# GROWTH AND NUTRITION OF PLANTS AS AFFECTED BY DEGREE OF BASE SATURATION OF MONTMORILLONITIC, KAOLINITIC AND ILLITIC TYPES OF SOIL COLLOIDS

By

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#### A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Department of Soil Science

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## CONTENTS

Introduction	Page 1
Review of Literature	2
Experimental	5
Materials Used	5
Preparation of Colloidal Clay	6
Electrodialysis	9
Plan of Greenhouse Experiments	10
I. Bentonite-sand mixtures	11
II. Kaolin-sand mixtures	14
III. Fox sandy loam	<b>1</b> 5
IV. Pure quartz sand	19
Analytical Methods	20
Results	21
Actual Base Status of the Treated Colloids	21
The Effect of Treatment on Soil Reactions	27
The Effect of Degree of Base Saturation on	
Crop Yields	<b>2</b> 8
I. Bentonite-sand mixtures.	28
II. Kaolin-sand mixtures	39
III. Fox sandy loam	49
IV. Pure quartz sand	54

The Effect of Degree of Base Saturation on	
the Mineral Content of Plants	55
I. Bentonite-sand mixtures	55
II. Kaolin-sand mixtures	61
III. Fox sandy loam	65
The Effect of Complementary Ions on the	
Growth and Mineral Composition of Plants	65
I. Bentonite- and Kaolin-sand mixtures	65
II. Fox sandy loam	73
The Effect of the Nature of Colloids on the	
Availability of Exchangeable Cations	77
Discussion	78
Summary and Conclusions	84
Literature cited	88

## GROWTH AND NUTRITION OF PLANTS AS AFFECTED BY DEGREE OF BASE SATURATION OF MONTMORILLONITIC, KAOLINITIC AND ILLITIC TYPES OF SOIL COLLOIDS

#### TSU SIANG CHU

Exchangeable bases held on the surface of soil colloids have been generally considered by many soil scientists and agronomists to be available to plants. Recent workers, however, have indicated that not all exchangeable bases held on the soil colloidal surface are equally available for plant absorption. Among the factors which affect the availability of exchangeable bases to plants, the nature of colloids, the degree of base saturation, and the nature of complementary ions are important.

In a study of some chemical properties of orchard soils in relation to satisfactory and unsatisfactory growth of peach trees, the writer (8) found that two groups of soils supporting trees of different growth vigor, although containing about the same amount of total exchangeable bases, varied greatly in the degree of base saturation due to the difference in their base exchange capacity. Soils supporting good growth of peach trees had a much higher degree of saturation of total as well as of individual exchangeable bases than those supporting poor growth of peach trees. Although the finding is not considered as a conclusive one in the case of peach trees, it is believed that there exists a relationship between the degree of base saturation of soils and plant growth.

The objectives of this investigation were to attain a better understanding of the significance of the degree of base saturation and the nature of complementary ions in relation to the growth and composition of certain crops, and to evaluate the effect of the nature of clay minerals on the availability of exchangeable cations.

## REVIEW OF LITERATURE

Probably one of the first investigators to study the effect of the degree of saturation on plant growth was Stoh≹mann (36). Using organic colloid, he found in 1864 that the yield of matured corn plant increased with the degree of base saturation. Since then, little knowledge has been accumulated regarding the effect of degree of base saturation of soils on the plant growth until recently when soil workers have taken a renewed interest in this problem.

During the past decade, many papers stressing the importance of degree of base saturation in relation to plant growth have been reported. Thus, Gedroiz (11) and several

other investigators working with soils and plant systems found that the exchangeable calcium is available for plant growth only as its degree of saturation is relatively high. Jenny and Cowan (19) found that the growth of soybean plants in Ca-H-clay suspensions was sharply reduced when the degree of calcium saturation fell below 30% of the total exchange capacity. Also working with soybean, Horner (16) found that with constant amount of calcium supply, the growth of the plants, as measured by both height and weight, increased markedly when the degree of calcium saturation increased from 40 to 60%. Albrecht (1), in discussing degree of calcium saturation of clay and nitrogen fixation, concluded that calcium from the same original total supply was delivered into the plants to a much larger extent when it was on a nearly saturated clay than on one only partly saturated. Similar conclusions drawn from the results of soybean experiments have also been reached recently by Mehlich and Colwell (26) and Mehlich and Reed (27).

According to the recent report of Bower and Turk (6), naturally occurring alkali soils high in exchangeable sodium may not furnish an adequate supply of calcium to plants despite the presence of CaCO<sub>3</sub>. This is in harmony with the finding of Gedroiz (11) that soils saturated with ammonium, sodium or potassium failed to support plant grow-

th even when  $CaCO_3$  was added to the cultures.

It has been suggested by some investigators that the kind of complementary ions present on the colloidal surfaces may affect the availability of the other exchangeable ions. Using purely chemical methods, Seatz and Winters (34) were able to prove that much more potassium was released from the exchangeable complex when the complementary ion was dominantly calcium than when it was dominantly hydrogen. Previous work done by Peech (31) has also substantiated this theory by chemical analysis.

The effect of the nature of complementary ion on the nutrient absorption by plants was also demonstrated by the experiments of Jenny and Ayres (18) using excised barley roots. Their results are in general agreement with those mentioned above. However, results conflicting to them have also been reported by many workers. According to Albrecht and Schroeder (2), the degree of H-ion saturation is in general a helpful factor in mobilizing calcium, magnesium and other cations into plants, although it does not affect the availability of potassium.

Contradictory results regarding the degree of base saturation in relation to cation availability to plants might be attributed partly to the difference in the nature of clay minerals. Elgabaly, et al. (10) found that the

uptake of Zn and K by barley roots was affected by the type of clay mineral.

Studies by Mehlich and Colwell (26) and by Allaway (4) showed that calcium uptake by plants was greater from soils or colloids representing the organic and 1:1 lattice type than from those representing the 2:1 lattice type. Recently, working with peanuts, Mehlich and Reed (28) found that for any given level of calcium, the calcium content of the peanut shells was highest when the plants were grown in the kaolinitic-type colloid, but, on the other hand, the highest content of calcium in the plants was found in those growing in the organic-type colloid.

#### EXPERIMENTAL

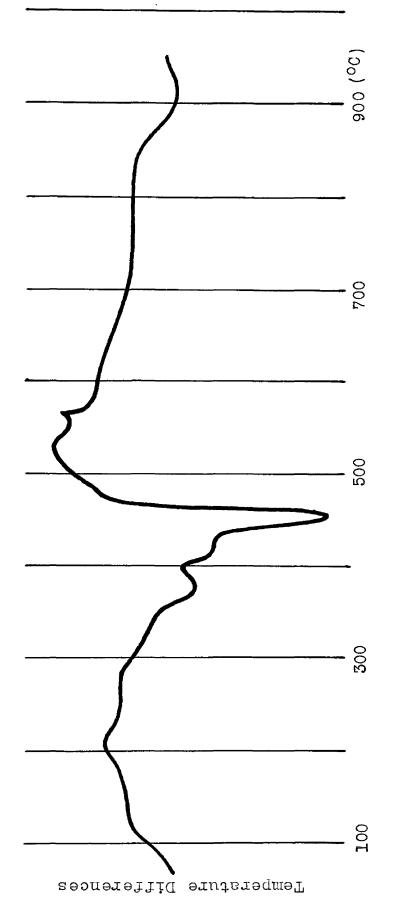
Materials Used. In the present investigation, a Wyoming bentonite from the American Colloidal Company, known as "volclay", was used as a source of montmorillonitic clay and a commercial kaolin, as a source of kaolinitic clay. The "volclay", as described by the producers, is 90% montmorillonite and in its natural state is predominantly saturated with sodium. The exchange capacity per 100 gms. of electrodialyzed bentonite, as determined by the usual ammonium acetate leaching method, was 86 m.e., and of electrodialyzed kaolin, 3.8 m.e.

Besides the two exchange materials mentioned above,

a soil having a relatively low degree of base saturation was also sampled from a peach orchard near Benton Harbor, Michigan. The soil is classified as a Fox sandy loam. It has an exchange capacity of 9.8 m.e. per 100 grams, and is about 25% saturated with bases. Differential thermal curves of the colloid fraction of the soil, as shown in Fig. 1, indicate the predominance of the clay mineral illite.

Pure quartz sand was mixed with the bentonite and kaolin in the greenhouse experiments. Rapid chemical tests on a dilute HNO<sub>3</sub> extract of the sand showed the absence of major cations and anions.

Preparation of Colloidal Clays. Much time was required to prepare the mineral colloids with the desired cation ratios. In the past, three methods have been used in preparing mineral colloids for such studies. In the first method, the colloids are first leached with a dilute acid, or electrodialyzed, or subjecting them to a powerful adsorbent, such as synthetic resins, and then the respective cations are introduced as hydroxides or salts in desired ratios. A serious objection to this method is that the cations do not necessarily react with the exchange complex in the ratio in which they are added. Some of them might exist in the system as free cations and would not be adsorbed by the colloids as exchangeable cations.





Fox sandy loam.

Geological Survey Division, for supplying this differential thermal curve). (The writer is indebted to Dr. Ralph E. Grim, Geologist, Illinois State

The second method is to saturate various portions of the colloids with the desired cations and then mix these in proper proportions. It is assumed that when the colloids with the respective cations are mixed together there would be an interchange of cations and ultimately not only a mechanical mixture would result but also a chemical complex containing the required cation ratios. However, this may not be true, because soil colloids together with their adsorbed ions, represent a Donnan system, and the attainment of a Donnan equilibrium may result in an unequal or non-homogeneous distribution of adsorbed ions.

In the third method, the colloids are leached with a solution of salts mixed in definite proportions. However, due to preferential adsorption of colloids for different cations, the ratio between cations adsorbed on the surface of colloids will not be the same as that existing in the original solution. The preferential adsorption also varies with the type of colloids, temperature, nature and concentration of the respective ions in leaching solution, etc. It is, therefore, very difficult to find out either theoretically or empirically the concentration of salts necessary to produce the desired ratio of cation mixtures. For a large scale experiment, the method is indeed, impracticable.

In the present study, the preparation of colloids with

desired cation ratios was done by the first method.

Electrodialysis. The electrodialyzing cell used was composed of three wooden chambers of the Bradfield type (7) arranged in a parallel manner. It had an inside dimension of 12 x 10.5 x 7.25 inches, and a maximum capacity of about 8,500 ml. in the central compartment and 2,500 ml. in each of the side compartments. Porous porcelain plates about 50 mm. or 0.25 inch thick were used as membranes. A perforated gold sheet having an area of 6 x 2.75 inches served as the anode and an ordinary copper wire screen having 9.5 x 6.5 inches area served as the The electrodes were placed about 20-22 cm. cathode. apart. An adjustable high resistance rheostat and an ordinary ammeter were connected in series with the cell with 220 volts, d.c., as the source of current. The rheostat was adjusted to keep the ammeter reading below 8 amperes and usually around 5. Too high temperature is soon reached with an amperage above 10. At times three such cells were connected in parallel and run simultaneously. By frequent renewal of the electrodialysates and stirring up of the colloidal suspension, the whole process of electrodialyzing a 3% suspension of bentonite could be completed in about 80 to 98 hours. In case of kaolin, a 8-10% suspension was used for electrodialysis, and the whole process was completed in a much shorter time.

The completion of the removal of bases was indicated by rather constant but very low current density (amperage per unit area of the electrode) and was confirmed by the phenolphthalein test on the cathode electrodialysate and pH measurement of the suspension. The unsaturated bentonite and kaolin suspension thus obtained had a pH of about 3.2 and 4.5 respectively.

After the electrodialysis had been completed, the flocculated suspension was removed from the cell and dried on a hot plate. The dried bentonite was ground in a steel mill to pass through a 100-mesh sieve. The pulverization of dried kaolin was affected by a wooden pestle in an open tray.

Since the natural content of exchangeable bases in Fox sandy loam was low, no pretreatment for their removal was attempted.

<u>Plan of Greenhouse Experiments</u>. Greenhouse experiments were conducted involving the growing of several different crops in four different cultural media, i.e., bentonite-sand mixture, kaolin-sand mixture, Fox sandy loam and pure quartz sand. On each of the four cultural media, two series of experiments were carried out for different purposes.

In the first series of experiments, plants were grown in the cultural media having different degrees of base

saturation but with the fixed ratios between the major exchangeable bases, i.e. exchangeable calcium, magnesium and potassium. The principal purpose of this experiment was to study the effect of degree of base saturation on the growth and nutrition of plants. In the second series of experiments, the base exchange capacity of the cultural media was held constant while the ratio between the major exchangeable bases varied within a certain range. The experiments were thus designed to supply information as to the mutual effect of the complementary ions on the growth and nutrition of plants.

Both series of experiments were laid out in the same general pattern. Glazed earthenware jars were employed throughout the investigation. With the exception of the experiments on peach seedlings in Fox sandy loam, which were replicated four times, all greenhouse experiments were run in triplicate. Equal rates of fertilizer applications, involving diammonium acid phosphate and ammonium nitrate, were made to all of the jars unless otherwise mentioned. Solutions of  $ZnSO_4$ ,  $FeSO_4$ ,  $H_3BO_3$  and  $MnCl_2$ were also added to each of the cultural jars to give concentrations of 2, 4, 3 and 8 p.p.m. of Zn, Fe, B and Mn respectively in the final clay-sand mixtures. All chemicals used were of c.p. grade.

I. Bentonite-sand mixtures.---From the known exchange

capacity of the electrodialyzed bentonite, calculations were first made as to the amount of bentonite required to give 4000 gms. mixtures of bentonite and sand with the desired base exchange capacity. For the first series of experiments, the treatments involved four levels of base exchange capacity, i.e. 2, 4, 6 and 8 m.e. per 100 gms. of the mixture, and each in combination with four degrees of total base saturation, i.e. 20, 40, 60 and 80%. For the second series of experiments, the difference between treatments was made only for the ratio between calcium, magnesium and potassium while the base exchange capacity was constant at 2 m.e. per 100 gms. for all of the treatments. A summary of the treatments for both series is given in Table I.

In setting up the greenhouse experiments the desired amount of colloids was first placed into one gallon jars, and solutions of calcium acetate, magnesium nitrate and potassium sulfate added in amounts to supply 20, 40, 60 and 80% of total base saturation with a Ca:Mg:K ratio of 75:15:10. The colloids were maintained as thick suspensions for a period of about three weeks with occasional mixing. After that, while still moist, they were thoroughly mixed with quartz sand to give desired levels of exchange capacity.

Two crops, Eaton Oats and Rosen Rye, were grown in

## <u>Table I</u>

A Summary of the Treatments of the Greenhouse Experiments

	T	(Income)						
Series	Exch. Cap., Base saturation, %				Start	End	Crops grown	
	m.e./100 g.	Ca	Mg	K	Total			
	ନ ଅ ଅ ଅ	15 30 45 60	3 6 9 12	<b>2</b> 468	20 40 60 80	4•5 4•6 5•0 5•3	4.6 4.8 5.9 6.1	Oats: June 27 to Aug. 8,
I	4 4 4 4	15 30 45 60	3 6 9 12	2468	20 40 6 <b>0</b> 80	4.5 4.6 4.9 5.1	4.6 4.8 5.7 5.9	1947 Rye: Sept. 20
Ŧ	0 0 0 0 0	<b>1</b> 5 30 45 60	3 6 9 12	2 4 6 8	20 40 60 80	4•4 4•5 4•8 5•0	4•5 4•7 5•4 6•2	to Nov. 31, 1947
	8 8 8	15 30 45	36 9	2 4 6	20 40 60	4•4 4•5 4•7	4.4 4.6 5.5	
	ର ଜୁ ଅନ୍ଦ ଅ	30 35 40 45 50	15 15 15 15	15 15 15 15 15	60 65 70 75 80	<b>4 • 3</b> <b>4 • 4</b> <b>4 • 6</b> <b>4 • 7</b> <b>5 • 0</b>	4•4 4•8 5•2 5•4 5•8	
II	2 *2 2 2	40 40 40 40 40	5 10 15 20 25	15 15 15 15	60 65 70 <b>7</b> 5 80	4.8 5.0 4.6 4.8 4.6	5.1 5.2 5.4 5.4	Rye: Sept. 20 to Nov. 31, 1947
	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	40 40 40 40 40	15 15 15 15 15	5 10 15 20 25	60 65 70 75 80	4 • 7 4 • 7 4 • 6 4 • 6 4 • 7	5.0 5.2 5.2 5.4 5.6	

on Bentonite-sand Mixtures.

\*Identical treatments, actually represented by the same

jars in the experiment.

succession in the experiment. A moisture content of around 12% was maintained for the growth of oats, and about 8% (start with 5%) for that of rye.

II. Kaolin-sand mixtures.----Due to its very low exchange capacity a considerable amount of kaolin had to be used in order to afford kaolin-sand mixtures with base exchange capacities comparable to those of bentonitesand mixtures. The mixtures, being high in kaolin, were low in apparent specific gravity. As a result, each lgallon jar could hold only 3500 gms. of the mixture.

By precisely the same way as described for preparing bentonite-sand mixtures, kaolin and pure quartz sand were mixed and treated to give two series of experiments. In the first series, the treatments involved two levels of exchange capacity, i.e., 1 and 2 m.e. per 100 gms. of mixture, each with four degrees of total base saturation, i.e., 20, 40, 60 and 80%, while the ratio of Ca:Mg:K was constant at 75:15:10. In the second series, the exchange capacity was fixed at 1 m.e. per 100 gms. for all of the treatments, while Ca:Mg:K ratio was varied as in the bentonite-sand mixtures. The fertilizer applications were the same as those for the bentonite-sand mixtures.

Rosen Rye was the first crop grown in the media. During its growth period, the moisture content of the media was maintained at about 12% for those having an

exchange capacity of 1 m.e. per 100 gms., and 16% for those having an exchange capacity of 2 m.e. per 100 gms.

After the rye was harvested, the contents of each jar were added to an equal amount of pure quartz sand and potted into 2-gallon jars in the following manner. Two thousand grams of sand was first spread on the bottom of the 2-gallon jar to facilitate drainage and aeration; then 7000 gms. of the kaolin-sand mixture was introduced; and finally an 1-inch layer of about 800 gms. sand was evenly spread over the surface. The purpose of further diluting of the mixture with sand and the manner of potting the mixture by layers was to improve the physical properties of the mixture and to prevent the formation of a surface crust.

The same fertilizer applications were made as were made originally to insure sufficient quantities of nitrogen, phosphorus, and minor elements. Moisture contents of the new mixtures were maintained at 10% for the low exchange capacity series, and at 12% for the high series. Oats were grown for a period of 70 days. Table II gives the summary of the actual plan of the greenhouse experiments for kaolin-sand mixtures.

III. Fox sandy loam.----No sand was added to the Fox sandy loam. The soil had a base exchange capacity of 9.8 m.e. per 100 gms., and is about 25% saturated with bases.

## Table II

A Summary of the Treatments of the Greenhouse Experiments on Kaolin-sand Mixtures.

	T	reatments				Mean pH		
Series	Exch. cap.,				Start	End	Crops grown	
	m.e./100 g.	Ca	Mg	ĸ	Total			gi 0wii
I	1 1 1 1	15 30 45 60	3 6 9 12	2 4 6 8	20 40 60 80	5•1 5•8 6•8	5.4 6.1 6.6 6.9	Rye: Sept.20- Nov. 31, 1947
-	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	<b>1</b> 5 30 45 60	3 6 9 12	24 6 8	20 40 60 80	5.2 5.9 6.9	5.4 6.3 6.9 7.2	Oats: Dec. 19, <b>1</b> 947 <b>-Feb</b> 26,1948
	1 1 *1 1 1	3 5 5 4 5 5 5 5	15 15 15 15	15 15 15 15 15 15 15 15 15	60 65 70 75 80	2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	6.4 6.5 6.6 6.7 6.7	
II	1 1 *1 1 1	40 40 40 40 40	5 10 15 20 25	15 15 15 15 15	60 65 70 75 80	3 3 3 3 5 5 5 5 5 6 6 6 6 6 6 6 6 7 6 7 7 7 7 7	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	Rye: Sept. 20- Nov. 31, 1947
	1 1 *1 1 1	40 40 40 <b>40</b> 40	15 15 15 15 15	5 10 15 20 25	60 65 70 75 80	6.4 6.9 6.5 6.5	6.54 6.4 6.4 6.4 6.4 7	

\*Identical treatments, actually represented by the same jars in the experiment. The first series of experiments was run with five levels of total base saturation, i.e., 25, 50, 75, 100 and 150%, each having the same Ca:Mg:K ratio of 75:15:10. The second series of experiments consisted of five treatments with varying ratios between Ca:Mg:K but with a constant degree of base saturation at 50%. One of the treatments was actually a part of the first series as is noted in Table III, which gives the summarized plan of the treatments.

Both series were first carried out in 4-gallon glazed earthenware jars, each filled with 20 kg. of the soil. Three young peach seedlings were transplanted into each jar, only one being retained after three weeks. A moisture content of about 15% was maintained during the experiment. At the end of 166 days, the total length of the main shoots of peach seedlings was determined.

After the removal of peach seedlings, the soil in each jar was allowed to dry and was remixed. Without additional fertilizer treatment, 9500 gm. portions of the soil from each jar were weighed into 2-gallon pots. Thus a total of eight 2-gallon pots could have been obtained from each quadruplicate of the same treatment in 4-gallon jars but only six of them were actually used for further experimental purposes. Each six of these 2-gallon pots, having the same treatment, were divided equally into two

## Table III

# A Summary of the Treatments of the Greenhouse Experiments

		Tre	eatmer	its		Mean pH				
Series	Exch.	Base sa	aturat	ion,	%			- Crops		
	cap., <u>m.e.</u> 100g.	Ca	Mg	K	Total	Start	End	grown		
	9•8	18.7	3.9	1.9	24.5	6:0	6.1	In 4-gal. jars: Peach seed-		
	<b>*</b> 9.8	37.5	7.5	5	50	6.2	6.0			
I	<b>9.</b> 8	56.25	11.25	7.5	75	6.4	6.3	In 2-gal. jars:		
	9.8	75	15	10	100	6.5	6.5			
	9.8	112.5	22.5	15	150	6.7	6.5	Proso, Oct. 23-		
	<b>*9.</b> 8	37.5	7.5	5	50	6.2	6.0	Nov. 27,1947		
	9.8	40	5	5	50	6.2	6.0	Oats, Dec. 19, 1947-Feb. 26, 1948		
II	9.8	35	5	10	50	6.3	6.2	Tomato, Aug.		
	9.8	30	10	10	50	6.2	6.2	27,1947-Jan. 29,1948		
	9.8	30	5	15	50	6.1	6.1			

on Fox Sandy Loam

\*Treatments actually represented by the same jars.

groups. One group was used for the growth of soybeans, proso and oats in succession and the other for the growth of tomatoes. Soybeans and proso were grown in the period from Aug. 28 to Oct. 23,1947 and from Oct. 23 to Nov. 27, 1947 respectively, with no artificial illumination of the greenhouse. Being short day plants, they all appeared dwarf in the vegetative growth and matured earlier than usual. Because of the limiting nature of the photoperiodicity to the growth of soybeans and proso, the results were not valid for direct interpretation. No measurement for their growth rate was, therefore, attempted during the experiment.

IV. Fure quartz sand.----The purpose of using pure quartz sand as cultural media was to afford comparisons with treatments made on bentonite and kaolin media so that a better interpretation of the results might be obtained. Rye and oats were grown in succession in 1-gallon jars, each filled with 4 Kg. of pure sand. Moisture content of the sand was maintained at about 5%. Every treatment represented in the both series of bentonite-sand and kaolin-sand mixtures was also made in the pure quartz sand cultures. The rate of applications given to each treatment at the start of the sand culture experiment was only two-fifths of the actual rate received by the bentonite-sand mixtures, the remaining three-fifths was sup-

plied after the first crop was harvested.

Analytical Methods. Harvested plant materials including oats, rye, and leaves of tomato were air-dried and ground in a small Wiley Mill to pass through a 20mesh sieve. One gram portions of the oven-dried tissue were then wet-ashed at a moderate heat with a mixture comprising of 4 ml. of 70%  $HClO_4$ , 15 ml. of concentrated  $HNO_3$  and 4 ml. of concentrated  $H_2SO_4$  (33). The extract was finally diluted with water to 25 ml. Aliquots of this extract were taken for the analysis of calcium, magnesium and potassium.

The determination of calcium was made volumetrically on the 5 ml. aliquot as oxalate, following the precedure of standard A.O.A.C. micro-method (5). Magnesium was determined photocolorimetrically, using 520 m/m filter in 0.2 ml. aliquot by thiazol yellow method (29), which was essentially the same as ordinary titan-yellow method (32). Potassium was determined on 1 ml. aliquot by the cobaltinitrite method using Peech's technique (30).

All pH measurements of soil and clay-sand mixtures were made potentiometrically with a Macbeth alternating current pH-meter using glass electrodes with a soil water ratio of about 1 to 2.

#### RESULTS

Actual Base Status of the Treated Colloids. In the previous sections, reference has been made to the possibility that with the present method of preparing colloids, the exchange reactions between the exchangeable hydrogenion of the electrodialyzed clays and cations of the introduced electrolytes are likely to be incomplete. In order to evaluate the actual status of the bases in the exchange materials, a series of laboratory experiments were carried out.

To 10 gm. portions of H-bentonite in suspension, different amounts of the solutions of calcium acetate, magnesium nitrate and potassium sulfate were added according to the calculated ratios. The systems were then allowed to stand in the laboratory, with occasional shaking, for a period of at least two weeks. Analyses of calcium, magnesium and potassium were finally made on the filtrate. From that, the actual percentages of base saturation were calculated. Similar experiments, using 50 gm. portions of materials, were also carried out for electrodialyzed kaolin and natural Fox sandy loam, only in the latter case the soil, after leaching with about 400 ml. alcohol, was used for analyses instead of the filtrate.

The results of these experiments, presented in Table  $IV_x$ , indicate that some of the bases added to the colloids were not held on the colloidal surface. The portion of the bases that existed in the free form varied with the nature of colloid, and electrolyte, and the symmetry concentration of the electrolyte added. The higher efficiency of replacement for H-ions was observed in the lower symmetry concentration of electrolytes. It is not the purpose of this paper to involve a discussion of exchange reactions except to mention the fact that the results obtained were in general agreement with many others (12).

Figures II, III and IV show exchange isotherms of calcium, magnesium and potassium with different types of soil colloids. As no similar laboratory experiment has been made for the treatments involved in the experiment series no. II of either bentonite-sand mixture or kaolinsand mixture or Fox sandy loam, the actual base status of those treatments were not precisely known. However, with aid of data shown in Table IV, it is perhaps possible to get a fairly close evaluation of them.

Inasmuch as the results of the present investigation, like many others along the same line, are likely to be qualitative in nature, the degree of base saturation referred hereafter in the tabulation of the results of greenhouse experiments will be the theoretical values

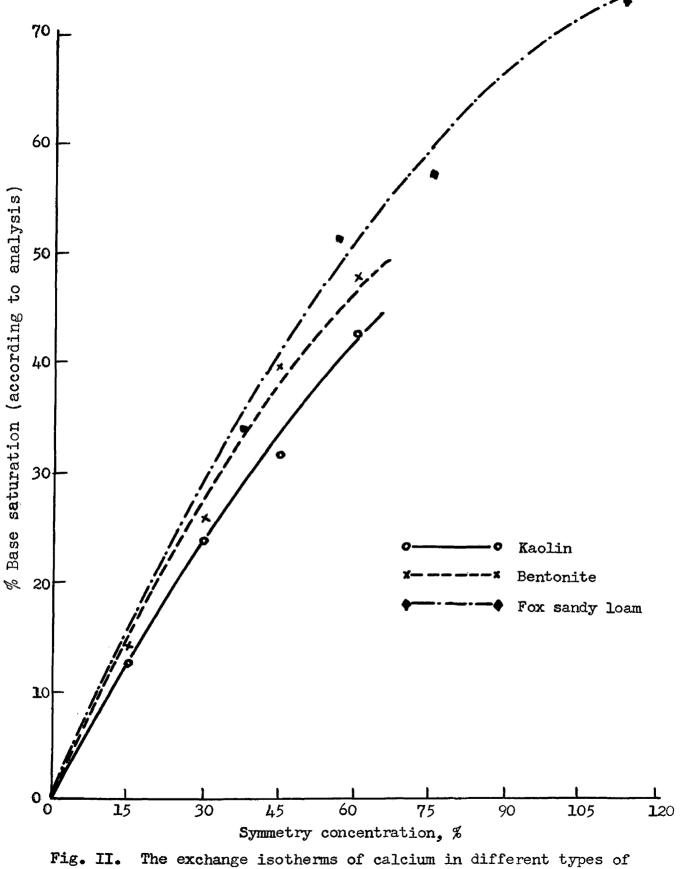
## Table IV

The Extent of Ionic Exchange Reactions of Bentonite,

Symmetry concentration,*			pH <b>val</b> ue	Actual base saturation, % (according to analyses)				
Ca	Mg	K	Total		Ca	Mg	K	Total
	Bento	nite	-Exch	. cap.=	-86 m.e	. per	100 g	ms.
15	3	2	20	3.82	14.2	2.7	1.6	18.5
30	6	4	40	4.21	26.0	5.6	3.1	34.7
45	9	6	6 <b>0</b>	4.83	40.3	7•9	5.0	53.2
60	12	8	8 <b>0</b>	5.40	48.1	9.2	6.1	63.4
	Kaol	inE	Exch.	cap.=-3	.8 m.e.	per ]	.00 gm	S.
<b>1</b> 5	3	2	20	5.18	12.8	2.2	1.3	16.3
30	6	4	40	5.86	24.3	4.5	2.3	31.1
45	9	6	60	6.41	32.3	6.4	3.7	42.4
60	12	8	8 <b>0</b>	6.72	42.9	8.0	<b>4</b> •8	55•7
Fo	x sandv	loam-	Exc	h. cap.=	<b>=9.</b> 8 m	1 <b>.e.</b> pe	er 100	gm <b>s</b> .
37.5	7.5	5	50	6.2	34.1			44.7
56.25	11.25	7.5	75	6.4	51.6	<b>9</b> •8	5.2	66.6
75	15	10	100	6.5	57.5	11.0	6.4	74.9
112.5	22.5	15	150	6.9	73.8	13.0	7.5	94•3

Kaolin and Fox Sandy Loam.

\*Symmetry concentration when expressed in terms of percentage is same as the percentage base saturation calculated according to the treatment received.



soil colloids.

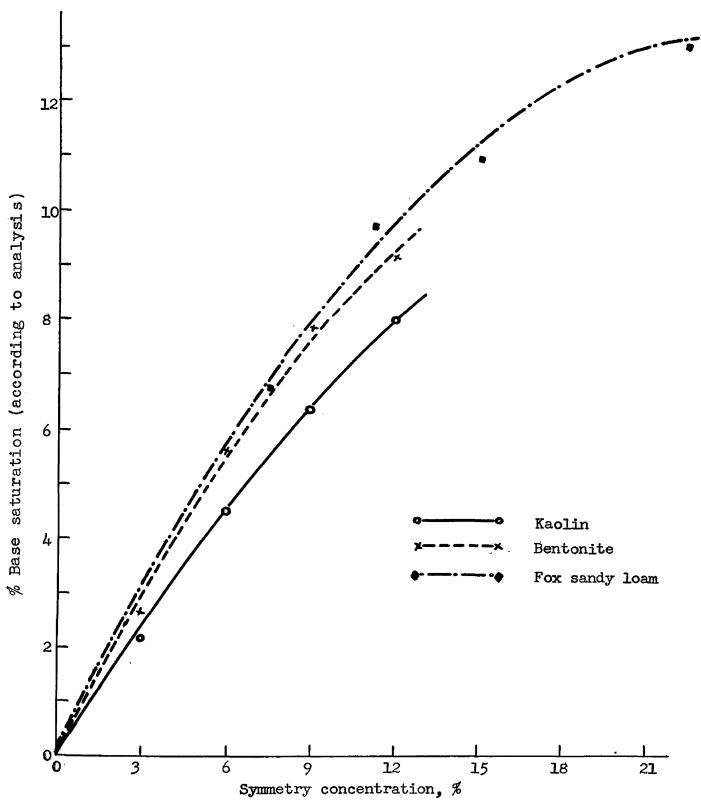
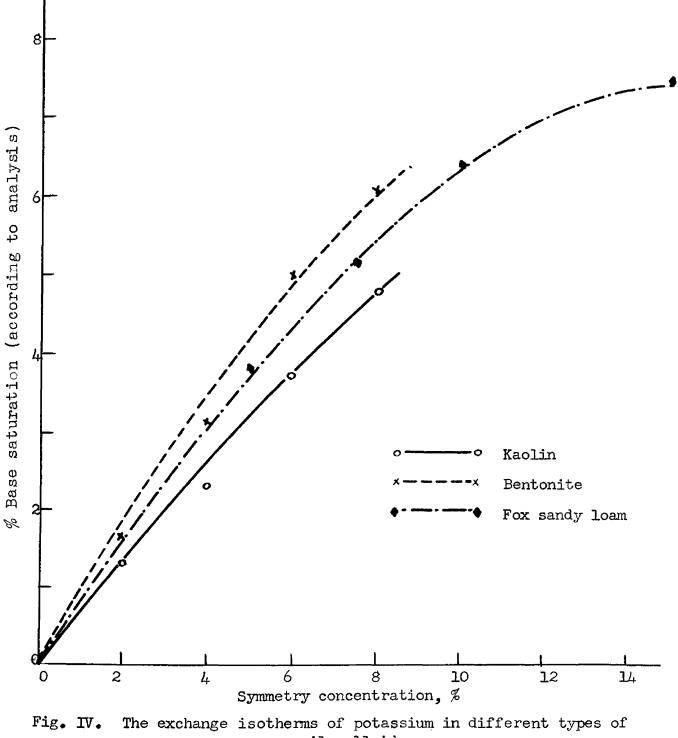


Fig. III. The exchange isotherms of magnesium in different types of soil colloids.



soil colloids.

indicated explicitly by the treatment according to calculation, rather than the actual value indicated implicitly by the treatment according to chemical analysis.

The Effect of Treatment on Soil Reactions. The pH of cultural media measured at the start and the end of the experiment are presented in Table I, II and III. A comparison of Table I and IV reveals that the pH values of pure bentonite suspension were different from those of bentonite-sand mixtures used for greenhouse studies. The difference is mainly due to the presence, in the bentonite-sand mixtures, of the large amount of sand which tends to raise their pH values.

The pH values of bentonite-sand mixtures were low as can be seen from Table I. Even with a total base saturation of 80%, the pH of the mixtures were still around 5.0 at the start of the experiment. The results thus indicate a rather high buffer capacity of bentonite at low pH levels which is in general agreement with Mehlich's findings (24, 25).

There were general increases in the pH values of the bentonite-sand media after crops had been grown on them, although the increases were slight where the degree of base saturation was low. On the other hand, noticeable pH increases were observed where the degrees of base saturation were high. No effort has been made to explore

the reasons for these increases. However, it is suspected that aside from the possibly unequal absorption of NH<sub>4</sub>-N and NO<sub>3</sub>-N by plants, the decomposition of acetic acid, which is formed as a result of base exchange reactions between calcium acetate and acid colloid, might be one of the main reasons.

The Effect of Degree of Base Saturation on Crop Yields.

I. Bentonite-sand mixtures.----The general growth of oats and rye as related to the total quantity of bases present in the bentonite-sand mixture is shown by the data in Table V. These results show that as the supply of exchangeable bases was increased, with a constant base exchange capacity, the yields of the crop increased. The increased yields for the increasing percentages of base saturation arrange themselves in a nearly straight line relation, as can be seen from the actual photographs of the growth conditions of the plants (Figs. V, VI, VII and VIII). A more effective comparison can be made for this relationship by reference to the graphs for the yields of oats and rye, shown in Figs. IX and X.

The four-levels of degree of base saturation, which represent a variation in both the supply of exchangeable bases and the hydrogen-ion concentration--the two variables which are reciprocally related--show that the

### Table V

The Effect of Different Levels of Exchangeable Bases on Yields of Oats and Rye Plants

Exchange capacity, m.e. per 100 gms. Base 4 б 8 2 saturation Yield in grams\* % Oats Rye Oats Rye Oats Rye Oats •55 •55 20 1.58 1.93 1.86 •54 1.83 •53 2.48 2.43 .86 2.80 .85 2.40 40 1.13 •77

1.09

1.30

60

80

1.85

2.59

3.39

4.24

in Bentonite-sand Mixtures.

\*Values represent average dry weights of the aboveground portions from three replicate pot cultures.

3.80

5.70

1.04

1.18

3.12

3.58

1.07

Rye

3.03



Fig. V. Growth of 17-day old oats in bentonitesand mixture showing the general plan of a part of the greenhouse experiment. Exchange capacity of the media varied from 2 m.e. to 8 m.e. per 100 gms. mixture. Treatments on base status were made to supply 20, 40, 60 and 80 % saturation of the exchange capacity, while Ca:Mg:K was kept constant. Experiments were set up in triplicate.

2 m.e. 2 m.e. 2 m.e. 2 m.e. 20% 40% 60% 80%

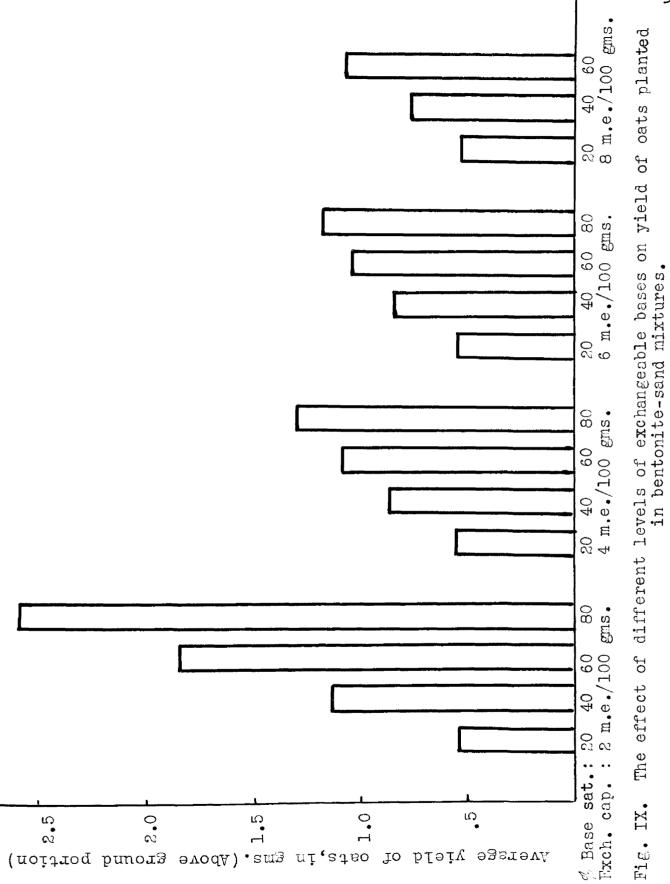
Fig. VI. Growth of 17-day old oats as related to degree of base saturation of the bentonitesand mixture with a base exchange capacity of 2 m.e. per 100 gms. of the mixture. (Increasing saturation from left to right).

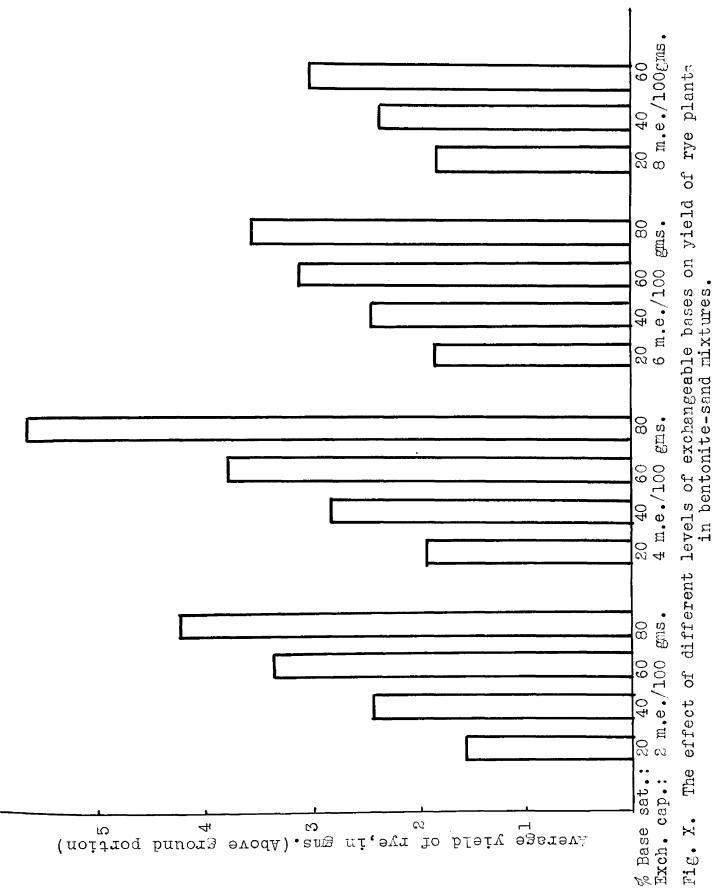


Fig. VII. Growth of rye at the end of 2 months as related to degree of base saturation of the bentonite-sand mixture with exchange capacity of 2 m.e. (left four jars) and 4 m.e. (right four jars) per 100 gms.



Fig. VIII. Growth of rye at the end of two months as related to degree of base saturation of the bentonite-sand mixture with exchange capacity of 6 m.e. (left four jars) and 8 m.e. (right three jars) per 100 gms.





growth of both oats and rye improved with a decreasing hydrogen-ion concentration and an increasing base saturation. Which of these two variables is the more significant factor is not evident in the yield data presented. However, the fact that both oats and rye are acid-tolerant crops is well known. According to Weir (39), oats and rye may grow normally at strongly acid soil with pH 4.8. The compilation of soil reaction preferences of plants by Spurway (35) shows oats and rye will tolerate a pH 4.5 without possibility of serious injury. Analyses of plant materials, as will be presented in the later sections, also give indications that the total amount of available bases is a more important factor in affecting the difference in growth than a variation in hydrogen-ion concentration.

The data in Table V also show that at 20% of base saturation, oats and rye yields were approximately the same, regardless of the exchange capacity of the media. A similar situation is observed at 40 and 60% base saturation levels except in the yields of oats from the 2 m.e. base exchange capacity jars, which were higher than the rest at corresponding base saturation levels. Photographs showing these facts are presented in Figs. XI and XII.

With the design of this experiment, it is possible

6 m.e. 20% 2 m.e. 4 m.e. 8 m.e. 20% 20% 20%

Fig. XI. Seventeen-day old oats showing, with the same low degree of base saturation, no effect on the growth by varying the base-exchange capacity of the bentonite-sand mixture.

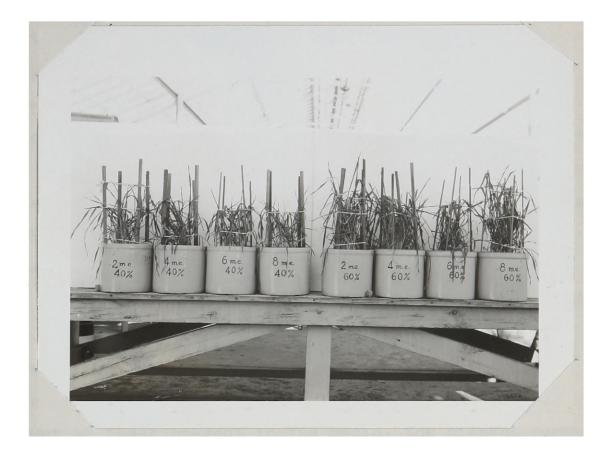
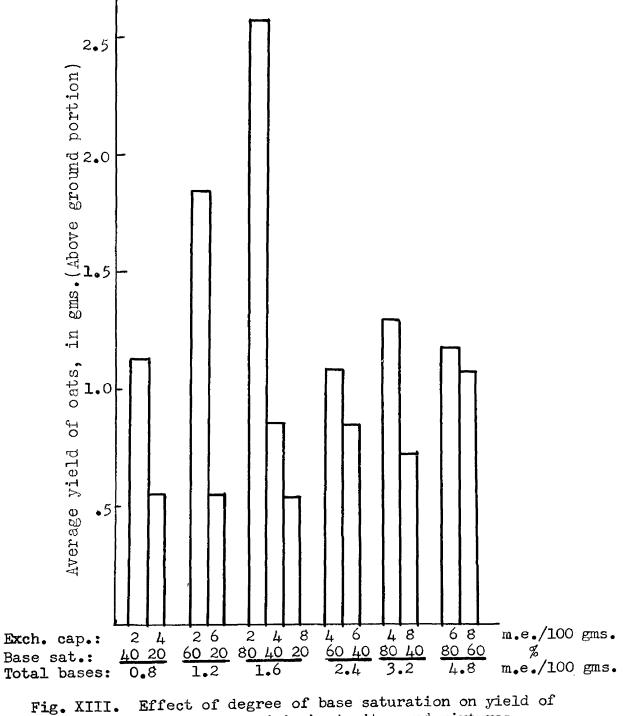


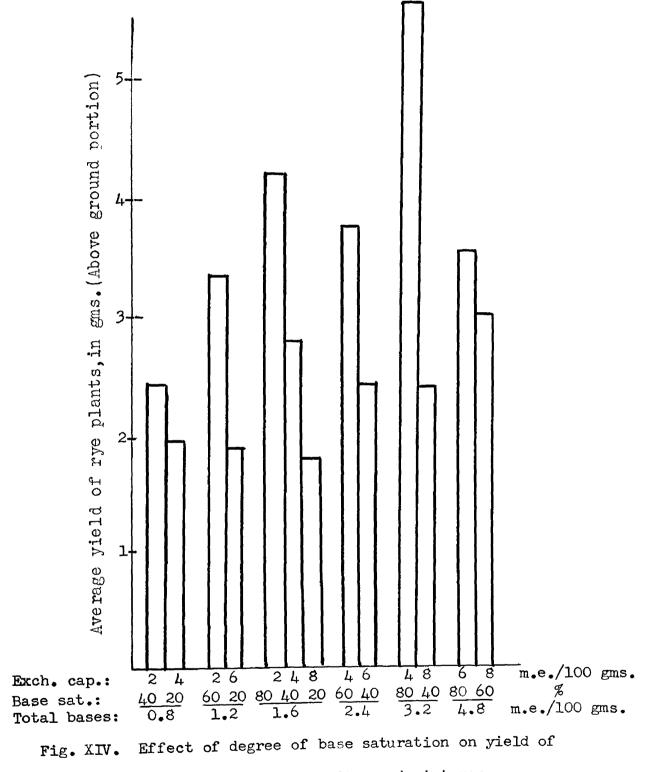
Fig. XII. Rye crops at the end of two months showing no significant difference of the growth by varying the base exchange capacity of the bentonite-sand mixture.

to make a further comparison between treatments. Out of the 15 different treatments listed in Table V, there were actually eight different levels of total bases contained in the cultural media, viz., 0.4, 0.8, 1.2, 1.6, 2.4, 3.2, 3.6 and 4.8 m.e. bases per 100 gms. of medium. Except for the levels 0.4 and 3.6 m.e., each level was made up, in more than one way, by varying the levels of the base exchange capacity, and the degrees of saturation. Thus, for instance, treatments made up by either of 2 m.e. exchange capacity, 80% saturation, or 4 m.e. exchange capacity, 40% saturation, or 8 m.e. exchange capacity, 20% saturation, all gave the same absolute amount of bases, i.e., 1.6 m.e. per 100 gms. of the bentonite-sand mixture. However, crop yields have shown different effects from these treatments. In all cases, with the same absolute amount of bases present in the media, the highest percentage of saturation gave the best yields of oats and rye. Futhermore, the greater the difference of degree of saturation, the greater the difference in yields. These facts, shown by the graphs in Figs. XIII and XIV, and by the photographs in Figs. XV and XVI, suggest that the growth of both oats and rye crops is more directly related to percentage saturation than to total amount of bases.

II. Kaolin-sand mixtures.---Yields of oats and rye showing the effect of varying levels of bases in the



oats planted in bentonite-sand mixtures.



rye plants in bentonite-sand mixtures



Fig. XV. Seventeen-day old oats showing the growth condition is more directly related to percentage saturation than to total amount of bases in bentonite-sand mixtures. All three jars contained 1.6 m.e. of bases per 100 gms. media.



Fig. XVI. Rye crops at the end of two months showing the growth condition is more directly related to percentage saturation than to total amount of bases in bentonite-sand mixtures. The two jars on the left contained 1.2 m.e. bases, the three in the middle contained 1.6 m.e. bases, and the two on the right contained 3.2 m.e. bases per 100 gms. media. kaolin-sand mixtures are given in Table VI. The increase of percentage saturation of the kaolin-sand mixtures in this experiment did not seem to have the same effects on the yields of oats and rye as it had produced in the bentonite-sand mixtures. There were some increases in the yields as the degree of base saturation increased from 20% to 40% at both levels of exchange capacity. But on the percentage basis the amount of increase was slight as compared with the percentage increases of yields in the case of bentonite-sand mixtures. The yields of rye were about the same at the corresponding levels of base saturation regardless of the exchange capacity, although the yields of oats were little higher at the 2 m.e. exchange capacity series after the mixture had been diluted with sand.

These facts suggest that a sufficient supply of available bases was supplied in the low saturation levels, and/or that some other factors besides the base status of the media were limiting the growth of the plants. It is evident from the data in Table II that the pH of the media is not sufficiently low to limit the growth of oats and rye. But it was noticed during the experiment that kaolin-sand mixtures exhibited poor physical properties. As water evaporated from the mixture, a very hard crust formed on the surface as if it had been

## Table VI

The Effect of Different Levels of Exchangeable Bases on Yields of Oats and Rye Plants

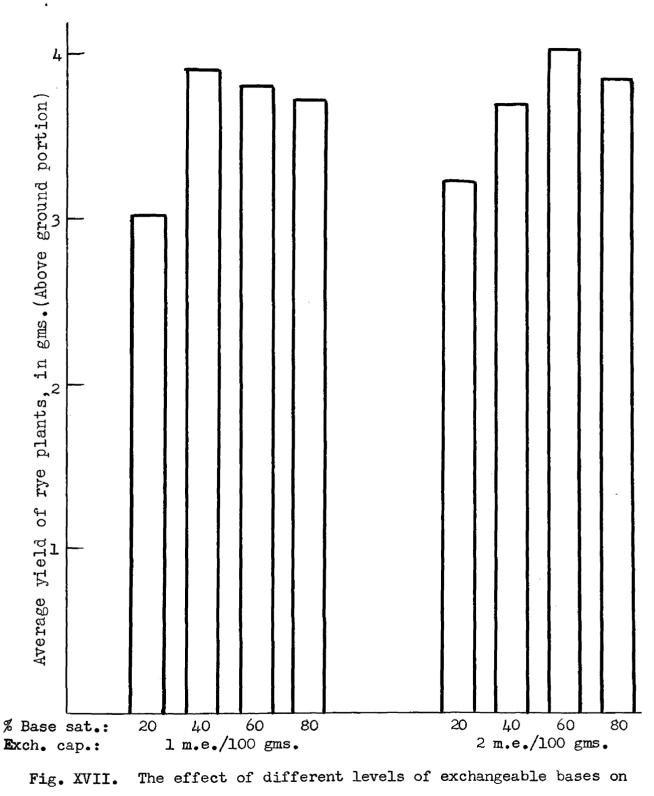
Perce	Exch	ange capacit	y, m.e. per l	00 gms.					
Base satu-		1		2					
ration	Yield in grams*								
%	Oats	Rye	Oats	Rye					
20	4.83	3.01	5.06	3.23					
40	5.77	3.90	6.82	3.81					
60	5.50	3.81	6.72	4.14					
80	6.03	3.72	6.35	3.98					

in Kaolin-sand Mixtures.

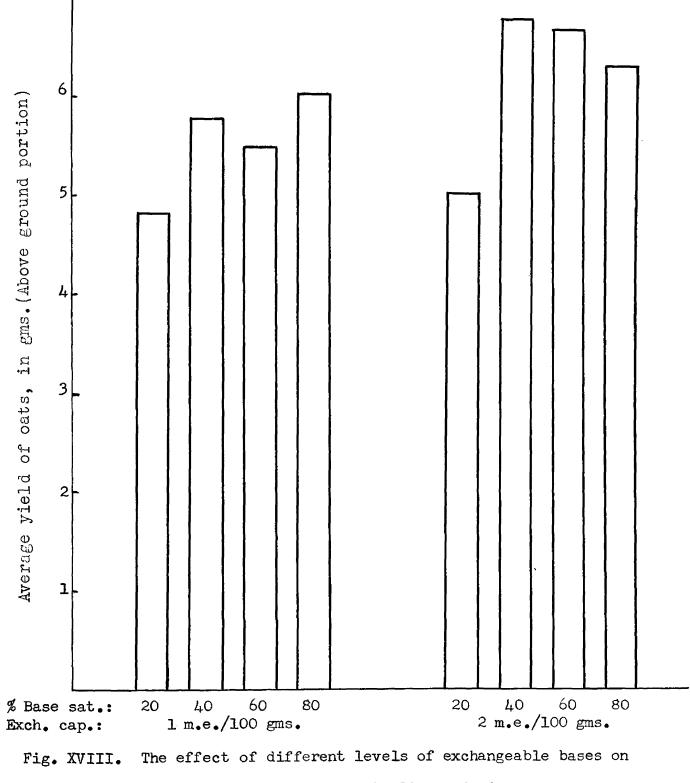
\*Values represent average dry weights of the aboveground portions from three replicate pot cultures.

subjected to pressure. Furthermore, cavities developed under the surface crust which might cause damage to the roots of the crops. All these indications lead one to suspect that the base status of the kaolin-sand mixture is not the only factor affecting the growth of oats and rye. However, the general similarity of the results between the yields of rye grown on the original kaolinsand mixtures and the yields of oats grown on the diluted kaolin-sand mixtures indicate that the growth of oats and rye are more closely related to the base status than to the physical properties of the media. It was observed that a 20% saturation of bases in kaolin-sand mixtures provided a sufficient supply of available bases for fair growth of oats and rye, and a 40% saturation supplied enough available bases for maximum growth of plants under the limitation of other factors existing in the experiment.

A comparison of treatments between 1 m.e. and 2 m.e. exchange capacity series reveals that with the same total supply of 0.4 m.e. bases per 100 gms. of the mixture, the 40% saturation of the 1 m.e. exchange capacity jars gave greater yields of oats and rye than the 20% saturation of the 2 m.e. exchange capacity jars (Figs. XVII and XVIII). On the other hand, no improvement of yields of the 80% saturation of the 1 m.e. exchange capacity jars over



yield of rye plants in kaolin-sand mixtures.



yield of oats planted in kaolin-sand mixtures.

those of the 40% of the 2 m.e. exchange capacity jars was obtained, although they all contained 0.8 m.e. total bases per 100 gms. mixture. These results again suggest that the growth of both oats and rye crops is more directly related to percentage saturation than to total amount of bases and that a 40% saturation of bases in kaolin-sand mixture is probably all that is needed for the growth of oats and rye under the experimental condition.

III. Fox sandy loam.----The general growth condition of peach seedlings as affected by the degree of base saturation is shown in Fig. XIX. The average total length of the shoots of peach seedlings after 5 months of growth in the treated soil was 29.1, 41.5, 25.7, 22.3 and 23.7 cm. for the 25% (untreated), 50%, 75%, 100% and 150% saturated soils respectively.

As can be seen in Fig. XIX, the growth of the peach seedlings in general was not very good. The best growth was at the 50% saturation level. Peach seedlings grown in the soil with the treatments supposed to give more than 75% saturation of bases appeared very poor in growth with only few leaves remaining on the top, and, of the four replications, two failed to servive at the 150% saturation level, and one at the 100% saturation level. During the early stages of the experiment, it was dis-



Fig. XIX. Growth of peach seedlings as influenced by the degree of base saturation of Fox sandy loam. Treatments from left to right are: No. 1 ---untreated natural soil(about 25 % saturation), No. 2---50 % saturation, No. 3---75 % saturation, No. 4---100 % saturation, No. 5--150 % saturation. covered that some of the peach seedlings developed abnormalities in growth. Their leaves became curled and the seedlings began to branch out with numerous small leaves. According to Tukey and Carlson (37, 38) these abnormalities are most probably due to insufficient length of the dormancy period of the peach seed and are frequently accompanied by the dwarfing effect. Although all the abnormal peach seedlings were finally replaced by normal ones during the experiment, the general unsuccessful growth did not yield dependable information as to the effect of degree of saturation on the growth of peach.

Because of the unfavorable photo-periodicity, as has been mentioned before, the growth of soybean and proso crops following the peach was also not successful. Consequently, no measurement for their response to the soil treatments has been made available for the discussion.

In Table VII is presented the results of the experiment on tomato and oats crops with the same treatments. A comparison of the height of the tomato plants, as affected by the various treatments, can be made by refering to Fig. XX. Differences in the yields of fruit and plant and also in the length of the main stalk were marked between the 50% and 75% saturation levels. Above

# Table VII

Yields of Tomato and Oats Crops as Affected by the Degree of Base Saturation of Fox Sandy Loam.

Base saturation					То	Oats		
Ca	Mg	K	Total		Wt. fruit*	Wt. plant*	Main stalk*	Wt. straw*
%	ħ	5/0	%		gms.	gms.	cms.	gm <b>s</b> .
18.7	3•9	1.9	24.5		582	32.1	105	4.5
37.5	7.5	5	50	•	59 <b>3</b>	36.1	1 <b>1</b> 8	5.7
56.25	11.25	7.5	75		692	50.2	150	5.5
75	15	10	100		670	44.2	123	5.8
112.5	22.5	15	150		653	42.7	115	5.5

\*Values representing averages from three replicated pot cultures.



Fig. XX. Growth of tomato plants at 90 days as influenced by the degree of base saturation of Fox sandy loam. Treatments from left to right are: No.1---untreated natural soil(about 25 % saturation),No.2---50 %, No.3---75 %, No.4---100 %, and No.5---150 % base saturated. 75% saturation levels, there were slight decreases in the yield of fruit and plant materials, accompanied by more marked decreases in the length of the main stalk.

The yield data of the oats show the same general trend as related to the base status of the soil as did the tomatoes except that the difference in yields is noticeable only between 25% (untreated) and 50% saturation levels. All these facts suggest that the growth of tomato and oats increases as the degree of base saturation of the soil increases but only up to a certain saturation level. For the present soil containing dominantly illitic type of mineral colloid along with some organic colloids, this limiting level seems to be at around 50% saturation for the oats and 75% for the tomato plant. The high critical saturation level for tomato plants as compared with that for oats has the support of the well recognized fact that in general tomatoes demand soils of higher fertility than do oats.

IV. Fure sand.----Generally speaking, the yield data of oats and rye in pure quartz sand were in the same order as those from bentonite-sand and kaolin-sand mixtures. They served as checks for the treatments in the bentonite-sand and kaolin-sand mixture and were not expected to give any direct information relating to the problem. Actual yield data, therefore, are not presented

here.

The Effect of Degree of Base Saturation on the Mineral Content of Plants.

I. Bentonite-sand mixtures.---The chemical analyses of the above-ground portions of oats and rye are summarized in Table VIII. Among the three mineral constituents, the greatest variation occurred in K. Figures XXI to XXVI show graphically the Ca, Mg and K contents of the oats and rye. The results show interesting relationships between the base status of the bentonite-sand mixture and the mineral composition of the crops.

From Figs. XXI and XXII, it can be seen that the Ca content of both oats and rye increased markedly from 15 to 30% Ca saturation levels (or from 20 to 40% saturation of total bases), but showed only a little increase from 30 to 45% Ca saturation levels (or from 40 to 60% saturation of total bases). Beyond that, there was practically no increase in Ca content. This situation is similar in all cases, regardless of the exchange capacity of the media. The results indicate that for a bentonite-sand mixture, a 15% saturation of Ca will not supply enough available Ca to meet the requirement of cats and rye. In order to afford an ample supply of readily available Ca from the exchange complex, the saturation level of Ca for a montmorillonitic clay has to be at least above 30%,

# Table VIII

Mineral Content of the Oven-dry Tissues of Oats and Rye as Influenced by Base Status of Bentonite-sand Mixtures.

	1	Base exchange capacity, m.e. per 100 gms. mixture											
Base		2			4		6			8			
sat.		M.e. per 100 gms. dry tissue											
%	Ca	Mg	K	Ca	Mg	ĸ	Ca	Mg	K	Ca	Mg	K	
						0a	ts						
20	18.2	3.1	13.2	<b>14.</b> 8	8.0	10.8	19.2	5.4	10.3	22.0	4.6	12.7	
40	28.0	9•3	23.9	31.3	11.5	17.8	40.2	8.5	14.0	41.3	7•4	16.1	
60	32.1	20.9	37•5	33.2	19.1	36.5	38.5	13.2	30.7	42.8	18.1	29.5	
80	32.3	22.6	52.3	34•5	22.0	44•7	40.2	20.3	36.0				
						$ ext{R}\mathbf{y}$	e						
20	11.1	3.0	11.7	11.9	7.2	21.0	18.5	7.0	9.2	15.2	8.1	21.5	
40	21.6	12.9	13.7	29.5	15.0	20.1	29.9	14.3	12.7	34.0	23.4	23.5	
60	29.8	20.2	41.1	34.0	16.5	37.3	32.6	23.3	25.8	35.2	26.5	49.2	
80	31.6	23.1	52.0	32.8	22.8	45.5	32.3	24.0	40.4				

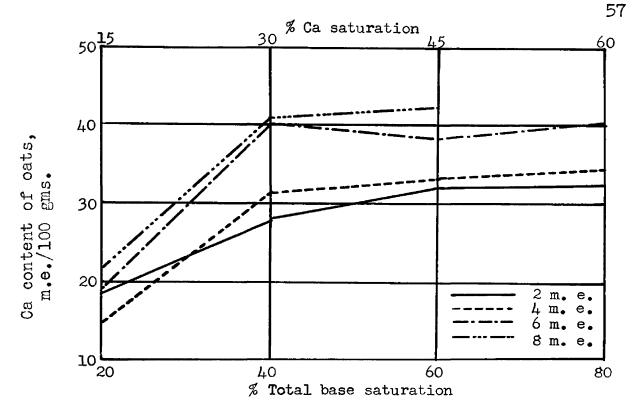


Fig. XXI. The effect of degree of base saturation on the Ca content of oats in bentonite-sand mixtures.

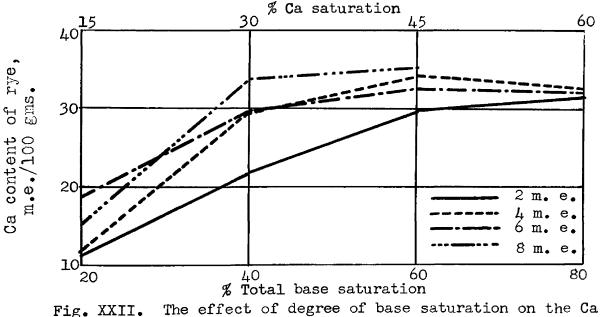
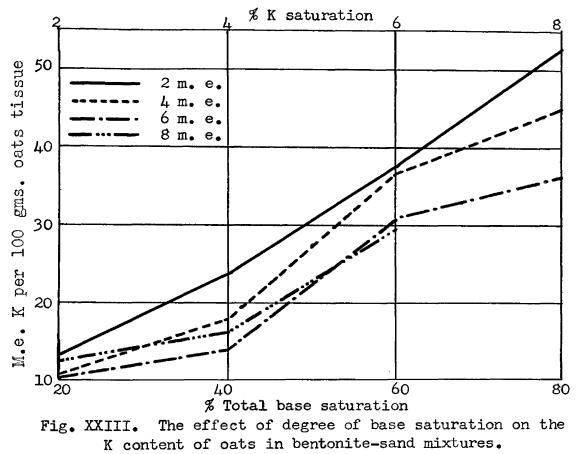
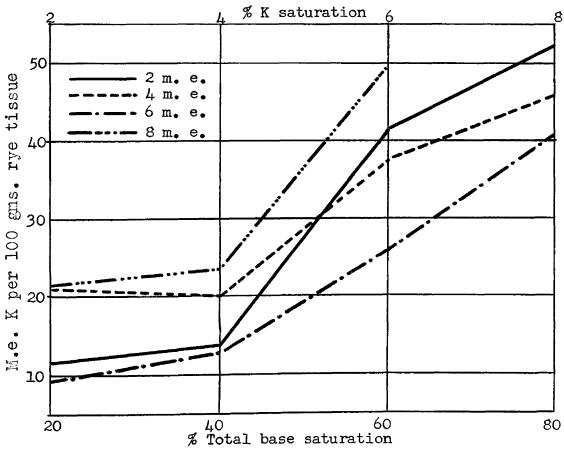
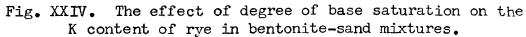


Fig. XXII. The effect of degree of base saturation on the Ca content of rye in bentonite-sand mixtures.







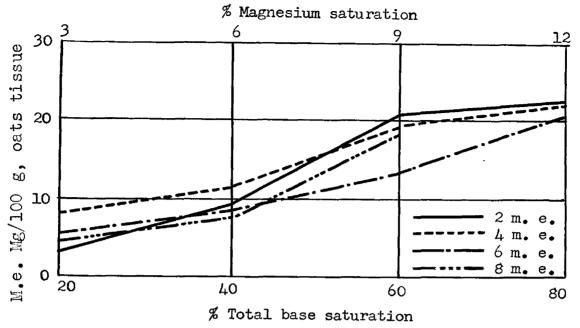


Fig. XXV. The effect of degree of base saturation on the Mg content of oats in bentonite-sand mixtures.

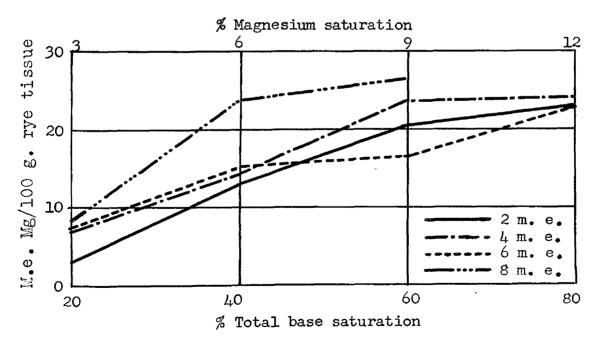


Fig. XXVI. The effect of degree of base saturation on the Mg content of rye in bentonite-sand mixtures.

or better 45%, of the exchange capacity.

With respect to the potassium curves shown in Figs. XXIII and XXIV, the following trend is noticeable. Generally, they all began to rise slowly at the beginning, and then rather steadily throughout the remaining range of the curves. Considering the usually greater error involved in the method of determining potassium, it is believed that the potassium content of the plants in question was probably not significantly affected by the base status of the medium until it reached a K saturation level of about 4% of the total exchange capacity. A considerable increase of K availability to the plants from a 4% to a 6% K-saturation level was evident from the curves. As the K-saturation level increased from 6% to 8%, the K-content of the plants increased still further, indicating a maximum availability of K has not yet been reached.

The Mg-curves (Figs. XXV and XXVI) also show general increases in the Mg content of the plant tissue as the saturation level of Mg in the medium increases. The trend is more or less like that of K rather than Ca, but the variation is within a smaller range.

In comparing the yields with the mineral composition of the oats and rye, it is suggested that the marked increase of Ca availability at the 40% level of total base

saturation is probably the main reason, for the increase of the yields at that level. Furthermore, the increase of yields beyond the 40% level seems to coincide with the continuous rise of the K and Mg curves. These facts give the indications that the differences in the growth of oats and rye are more closely related to the degree of base saturation, through its combined effects on the availability of different cations, rather than the pH values as such.

Furthermore, the data reveal that the mineral contents of the plants, like the yields, were more directly related to percentage saturation than to total amount of bases present in the montmorillonitic colloids.

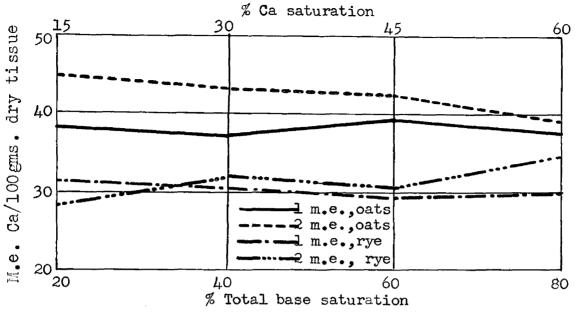
II. Kaolin-sand mixture.---The effect of the variations in the level of base saturation upon the mineral content of the plants in kaolin-sand mixture is given in Table IX and Figs. XXVII, XXVIII and XXIX. There was no significant increase in the calcium content of the plants as the saturation level increased. This indicates that a 15% level of Ca saturation supplies enough available calcium for the nutritional requirement of oats and rye.

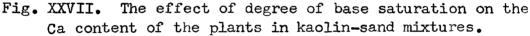
The potassium curves show that there was a general increase in the potassium content of the plants as the level of K saturation in the kaolinitic colloid increased from 2, through 4 to 6% of the total base exchange capaci-

## Table IX

Mineral Content of the Oven-dry Tissues of Oats and Rye as Influenced by Base Status of Kaolin-sand Mixtures.

	Base exchange capacity, m.e./100 gms. mixture							
Base	<u></u>	l		2				
saturation	M.e. per 100 gms. dry tissue							
%	Ca	Mg	K	Ca	Mg	K		
	Oats							
20	38.1	10.1	5•5	45.0	13.3	10.1		
40	37•3	18.2	17.1	43.1	19.2	18.5		
60	39.1 16.2		18.5	42.2	21.1	21.3		
80	37.8	17.3	23.0	39.2	19.8	22.8		
	Rye							
20	31.1	9.1	2.5	28.2	12.5	8.5		
40	<b>30.</b> 8	10.2	13.5	31.9	<b>15.</b> 8	12.4		
60	29.2	14.0	18.7	30.5	17.3	19.6		
80	29.9	15.7	19.3	34.8	16.2	18.0		





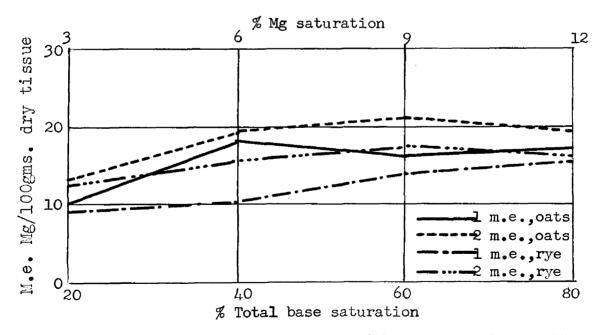


Fig. XXVIII. The effect of degree of base saturation on the Mg content of the plants in kaolin-sand mixtures.

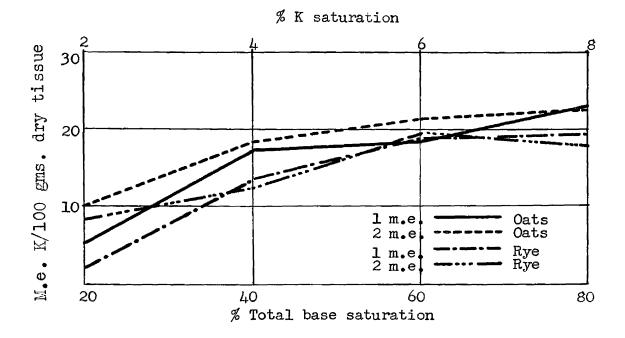


Fig. XXIX. The effect of degree of base saturation on the K content of the plants in kaolin-sand mixtures.

ty. However, no significant increase was noticed above the 6% saturation level. The Mg situation was much the same as the K. Therefore, it is believed that a sufficient supply of K and Mg had been reached at the level corresponding to 60% saturation of total bases.

III. Fox sandy loam.----The results of the chemical analyses of tomato leaves and oats grown on Fox sandy loam are shown in Table X and in Figs. XXX, XXXI and XXXII. Appreciable increases of the Ca content in the plants were observed when the level of total base saturation was increased from about 50 to 75% of the total exchange capacity (Fig. XXX). However, above that level, the increase of Ca content in plants was overshadowed by the rapid increase of K (Fig. XXXII). The Mg curves (Fig. XXXI) were not as regular as Ca and K curves. In general, the Ca curves agreed fairly well with the yield data.

The Effect of Complementary Ions on the Growth and Mineral Composition of Plants.

I. Bentonite- and kaolin-sand mixtures.----The yield and composition of rye in the bentonite- and kaolin-sand mixtures are given in Table XI. The fifteen treatments listed in the table can be divided into three groups according to the design of the experiment. The first five treatments gave the same degree of Mg and K satura-

## Table X

The Effect of Degree of Base Saturation on the Composition of Oats and Tomato Plants Grown on Fox Sandy Loam.

Base	saturation*	Tom	ato le	aves	Oats			
		Mine	Mineral content, m.e. per 100 gms.					
	%	Ca	Mg	K	Ca	Mg	K.	
	24.5	34.1	22.4	13.5	28.1	16.2	18.5	
	50	35.4	22.3	16.0	20.3	19.4	21.2	
	<b>7</b> 5	63.6	21.4	16.9	40 <b>•4</b>	17.1	25.6	
	100	65.2	32.5	21.1	45.3	22.3	43.8	
	150	59•3	35.6	26.9	45•9	20.4	40.8	

\*Ratios of Ca:Mg:K are shown in Table III.

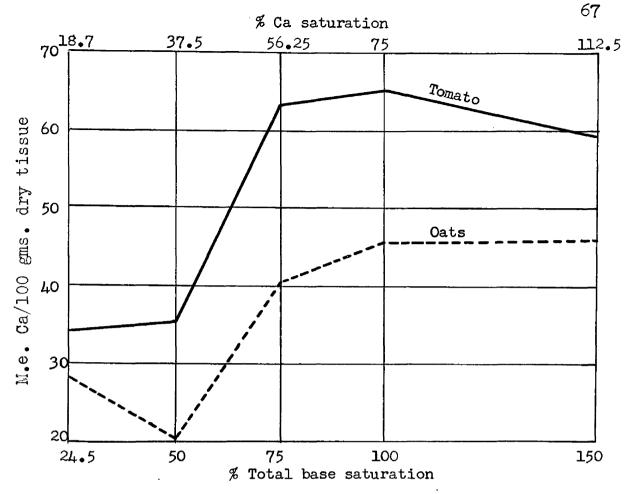


Fig. XXX. The effect of the degree of base saturation on the Ca content of tomato and oats plants in Fox sandy loam.

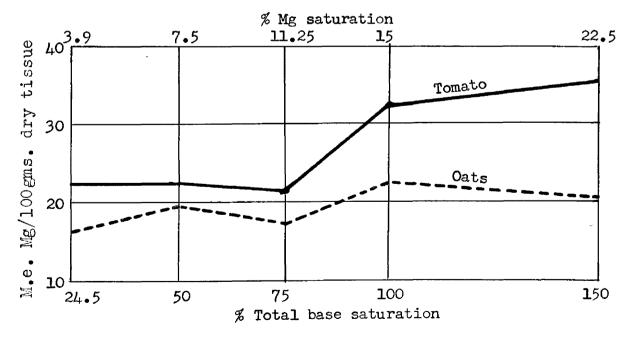


Fig. XXXI. The effect of the degree of base saturation on the Mg content of tomato and oats plants in Fox sandy loam.

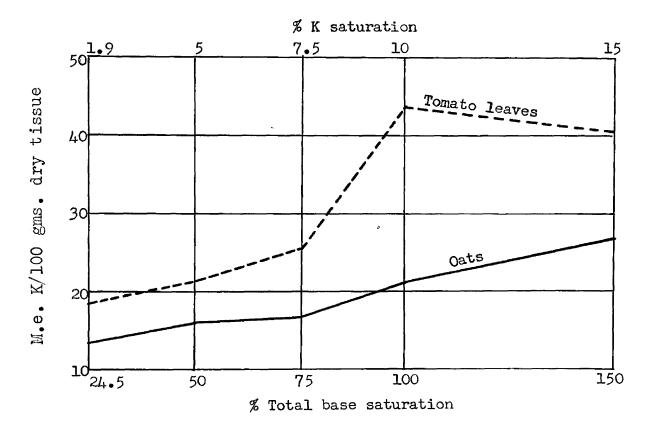


Fig. XXXII. The effect of the degree of base saturation on the K content of tomato and oats plants in Fox sandy loam.

tion, but varied in the degree of Ca saturation or its concomitant, the degree of hydrogen saturation. In the second five treatments, the degree of Mg saturation varied, and lastly in the third group of treatments, the degree of K saturation varied. The yield data of the plants showed little differences within the groups or among the three groups. Only the last group of five treatments showed consistently increasing yields as the degree of potassium saturation increased.

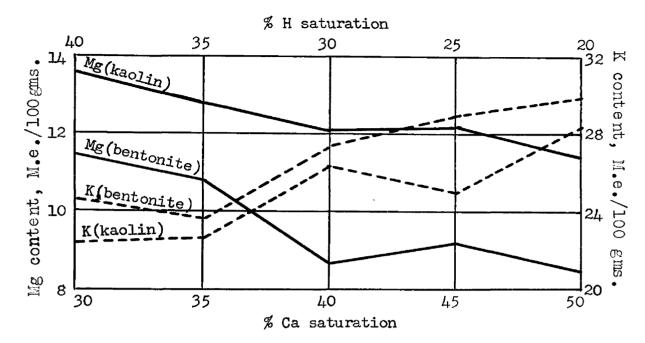
Figures XXXIII, XXXIV and XXXV are the graphs showing the effect of degree of saturation of the complementary ions on the mineral nutrition of plants. From Fig. XXXIII, it can be seen that the presence of more Ca ions on the clay particle brought about a gradual decrease in the Mg and an increase in the K content of rye. More K was also absorbed by rye when complementary hydrogen ions were increasingly replaced by the magnesium ions on the colloidal particles (Fig. XXXIV). The results agree with the findings reported by Peech and Bradfield (31).

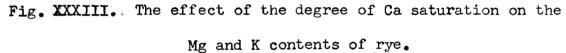
The Ca content of the plant was decreased by increasing Mg-saturation, or by, its concomitant decreasing of H-saturation (Fig. XXXIV). It is also observed, that as complementary ions to exchangeable Ca and Mg, increasing increments of K-ions resulted in less absorp-

# <u>Table XI</u>

The Effect of Complementary Ions on Yields and Composition of Rye in Bentonite- and Kaolin-sand Mixtures.

		6		Yield,	gms.	Composition, m.e./100gms.dry tissue						
Saturation			on	Ben-	Kao-	Bentonite			Kaolin			
Ca	Mg	ĸ	H	tonite	lin	Ca	Mg	K	Ca	Mg	K	
30	15	15	40	3.53	3.05	13.3	11.5	<b>24</b> .8	24•5	13.6	22.5	
35	15	15	35	3.25	3.38	18.1	10.8	23.8	28.3	12.8	22.8	
40	15	15	30	3.53	3.04	24.4	8.7	27.5	26.8	12.1	26.4	
45	15	15	25	<b>3.0</b> 6	3.48	28.6	9•2	29.0	25.6	12.2	25.1	
50	15	15	20	3.18	3.23	26.8	8•5	29.7	29•7	11.4	28.4	
40	5	15	40	3.01	3.05	25.5	8.4	27.2	29•3	8.9	22.4	
40	10	15	35	3.91	3.36	26.1	10.2	28 <b>.0</b>	26.8	9.6	24.2	
40	15	15	30	3.53	3.04	24.4	8.7	27.5	26.8	12.1	26.4	
40	20	<b>1</b> 5	25	3.99	3.33	21.5	9.6	30.4	24.4	11.5	27.6	
40	25	15	20	3.38	3.31	20.5	15.3	31.7	23.5	14.6	26.9	
40	15	5	40	3.20	3.00	29.3	10.7	16.5	27.6	14•4	11.7	
40	15	10	35	3.07	3.22	28.0	10.3	24.1	26.2	12.5	29.4	
40	15	<b>1</b> 5	30	3.53	3.37	24.4	8.7	27.5	<b>26.</b> 8	12.1	26.4	
40	15	20	25	4.09	3.48	23.2	8.0	34•4	21.0	11.3	31.7	
40	15	25	20	3.91	3•53	22.7	8.3	37.8	20.5	10.8	28.5	





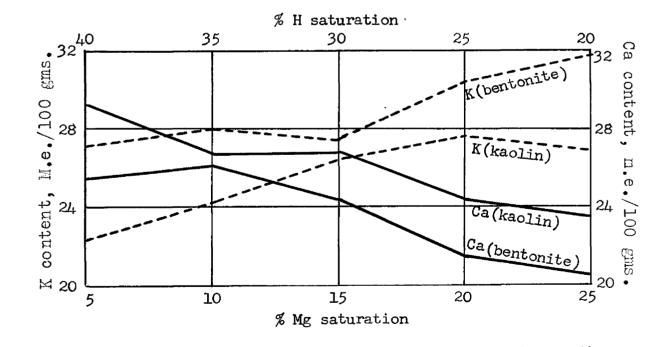


Fig. XXXIV. The effect of the degree of Mg saturation on the Ca and K contents of rye.

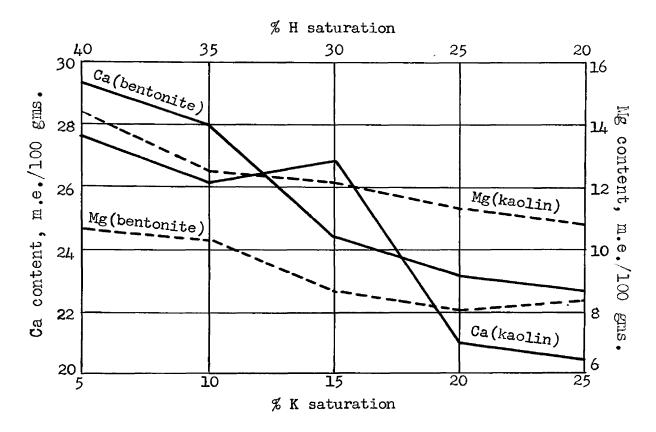


Fig. XXXV. The effect of the degree of K saturation on the Ca and Mg contents of rye.

tion of Ca and Mg by the plant (Fig. XXXV). In other words, the increase of the degree of H-ion saturation as compared with K-ion saturation is in general a helpful factor in mobilizing Ca and Mg ions into plants.

Figure XXXVI shows the Ca, Mg and K contents of rye as influenced directly by the degree of saturation of Ca, Mg and K respectively. The results are in general agreement with those mentioned previously. Some deviations might be due to the differences in the ratio between the three major exchangeable cations.

II. Fox sandy loam.----The yields of tomato and oat plants together with their mineral composition are presented in Table XII. Figure XXXVII shows the actual growth condition of tomato plants at the end of 90 days. The maximum yield of tomato fruits was obtained when the soil was at the level of 35% saturation with Ca, 5% with Mg and 10% with K (i.e. a ratio 7:1:2). The yield data of the tomato plants, however, did not coincide with those of fruits. No significant difference in the yields of oats was noticed.

The analyses of the mineral composition of the plants show that with the same degree of K saturation, the replacement of a part of Mg by Ca as complementary ions, increased the potassium content of the plants. Aside from that, the results are not available for

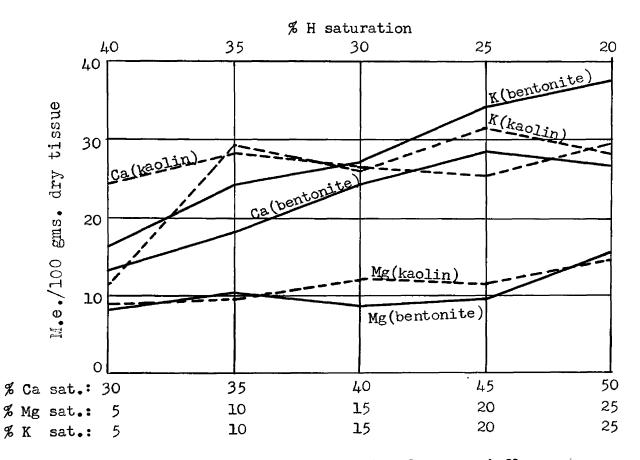


Fig. XXXVI. The Ca, Mg and K contents of rye as influenced directly by the degree of saturation of the respective cations.

## Table XII

The Effect of Complementary Ions on Yields and Composition of Oats and Tomato Plants Grown on Fox Sandy Loam.

	70			Yield,	* gm <b>s</b> .	Composition, m.e. / 100gms.dry tissue					
Sa	tura	tic	on	Tomato	Oats	Tomato leaves			Oats		
Ca	Mg	K	H			Ca	Mg	K	Ca	Mg	K
37•5	7•5	5	50	36 <b>.1</b> 593	5•7	35•4	22.3	16.0	20.3	19.4	21.2
40	5	5	50	41.6 597	5•9	58.2	20.1	20.4	25.4	17.3	22.5
35	5	10	50	33•3 678	5.5	42.3	18.4	31.5	22.1	16.2	42.7
30	10	10	50	<b>29.</b> 4 618	6.0	35.6	24.4	29.1	26.2	21.4	39•7
30	5	15	50	34.9 608	5.2	37.4	<b>2</b> 2.6	32.4	20.0	15.1	40.4

\*Averages of the triplicate replications. Two values are given for the yields of tomato. The upper values represent the dry weight of plant materials and the lower values the fresh weight of fruits.



Fig. XXXVII. The growth of tomato plants in Fox sandy loam at the end of 90 days. Treatments involve variations in the degree of saturation of Ca, Mg and K.

No.2--Saturation of Ca,37.5%; Mg,7.5%; K, 5 %. No.6--Saturation of Ca, 40 %; Mg, 5 %; K, 5 %. No.7--Saturation of Ca, 35 %; Mg, 5 %; K,10 %. No.8--Saturation of Ca, 30 %; Mg,10 %; K,10 %. No.9--Saturation of Ca, 30 %; Mg, 5 %; K,15 %. further interpretation because of the design of the experiment.

The Effect of the Nature of Colloids on the Availability of Exchangeable Cations. Since most of the relationships between the nature of mineral colloids and the effects of degree of base saturation on the growth and mineral composition of plants have already been mentioned in the previous sections, only a few remarks need to be added here to complete the picture. It has been mentioned in Table I that rye was grown on the bentonite- and kaolin-sand mixtures at the same period during the experiment. As a result, data are available for making direct comparisons between the effect of the degree of base saturation of montmorillonitic colloids and that of kaolinitic colloid on the growth and mineral composition of the plants. In reference to the data shown in Table V and Table VI, it is observed that the yields of rye were all higher in kaolinitic than in montmorillonitic media when the base saturation was below 60% level of the total exchange capacity of 2 m.e. per 100gms. Furthermore, a comparison of the data in Table VIII and IX reveals that the Ca and Mg contents of the rye grown in kaolin-sand mixture were higher than that grown in bentonite-sand mixture when both were at the levels below 60% of base

#### DISCUSSION

The most outstanding fact demonstrated in this investigation is the marked influence of the nature of soil colloid upon response to increasing degree of base saturation. Yields from montmorillonitic colloid increased with each increment of base saturation reaching a maximum at 80% saturation, the highest experimental level. Growth in kaolinitic colloid increased from 20 to 40% saturation but shows no rise beyond this point. The illitic colloid gave results which are intermediate between them. Mehlich and Colwell (26), working with soil containing montmorillonitic and kaolinitic type of colloids, have found similar results.

The mineral composition data show that only within a certain range of base saturation is the mineral composition of plant a function of the degree of base saturation. The ranges of Ca, Mg and K are all higher in montmorillonite than in kaolinite colloids. This fact suggests that with a given degree of base saturation, more exchangeable cations are available to plants in kaolinitic colloid than in montmorillonitic colloid. Exchangeable Ca and K held by illitic colloid seem to be even less available than those held by montmorillonitic colloids at the same degree of base saturation.

From the structural consideration, Marshall and Krindill (23) classified montmorillonite, beidellite, nontronite, saponite, and attapulgite as colloidal electrolytes whereas the clays of the illite and kaolin groups as non-electrolytes. Using the potentiometric titration method and conductance measurement, Marshall (22) and his coworkers (23) recently concluded that for the three cations, Na<sup>+</sup>, K<sup>+</sup>, and NH<sup>+</sup>, the ionization of the clay "salts" follows the order: kaolinite > montmorillonite > beidellite > illite, whereas the apparent strengths of the clay "acids" as judged by their dissociation of H<sup>+</sup> are in the order: montmorillonite > beidellite > illite > kaolinite. Adopting Marshall's idea of cationic activity (21) in explaining the relative uptake of exchangeable bases by plants, it can be seen that the results of the present investigation coincide with the results found by Marshall and his coworkers in their laboratory studies.

From the view point of practical agriculture, it is of interest to note that in order to increase the Ca uptake by growing plants higher saturation levels of Ca and K are needed for illitic clay than for montmorillonitic clay. In the case of kaolinite, the Ca uptake by plants was as great at low as at high degrees of Ca saturation and increasing amounts of K at the lower

degrees of K saturation resulted in a slight but gradual increase in the uptake of K by plants. Hence on kaolinitic soils only a relatively small amount of lime would be necessary to react with a small percentage of the exchangeable hydrogen in order to give a good crop response, while on montmorillonitic and illitic soils, much larger quantities would be needed to give higher levels of Ca saturation for improving the Ca nutrition of plants. The fact that illite, according to Grim(13), is one of the main constituents of the glacial materials of the United states, might partly explain the need of heavy liming in some of Michigan Soils.

The advantage of localized application of fertilizers, particularly in montmorillonitic and illitic soils, is clearly indicated by the results. Greater uptake of exchangeable bases and better growth of plants were obtained when the degree of base saturation was relatively high.

Of great importance also in soil-plant relationships are the effects of complementary ions on the uptake of exchangeable bases by plants. The results of this investigation indicate that neutralizing an acid soil with Ca or Mg should render K more available. This serves as another reason for the general superiority of Ca-clay over H-clay. However, excess application of K fertilizers to

an acid soil may prove to be undesirable, because as complementary ions, K tends to inhibit the uptake of Ca by plants.

Turning to the theoretical aspects, let us now review . briefly some of the theories which have been offered to explain the difference in availability of various exchangeable bases. Explanations given by Horner (16) attributed the difference to the relative energy of adsorption of different exchangeable bases on the surface of clay particles. However, no numerical value or exactly relative order of energy of adsorption was given by Horner. Jenny (17), in his equation illustrating the quantitative relationship between the interchanging cations and the complementary ions, used oscillation volume as a measure of adsorbability. The greater the oscillation volume, the smaller the adsorbability, and consequently the greater the availability of the ion to the plant. Later, Jenny and Ayres(18) were able to evaluate the ratio of oscillation volumes of some of the exchangeable ions.

Recently Marshall employed various methods for the measurement of cationic activity of the exchangeable bases, and used the term "cationic activity" almost synonymously as "ionic dissociation" or "availability". Cooper and his co-workers (9) have repeatedly proposed and presented evidence for the theory that the intensity

of removal of cations from soil colloidal complexes is largely a function of the normal electrode potentials of the element concerned. All the theories proposed by various workers are, in reality, essentially the same but with different terminology.

No satisfactory explanation has yet been advanced for the different availability of exchangeable bases because of the difference in the nature of colloids. In the following sections, the writer offers his own explanations from the theoretical point of view.

The physico-chemical behavior of the surface of a colloidal particle is a function of both the geometrical and electrical properties of this surface. From the geometrical viewpoint the surface may be of the convex, plane or concave type. These differences in geometric shape of colloidal particles will result in different distribution of electrostatic attractive force in the surface of the colloidal particle. Declaux (3) has calculated the distribution of ions around a spherical particle (convex field) of opposite charge. Winterkorn (40) made studies on the surface behavior of platy-shaped clays (planar surface). An analysis of the equations for the convex field shows that the ionic concentration is very high close to the surface and falls off rapidly with increasing distance. This decrease becomes more rapid with increas-

ing charge of the ions. In the case of the planar surface the concentration stays practically constant with increasing distance from the surface. For clays of different shape, these facts may account for a part of the different availability of exchangeable bases on different colloidal clays. But since the three colloids used in this experiment are all platy in shape, this factor of the shape of clay minerals does not actually exist in the present case.

According to Hendricks (15) there are two forces which exercise the attraction of exchangeable cations on the surface of colloidal crystals. One is the Couloumb's force due to electrostatic attraction and the other is the Van der Waals force. Van der Waals force varies primarily with the nature of the ions (or molecules) which come upon the surface of a clay mineral as adsorbed particle. while Couloumb's force varies with the nature of ions. the crystal structure of the mineral and the distance between the crystal surface and the seat of isomorphous replacement within the crystal lattice. For certain structural reasons (14), isomorphous substitution within the crystal lattice of kaolinite is believed to be absent. The exchangeable bases are held on the surface of kaolinite mostly through the direct replacement, by cations, of H in OH groups of the lattice surface (20). But in montmoril-

lonite, a 2:1 type clay mineral. due to its structural characteristics, seats of replacement are offered to the cations. The difference in the forces of attraction thus created may account for at least a part of the difference in the availability of exchangeable bases on the surface of montmorillonitic and kaolinitic types of clay minerals.

### SUMMARY AND CONCLUSIONS

This investigation was undertaken to attain by means of pot cultures a better understanding of the significance of the degree of base saturation in relation to the growth and mineral composition of certain crops.

Two relatively pure mineral colloids, bentonite and kaolin, and a Fox sandy loam containing illite were used for the studies. Bentonite and kaolin were first electrodialyzed and then mixed with different amounts of pure quartz sand to give different levels of base exchange capacity. Treatments were made to all three cultural media for varying degrees of base saturation and also, in a separate experiment, for varying ratios between one of the three major exchangeable cations and exchangeable hydrogen. Oats and rye were grown in succession in montmorillonitic and kaolinitic media, while peach, soybean, proso, tomato and oats were grown in the Fox sandy loam. Dry weights and contents of certain mineral constituents of oats, rye

and tomato were determined.

Yield data from the montmorillonitic media showed nearly linear relationship between the degree of base saturation and the growth of the plants. In the kaolinitic media the increase of yield was only noticeable from the first increment of bases, effects above 40% total base saturation being insignificant. The results from illitic soil was intermediate between those mentioned above, i.e., the highest yield of tomato obtained at the 75% saturation level.

The yield data further indicate that the growth of plants was more closely related to the degree of base saturation than to the total supply of exchangeable bases. With the same amount of bases and at the levels below 60% base saturation, the yields of rye in the kaolinitic colloid were higher than in the montmorillonitic colloids.

In the montmorillonitic media, the increase of Ca uptake by the plants from the first increment of Ca was pronounced with only little effects above 30% Ca saturation (or 40% level of total base saturation). The K content of the plants was increased appreciably at only the higher levels of base saturation, while significant increases of the Mg content of the plants occurred at lower levels (i.e. below 60% base saturation level).

In the kaolinitic media, no appreciable change of Ca and Mg contents of the plants was noticed. This is an interesting contrast to the results obtained with the montmorillonitic media. However, there were definite increases in K content of plants with increasing increments of K at the lower levels of saturation.

The higher contents of Ca and Mg in the plants were found in kaolinitic media rather than in the montmorillonitic media provided that the total base saturation level was under 60 % of the exchange capacity. On the other hand, the K content of the plants from montmorillonitic media was invariably higher than that from kaolinitic media.

In the illitic soil, the most marked increase of Ca content in plants occurred when the degree of base saturation increased from the 50 % to the 75 % level. Beyond that point, no appreciable increase was noticed. As the degree of base saturation of illitic soil increased, the K and Mg percentages in the plants increased also.

The effect of complementary ions on the availability of the exchangeable bases was indicated by the mineral composition of the rye grown in montmorillonitic and kaolinitic media receiving the same treatments. The results all show that referring to H-ion as standard, the Ca-ion and Mg-ion tended to increase the availability of exchange-

able K, while the K-ion exhibited the reverse effect on exchangeable Ca and Mg. The well recognized fact that Ca and Mg ions have the mutual repressive effect was also observed in the experiment.

The study also discusses, from the theoretical point of view, some of the factors involved in determining the availability of exchangeable bases.

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