	232	258	270
7	173	231	231	249	250
8	258	323	322	334	340
9	42	70	70	79	79
10	61	88	92	92	90
11	46	75	76	78	77
12	34	63	64	73	74
13	--	122	124	120	130
14	--	153	154	154	158
15	--	138	196	191	190

TABLE V AVAILABLE POTASSIUM AT VARYING INTERVALS
IN SOIL SAMPLES STORED UNDER AIR DRY
CONDITIONS AT ABOUT 25° C.

Soil No.	Available potassium in dry soil						
	Initial ppm.	After 48 hours ppm.	After 7 days ppm.	After 5 weeks ppm.	After 7 weeks ppm.	After 13 weeks ppm.	After 18 weeks ppm.
1	195	170	158	140	138	154	160
2	183	163	151	133	132	150	150
3	236	221	208	168	187	203	200
4	288	271	246	208	205	237	241
5	201	202	179	153	164	189	192
6	230	218	202	172	188	201	203
7	231	206	196	171	175	199	200
8	323	287	268	227	236	259	267
9	70	56	60	58	52	58	56
10	88	78	71	73	67	78	80
11	75	60	63	58	58	49	53
12	63	53	51	57	51	49	54
13	122	102	97	102	--	--	--
14	153	144	133	145	--	--	--
15	188	177	156	135	--	--	--

A study of Table IV shows that the available potassium increased in all soils with time after moistening, with the change more or less following the course of a logarithmic function. This is in good agreement with the results found by other investigators (8, 20, 34) for different soils as discussed in the review of the literature since the quantities of available potassium in all soils in this experiment were below the level where a fixation during moist storage has been found.

TABLE VI AVAILABLE POTASSIUM AT VARYING INTERVALS
IN SOIL SAMPLES STORED IN AN OVEN AT A
TEMPERATURE OF 110°C.

Soil No.	Available potassium in dry soil					
	Initial	After 48 hours ppm.	After 7 days ppm.	After 7 weeks ppm.	After 13 weeks ppm.	After 18 weeks ppm.
1	195	160	160	144	165	167
2	183	150	146	133	164	162
3	236	208	204	192	281	229
4	288	242	240	216	248	243
5	201	195	196	184	215	215
6	230	197	196	191	229	228
7	231	188	188	184	201	207
8	323	236	231	223	244	251
9	70	48	50	54	63	60
10	88	64	62	55	80	82
11	75	48	52	43	57	60
12	63	40	43	35	55	59
13	122	99	101			
14	153	142	134			
15	188	160	158			

The approach of a constant level of available potassium seemed to proceed more rapidly in the soils with the lower content of available potassium. The Durant soils (13, 14, 15) showed practically no variations in the available potassium content after 7 weeks of moist storage. The Parsons silt loam (9, 10) and the Bates very fine sandy loam (11, 12) had a very pronounced increase in available potassium content during the

first 7 weeks, while the rest of the soils showed a more gradual increase, especially in the case of the Kirkland silt loam (5, 6) which did not seem to reach a constant level during the 18 weeks period covered by these experiments.

Data on the changes in the amount of available potassium in soils stored under air dry conditions are given in Table V. It will be observed that the general trend is the same for all soils. The amount of available potassium decreased gradually, passed through a minimum and increased again with the minimum reached after 5 to 13 weeks. The time for reaching the minimum seems to be correlated with the quantity of available potassium. (Bates very fine sandy loam with initial 75 and 63 ppm. of available potassium respectively, reached a minimum after 13 weeks.)

The figures given in Table VI for soils stored at 110°C show the same general trend as those in Table V. Minimum values occurred with one exception, after 7 weeks, but the rate of change differed in such a way that a more rapid decrease occurred at the beginning followed by a more gradual change. The minimum reached in Series B was higher when compared with soils high in available potassium and lower for soils low in available potassium. After 18 weeks the content of available potassium was higher in the soils of Series B with one exception (Albion silt loam, No. 8).

RATE OF CHANGE OF POTASSIUM INTO AVAILABLE FORM
UNDER DIFFERENT PERCENTAGES OF BASE SATURATION.

Three 300 gram samples of oven dry soil from each of soils number 3 and 4 (St. Paul very fine sandy loam) and 9 and 10 (Parsons silt loam) were weighed into 1000 ml. Erlenmeyer flasks. To one sample from each soil 500 ml of .1 normal hydrochloric acid was added, and to the other two samples 500 ml of normal calcium chloride. The flasks were placed on a hot plate for one hour and agitated four times, cooled, filtered under vacuum and washed two times with 250 ml of the respective .1 normal acid and normal calcium chloride solutions, and thereafter with four 250 ml portions of distilled water.

One of the calcium saturated samples from each soil was treated with 200 ml of hydrochloric acid of a concentration corresponding to 30% of the base exchange capacity of 300 grams of the respective soils. After two hours and with several agitations the samples were filtered again and washed twice with 250 ml distilled water.

All soils were allowed to air dry for 24 hours, were passed through a coarse screen and uniformly mixed. Finally they were stored in glass flasks, plugged air tight with rubber stoppers and kept at the laboratory temperature (about 25°C).

Analyses for available potassium were made at certain intervals. The moisture contents and the quantities of available potassium in the samples after drying in the oven at 110°C for 48 hours also were determined. The results of these analyses are given in Table VII.

TABLE VII RATE OF CHANGES IN AVAILABLE POTASSIUM IN FOUR SOILS UNDER THREE DIFFERENT PERCENTAGES OF BASE SATURATION AT A TEMPERATURE OF 25°C.

Percentage solution	Soil No.	Available potassium in ppm. of dry soil after indicated number of days after treatment											
		3	6	10	14	17	21	26	31	38	45	52	*
Calcium saturated	3	76	86	92	95	90	94	100	87	95	88	88	137
	4	82	92	99	102	99	99	99	97	95	91	91	134
	9	29	36	40	42	35	35	36	29	32	28	32	49
	10	33	40	46	49	42	42	42	33	32	37	37	50
30% H 70% Ca	3	69	88	103	113	92	90	90	84	87	88	92	161
	4	90	105	121	129	110	105	113	105	100	94	87	168
	9	26	36	41	45	35	29	31	32	31	32	32	42
	10	29	33	46	52	30	33	33	33	32	33	33	47
Hydrogen saturated	3	62	72	94	98	78	83	86	100	103	88	92	123
	4	73	85	105	105	84	82	91	101	97	89	85	117
	9	21	28	39	38	28	25	25	31	34	28	28	38
	10	22	33	44	41	29	29	30	37	40	33	37	42

The quantity of available potassium occurring in the St. Paul and Parsons soils after leaching with .1 normal hydrochloric acid and the calcium chloride solution is given in Table VII. It will be observed that the chemical treatment removed more of the available potassium from the

* Samples oven dried for 48 hours, 6 days after treatment.

St. Paul soil then from the Parson soil (compare Table III).

It is quite evident that calcium chloride leaching, and treatment with dilute hydrochloric acid did not remove all of the available potassium from these soils since such a high amount of available potassium was found three days after treatment. A further increase occurred until a maximum was reached for most soils after about 14 days, followed by a gradual decrease in the available potassium content throughout the experiment.

It seems difficult to offer an explanation for the change in available potassium which was observed in this experiment. The theory of fixation by means of microorganisms, suggested by some investigators, and discussed in the review of the literature may have some merit, but so long as potassium only is known to be present in a water soluble form in organic matter, further knowledge about that problem would be required before such a theory could be proposed.

EFFECT OF EXTRACTING SOILS FOR SIX
DAYS WITH AMMONIUM ACETATE AT 25°C
AND 70°C ON AVAILABLE POTASSIUM.

The effect of extracting soils for six days at 25° and 70°C compared to ordinary extraction at 70°C for one hour was determined for Soil No. 4, Series A, B, and C (virgin St. Paul very fine sandy loam). The extraction tubes were carefully plugged and agitated once a day.

TABLE VIII COMPARISON BETWEEN ORDINARY AND SIX DAYS EXTRACTION ON THE QUANTITY OF AVAILABLE POTASSIUM REMOVED FROM A VIRGIN ST. PAUL VERY FINE SANDY LOAM.

Moisture condition	Available potassium, ppm.		
	Ordinary extraction	Six days at 25°C	Six days at 70°C
A. Moist soil	288	234	314
B. Air dried for seven days	205	227	233
C. Oven dried for seven days at 110°C	216	248	251

The data in Table VIII show that six days extraction at room temperature was about equal to one hour extraction at 70°C for moist soil. A slight increase from longer extraction was obtained on the air dry and oven dry soil, but the quantity of available potassium was less than that obtained from moist soil. Six days extraction at 70°C increased the

quantity of extracted potassium about 11% for the moist soil while only a slight increase occurred for the air dry and oven dry soils. The amount of potassium fixed respectively by air drying and oven drying was not recovered by the extended extraction even at the higher temperature.

AVAILABLE POTASSIUM REMOVED BY REPEATED
EXTRACTIONS WITH .1 NORMAL HYDROCHLORIC ACID.

Soil No. 1 (cultivated Norge very fine sandy loam) and Soil No. 11 (cultivated Bates very fine sandy loam) from Series A (moist soils) were extracted with equal quantities of .1 normal hydrochloric acid (1 ml acid to 1 g. soil for 1 hour at 70°C, filtered and washed with an equal quantity of distilled water. After washing the soils were analyzed for available potassium by the standard method, and the extracting procedure was repeated.

The moisture content of the soils at the start was around 20% (calculated on oven dry basis) and about the same quantity of moisture remained in the soil after filtering, which would leave about one sixth of the filtrate in the soil. Washing with distilled water reduced this amount to one sixth again, which would be about one thirty-sixth of the available potassium in the previous extraction or approximately three percent. This value is within the realm of accuracy of the analytical procedure.

TABLE IX EFFECT OF REPEATED EXTRACTIONS WITH .1
NORMAL HYDROCHLORIC ACID ON THE AVAILABLE
POTASSIUM IN NORGE AND BATES VERY FINE
SANDY LOAM SOILS.

Number of extraction	Available potassium, ppm. of dry soil	
	Norge very fine sandy loam	Bates very fine sandy loam
0	195	76
1	75	23
2	53	23
3	39	15
4	35	11
5	30	11
6	46	12
7	29	12
8	31	14
9	29	10
10	24	10
11	24	10
12	29	10
13	29	10
14	29	10
15	29	10
16	24	10
17	24	10
18	24	11
19	24	10
20	23	11
21	24	10
22	24	10
23	--	11
24	--	10
25	--	10
26	--	10
27	--	10

Data on the available potassium removed from these soils are given in Table IX. The extractions were carried on until all of the original 300 grams of soil were used for the analyses. It will be observed that the amount of available potassium was rapidly reduced to a low level, where it remained relatively constant throughout the experiment. Occasional variations are probably due to the fact that the intervals between extractions, during which the soils were kept at room temperature, varied from one hour to three days.

The results seem to indicate an ability of these soils to continue to provide a relatively uniform quantity of potassium upon continued extractions with .1 normal hydrochloric acid although differences in the extracting ability of hydrochloric acid and molar ammonium acetate were apparent and may have had some influence on the results obtained in this experiment.

REPEATED EXTRACTIONS WITH MOLAR AMMONIUM ACETATE AND
RATE OF LIBERATION OF DIFFICULTLY AVAILABLE POTASSIUM
AFTER COMPLETE REMOVAL OF AVAILABLE POTASSIUM.

Soil samples from Soil No. 8 (virgin Albion silt loam) and No. 15 (virgin Durant loam) Series A (moist soils) were extracted at 70°C for one hour with molar ammonium acetate using two parts of extracting solution and one part of soil (by weight). The soil was allowed to settle and 65% of the total extract was decanted and analyzed for available potassium with the flame photometer. The same quantity of ammonium acetate solution (as decanted) was added and the procedure was repeated.

In this procedure, 35% of the potassium extracted at one extraction, evidently remained in the next extraction, and in order to find the quantity of potassium released by a certain extraction, 35% of the quantity of potassium found in the preceding extraction must be subtracted from the quantity found in the succeeding extract.

It also might be noted that the higher concentration of potassium in the extract has an influence on the equilibrium between potassium in solution and the potassium on the exchange complexes, and that this method probably would require more extractions to reach a potassium free extract than a combination of extraction with subsequent leaching of the soil before a succeeding extraction is made. On the other hand the method is fast and very accurate.

When potassium free extracts were obtained, the soils were filtered and washed with distilled water until the filtrates were free from ammonium. The soils were allowed to air dry for 24 hours. Then they were passed through a coarse screen, mixed to uniformity and stored in air tight glass flasks at a laboratory temperature of 25°C.

Within certain intervals, as indicated in Table X, the soils were tested for available potassium.

TABLE X AVAILABLE POTASSIUM REMOVED FROM SOILS BY
REPEATED EXTRACTIONS WITH MOLAR AMMONIUM
ACETATE.

Number of extraction	Available potassium in the extract, ppm. of dry soil		Available potassium after correcting for potassium remaining from the preced- ing extraction, ppm.	
	No.8 Albion silt loam	No. 15 Durant loam	No.8 Albion silt loam	No. 15 Durant loam
1	261	160	261	160
2	124	67	33	11
3	48	29	5	6
4	21	13	4	3
5	8	6	1	1
6	3	3	0	1
7	0	0	0	0
8	0	0	0	0

TABLE XI RATE OF CHANGE OF DIFFICULTLY AVAILABLE POTASSIUM INTO AVAILABLE FORM AFTER COMPLETE REMOVAL OF AVAILABLE POTASSIUM

Soil	Available potassium, ppm. and indicated time in days					
	4	9	15	22	35	(2 at 110°C)
Albion silt loam	15	19	15	16	15	27
Durant loam	11	16	11	14	14	23

The results in Table X show that only one-tenth of the available potassium remains in the soil after the first extraction. It might be still less if the fact is considered that part of the potassium obtained in the succeeding extractions might be liberated from a difficultly available form during the course of the extractions.

Practically all of the available potassium was removed after four extractions.

A rapid change of potassium from difficultly available into available form occurred upon storing the soil in a moist condition as indicated in Table XI. The results obtained were similar to those obtained in a preceding experiment (Table VII), a maximum being reached after a short time followed by a slow decrease. Drying the soil at 110°C for 48 hours caused a much greater increase in the amount of available potassium than moist storage for 35 days.

CONCLUSIONS

In dealing with the problem of different forms of potassium in soil, it must be recognized that a soil is not a static formation, but must be considered as a system in which many chemical and physical processes of constantly changing intensity are continuously going on, bringing about a dynamic condition which seldom reaches an equilibrium.

Although theoretical speculations and conclusions may make a theory or experimental data more or less acceptable, it always has to be proved under given conditions whether they have a broad application. For example, in some experiments it has been found that liming a soil renders potassium more available while in other instances liming has decreased the amount of available potassium. These different observations do not mean that any of the results were wrong. It means that more information is required to explain why different results were obtained. A similar situation may exist for other phases of this complex problem where different opposing theories are proposed.

The first part of this experiment which dealt with exchangeable potassium in soils stored under moist conditions, seems to support the theory of established equilibrium. An equilibrium in a chemical sense involves only reversible reactions proceeding at the same rate in

opposite directions. Dealing with such a complex substance as a soil, however, it is not very likely that all reactions involved could be reversible, and since most reactions performed in the same medium usually have a mutual influence on each other, it is very unlikely to find a true equilibrium established in any soil. Considering one single element such as potassium it might participate in two or more different reactions, each of which might be irreversible; and a constant quantity of this element can be maintained as long as the reactions liberating and fixing this element proceed at the same speed, and something that could be called a false equilibrium might be established. A theory of two simultaneous reactions in the soil, one fixing and one liberating potassium into available forms may explain the behaviour of the soils under air dry and oven dry conditions, where drying and increased temperature might accelerate the fixation reaction more than the reactions involving liberation of available potassium. When these two reactions proceed at different rates, the quantity of exchangeable potassium as measured by base exchange reactions may increase or decrease in a soil.

SUMMARY

A study of the available potassium in fifteen soils from different parts of Oklahoma was performed.

The soils were brought to equal moisture contents, divided into three parts, and stored under different conditions. The soils were analyzed for available potassium at varying intervals. The moist soils, stored in air tight glass jars at 5°C showed an increase in available potassium and approached a constant level which appeared more rapidly in the soils lowest in available potassium.

Soils stored under air dry conditions at 25°C showed a decrease in available potassium which reached a minimum and then increased slowly.

Soils stored in open containers at 110°C showed a more rapid decrease in available potassium followed by an increase to a slightly higher level than under air dry conditions.

Ignition at 550°C caused a large increase in available potassium content.

The rate of change in available potassium under three different conditions in percentages of base saturation was studied in four soils. No significant differences were observed between soils saturated with calcium, hydrogen, and 70% calcium - 30% hydrogen. In all cases an increase occurred in the content of available potassium reaching a maximum in 14 days followed by a slow decrease.

A comparison was made between ordinary extraction with normal ammonium acetate at 70°C for one hour, and six days extraction at 25° and 70°C respectively, using moist, air dry, and oven dry soils. The quantity of available potassium increased with extended time and increasing temperature, the time factor being most important for the dry soil and the temperature most important for the moist soil.

Repeated extractions with .1 normal hydrochloric acid were made on two soils, and the available potassium determined between each extraction. A constant level of available potassium was reached after a few extractions, which was maintained through the experiment.

Repeated extractions with normal ammonium acetate were made on two soils. A complete removal of available potassium was obtained after five extractions. The soils free from available potassium were stored moist at 25°C and analyzed for available potassium at varying intervals. A rapid increase in available potassium content occurred during the first four days after treatment with little change occurring during the next 31 days. Heating the leached soil for 2 days at 110°C greatly increased the amount of available potassium obtained from these soils.

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