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J. H. LONGWELL, *Director*

PLANT NUTRITION AND THE HYDROGEN ION

VII. *Cation Exchange Between Hydrogen Clay and Soils*

D. A. Brown and Wm. A. Albrecht



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CONCLUSION

Theoretical and experimental aspects supporting the use of cation exchange materials for measurement of the most active suite of cations in soils were presented. Data were given to show the effect of the ratio of the exchangeable cations of the soil to the exchangeable hydrogen ions of the electrodialyzed clay upon (a) the total cations exchanged, (b) the fraction of the total cations in the soil that was exchanged, and (c) the suite of exchanged cations. The fraction of the total cations exchanged at the higher cation:hydrogen ion ratios gave values of the same order as the active fraction for cations determined by the clay membrane technique. Data were also presented showing the effect of the time intervals allowed for cation exchange reactions upon the fraction of total cations exchanged, and upon the suite of cations exchanged. By adjustment of the cation:hydrogen ion ratio and the time interval for exchange, the suite of cations exchanged by this technique becomes more representative of that which may be exchanged from the soil to the plant roots. The possibilities of using both cation and anion exchange materials for study of the changes in the suite of ions in the soil become apparent from the data presented.

PLANT NUTRITION AND THE HYDROGEN ION

VII. Cation Exchange Between Hydrogen Clay and Soils¹

D. A. BROWN² AND WM. A. ALBRECHT³

Attempts to explain plant nutrition in terms of soil fertility have brought about many difficult and challenging problems. Of these, that of finding methods for quantitative measurements of that fraction of the exchangeable ions which actually dominates the reactions between the soil and the plant root seems most hopeful. Quantitative measurement of the ionic exchanges between the plant root and the soil colloid calls for a technique which will most nearly duplicate properties exhibited by the surface of the plant roots.

For the sake of clarification, the process of nutrient uptake by plant roots may be divided into two steps; first, the movement of nutrient cations from the surface of the colloidal clay to that of the plant root; and second, their absorption and subsequent roles in the metabolic processes of the plant. The uptake of nutrients involves, therefore, considerations not only of the exchange properties of both the clay colloid and the plant root surfaces, each with its suite of exchangeable cations, but also of plant metabolism as it moves the ions into the plant from the root surface. As a result of this metabolism, the potential for ionic movement from the clay surface to that of the root is maintained.

Significant progress has been made in characterizing the exchange properties of the clay minerals. The importance of the type of mineral, of its structure, of the percentage saturation by cations, and of the complementary ion effects as factors in plant nutrition has become evident through many investigations (8, 10, 11, 12, 13, 15, 17, 20, 23)*. In contrast, however, to this more abundant knowledge of the cation exchange

¹Part of dissertation submitted by the senior author to the Graduate School, University of Missouri, in partial fulfilment of the requirements for the degree of doctor of philosophy.

²Assistant Professor of Agronomy, University of Arkansas, formerly graduate assistant, University of Missouri.

³Professor of Soils, University of Missouri.

*Numerals refer to list of references, page 23.

properties of the clay minerals, there is a meager understanding of those properties of the plant root.

Recent investigations, however, support the view that plant roots possess an exchange capacity (6, 24). Additional evidence shows that it is a definite property of the root surface since cation exchange is exhibited even in the absence of plant metabolism (11, 21). While this does not deny the influence of plant metabolism on the exchange reaction, it does provide a means of studying the exchange properties of the plant root independently of its complex metabolic processes. In view of the extremely complicated influence of the metabolic reactions, it would seem logical to study first the experimental techniques for duplicating the exchange of cations from the soil colloid to the root surface, and to leave the interactions of plant metabolism upon these exchange reactions for subsequent study.

Cations moving from the clay colloid surface to the root surface will be (a) adsorbed on the root surface, (b) absorbed into the plant, or (c) removed from the root surface through secondary exchange reactions with the clay colloid. Thus, the suite of cations which reaches the surface of plant root becomes a major factor in nutrient uptake. It is this suite with which the plant must enter into exchange reactions and from which it must obtain those inorganic elements necessary for growth and reproduction.

The ultimate goal in the investigation of nutrient uptake by plants, of course, would be the preparation of a synthetic plant root which would duplicate the cation exchange reactions of the plant root in conjunction with plant metabolism. The present state of our knowledge does not permit our even conceiving a method which will duplicate the metabolic processes of the plant. It is, however, possible to make progress toward duplicating the exchange reactions of the plant root by substituting for the exchange properties of the plant root a cation exchange material.

It was the objective of this investigation to make an experimental approach toward duplication of the surface exchange reactions between the soil colloid and the plant root. This involved the substitution of a colloidal hydrogen clay with its ionizing hydrogen ions for those of the plant root. Using a suitable membrane to separate the colloidal hydrogen clay from the soil under test, the exchange of hydrogen ions from the clay for the cations of the soil was measured quantitatively. Cations exchanged by this technique should represent the most active fraction of the exchangeable cations in the soil. Therefore one should be able to obtain a quantitative expression of the exchange reactions occurring between the soil colloid and the plant root.

This procedure assumes certain similarities between the plant root and the soil colloid insofar as their surface exchange properties are concerned. It eliminates any attempt to measure the effect of plant metabolism upon the soil-root equilibrium. It is analogous to measuring the initial exchange reaction occurring in nutrient uptake; i. e., the movement of cations from the cationic environment of the soil colloid to that of the

root surface. It does not imply that a stoichiometric exchange of hydrogen ions from the plant root for the cations of the soil will necessarily mean a stoichiometric uptake of them by the plant. It implies that the hydrogen being ionized from the colloidal clay will exchange first for these cations of the soil which are held with the least energies of adsorption.

SOME THEORETICAL CONSIDERATIONS

The measurement of cation exchange reactions in soils by means of a standardized cation exchanger involves several important considerations. These include (a) the use of the hydrogen as the principal ion exchanging for the cations of the soil, (b) the ratio of the exchangeable cations of the soil to the total exchangeable hydrogen ions of the colloidal hydrogen clay, (c) the stage to which the exchange reaction between these two is allowed to proceed, (d) the moisture content of the soil under study, (e) the concentration and type of clay mineral composing the hydrogen clay suspension, and (f) the characteristics of the membrane used to separate the soil and the hydrogen clay.

As a consequence of root respiration by growing plants and the decomposition of sloughed-off organic materials, the hydrogen ion is most likely to be the dominant cation which the plant root surface exchanges for the adsorbed cations of the soil (9). That a significant concentration of hydrogen ions in the soil is an important factor in plant nutrition has been shown by Albrecht and Schroeder (2). Other investigations (6, 24) indicate that the plant roots may be characterized by an atmosphere of cations held and exchanged in a manner similar to those of the soil colloid. There is the distinction, however, that the ionic environment of the plant root probably consists primarily of hydrogen ions, while that of the soil colloid contains varying percentages of all the exchangeable cations. For the sake of better comprehension, the ionic environment of the soil colloid may be visualized as divided into an infinite number of arbitrary planes cut parallel to and extending from the surface to an indefinite point in the ionic environment of the soil colloid as shown diagrammatically in Figure 1. Since cations differ in their energies of adsorption, these arbitrary planes should show progressive changes in the suite of cations (percentage distribution of individual cations in each plane) with increasing distance from the colloidal surface. Thus, in a montmorillonitic type of clay we might visualize the suite of cations in the plane closest to the colloid's surface as containing 70% calcium, 13% hydrogen, 12% magnesium, 3% sodium and 3% potassium. At some indefinite point out in the ionic environment the suite of ions would be significantly altered, perhaps showing only 40% calcium, 5% hydrogen, 7% magnesium, but 28% sodium, and 20% potassium. Changes in the percentage distribution of a given cation in any one of these suites grades insensibly from one plane to the other, thus making these divisions purely arbitrary. Due to the difference in the energies of adsorption, however, the inner planes of cations should be relatively richer in hydrogen, calcium, and magnesium while the planes in the outer edge should be relatively richer in sodium and potassium.

The exchangeable cations of the soil colloid are held within its ionic

environment and are not removed without the energy of an exchanging ion from the plant root or the intermicellular solution. An intermicellular water film of varying thickness exists between the two colloidal surfaces, and cation exchange may take place through this layer of water molecules by (a) an overlapping of the ionic environments of the root and clay colloid, permitting contact exchange (14, 15, 16); (b) by hydrolysis and subsequent diffusion through the aqueous phase; and (c) by secondary equilibrium reactions with the non-adsorbed cations of the intermicellular solution. In either case a potential for cation exchange exists. If we consider the ionic environment of the plant root overlapping that of the soil colloid, as shown in Figure 1, a potential is established for cation exchange between the two cationic environments. The hydrogen ion, therefore, represents an effective means by which the plant roots may remove nutrient cations from the environment of the soil colloid.

As a means of duplicating the surface exchange properties of the plant root let us consider the substitution of a cation exchanger, such as an electro dialyzed hydrogen clay, with its diffuse double layer of exchange-

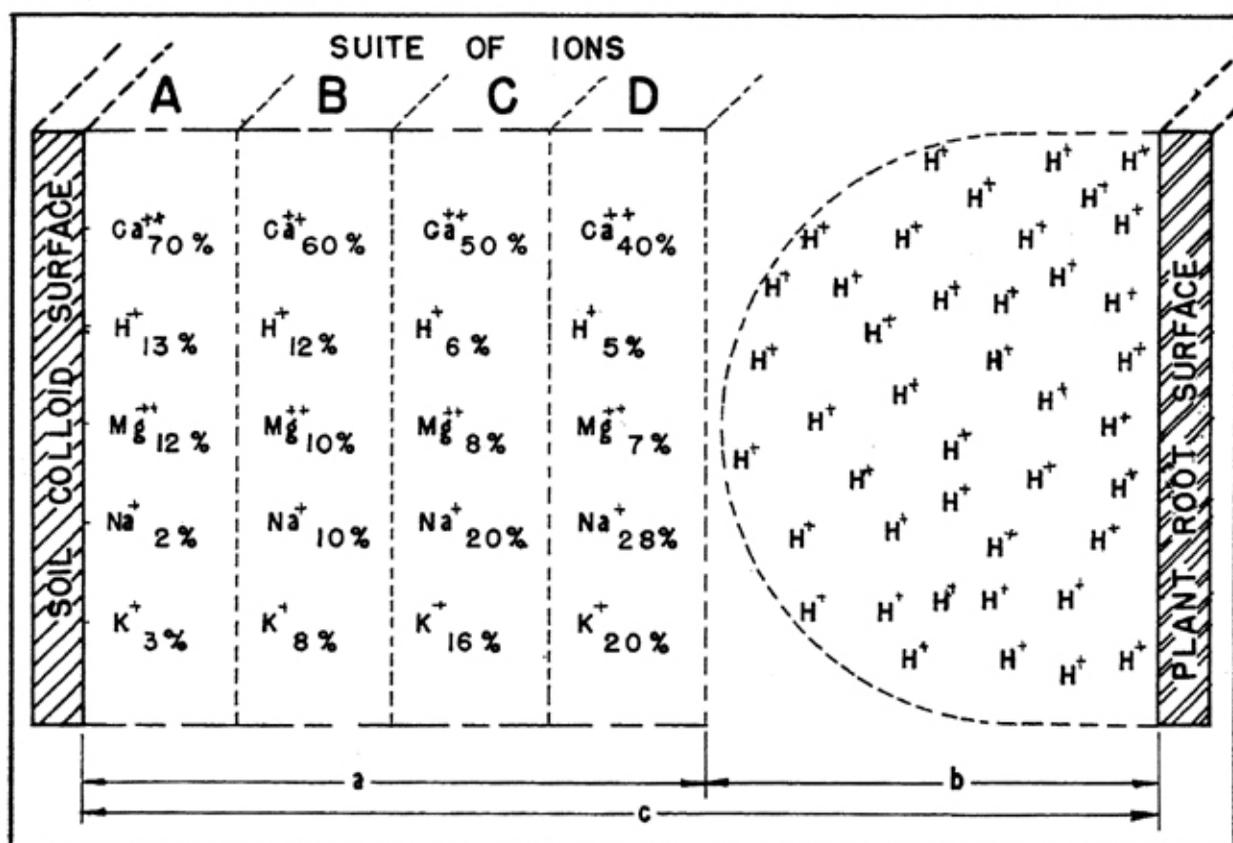


Figure 1. Cross-section of the ionic environment of the soil colloid and the plant root. A, B, C, and D represent the changing suites of cations through arbitrary planes of the diffuse double layer (a) of the soil colloid. The ionic environment of the plant root is represented by (b), and the layer of water molecules by (c).

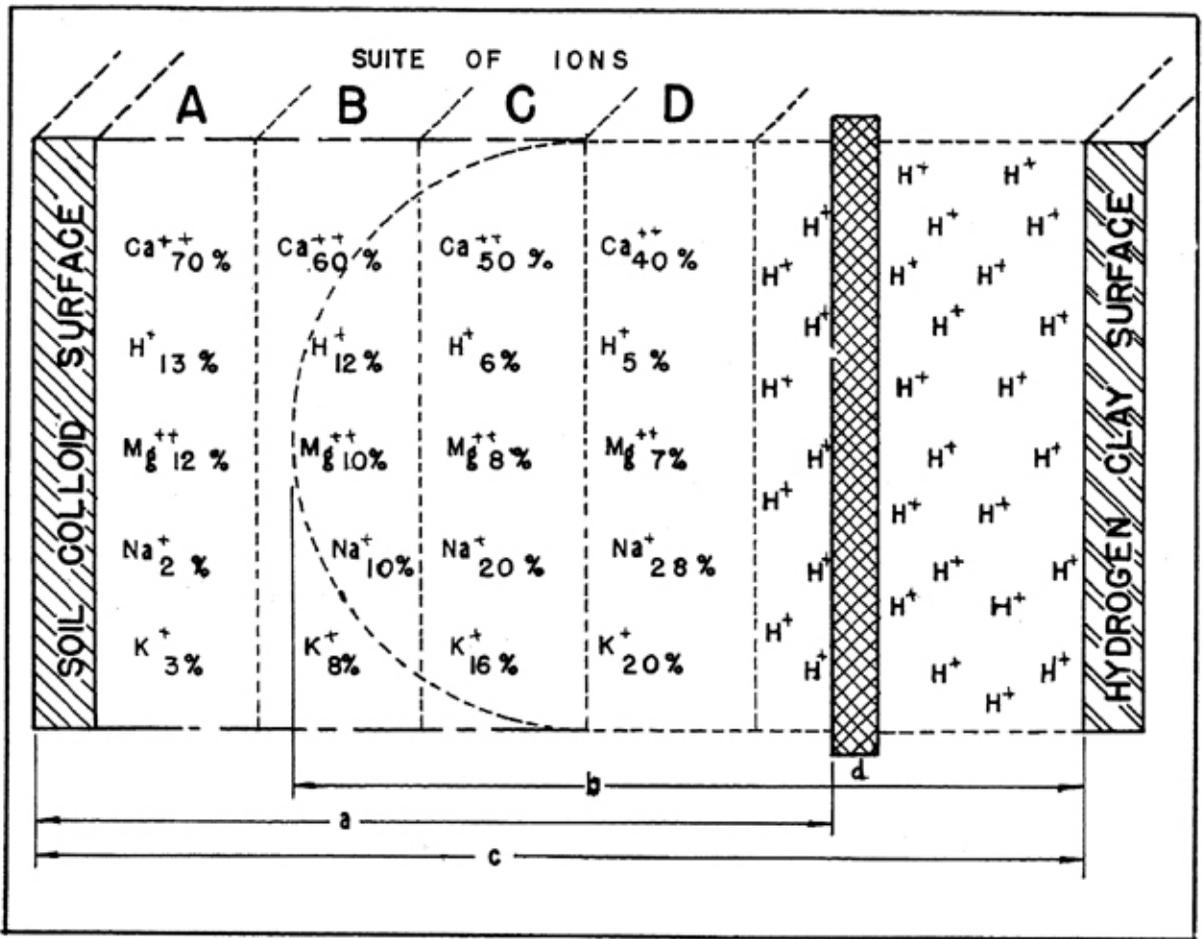


Figure 3. Cross-section of the ionic environment of the soil colloid and hydrogen clay illustrating the extent of effective penetration of hydrogen ions into the diffuse double layer under conditions established for a low cation:hydrogen ion ratio. (Legend same as in Figure 1.)

the acid clay be possible, due to the limited amount of cations in the soil.

The exchange reaction will also be limited in the second case, Figure 4, when conditions exist for a high cation:hydrogen ion ratio. This defines a relatively large number of exchangeable cations in the soil in contrast to a small number of hydrogen ions on the acid clay. It implies that the hydrogen ion becomes the limiting factor in the exchange reaction and that only a small fraction of the total exchangeable cations of the soil will be removed.

In view of the progressive changes in the suites of cations with successive planes outward from the colloidal surface, it becomes obvious that hydrogen ions which penetrate the diffuse double layer of the soil colloid surface will exchange for those cations in the outermost plane first. Thus, under a low cation:hydrogen ion ratio it may be that 80 to 90 per cent of all cations will be removed (Figure 5). The suite of cations exchanged from the soil in the case of a high cation:hydrogen ion ratio will be limited largely to those suites held in the outer planes of the diffuse layer. Those removed should be significantly higher in the monovalent cations. Under

a low cation:hydrogen ion ratio the suite removed from the soil should be relatively richer in the divalent cations.

Such cation:hydrogen ion ratios can be expected between the soil colloid and the plant root. They may therefore modify significantly the suite of ions exchanged to the root. It must be realized that any attempt to establish a definite distance from the soil colloid surface into its surrounding ionic environment which would separate the more active cations which plants can be expected to utilize most, and those cations held firmly by the clay against the attractive force of the root is, of necessity, purely arbitrary. Through the use of a high cation:hydrogen ion ratio, a sensible approach can be made, however, toward measuring this most active suite of cations.

Stage of Cation Exchange. The extent to which the cation exchange reactions between the soil and hydrogen clay are allowed to proceed will obviously modify the suite of exchanged cations. Since the hydrogen clay is originally made to have an initial pH of 3.2, it will enter into measurable exchange reactions with the soil only to the extent of its approach to a pH near 7.0.

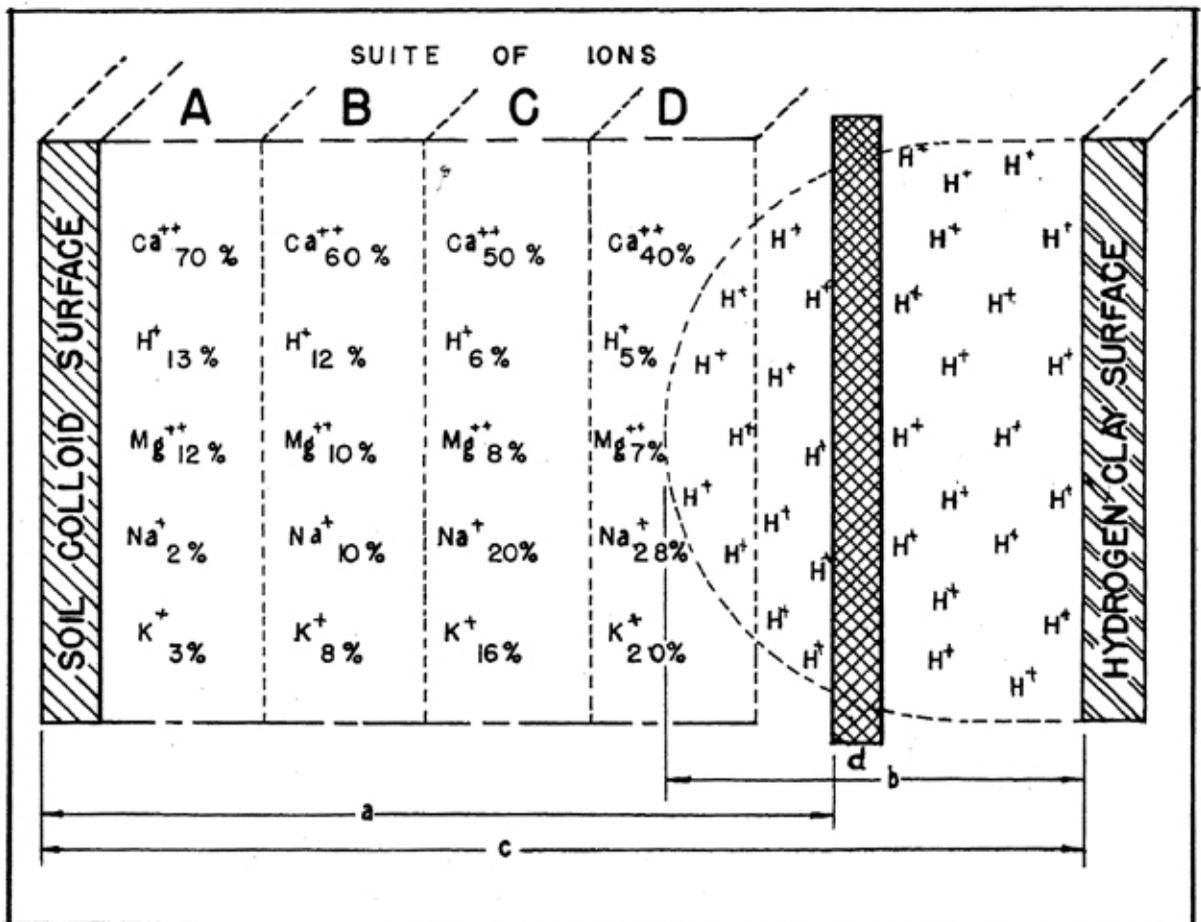


Figure 4. Cross-section of the ionic environment of the soil colloid and hydrogen clay illustrating the extent of effective penetration of hydrogen ions into the diffuse double layer of the soil colloid under conditions established for a high cation:hydrogen ion ratio. (Legend same as in Figure 1.)

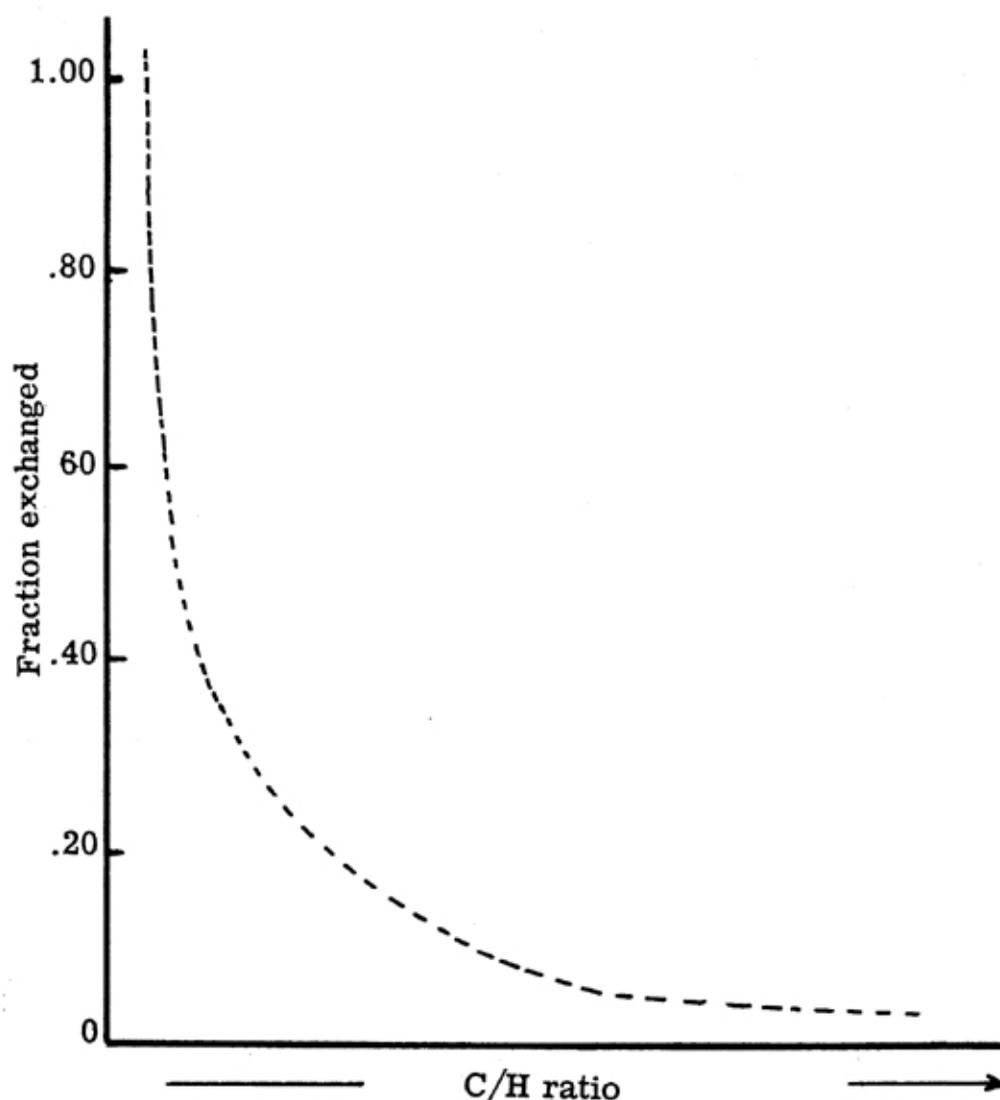


Figure 5. The effect of an increasing ratio of exchangeable cations to hydrogen ions upon that fraction of the total cations exchanged from the soil as a result of the establishment of a potential for cation exchange between the soil colloid and hydrogen clay.

For short time intervals of exchange, the reactions will involve the cations held in the outermost portion of the cationic environment of the soil colloid. The suite of cations so exchanged will differ greatly from that which is removed through contact over a longer time interval. The suites exchanged during short intervals should be relatively richer in monovalent cations, while those during a long time interval should be relatively richer in divalent cations. The suites of cations removed through various time intervals will follow the same general results obtained by fractional electro dialysis, except that in the use of a cation exchange material many of the variables associated with electro dialysis can be eliminated. The time interval for exchange can be selected to duplicate that of the plant root contact with a given clay surface. Thus, the suite of ions exchanged from the soil by a hydrogen clay may be made to represent rather closely the

suite of cations which the plant root obtains by exchange during either short or long time intervals of contact.

Moisture Content of the Soil. The effect of the moisture content of the soil upon the exchange reactions is of decided significance in arid soils which contain large quantities of soluble and sparingly soluble salts. Eaton and Sokoloff (5) and Reitmeier (22) have shown the effect of an increased moisture content upon the exchangeable cations of the soil. Experiments carried out on highly diluted soil suspensions cannot be expected to give a true picture of the cationic environment of a soil colloid. Thus it becomes important to measure the suite of readily exchangeable cations of a soil under optimum moisture conditions. There is also some danger in highly diluted soil suspensions giving some error in the most readily exchangeable cations of humid soils, since they may contain complexes of calcium and magnesium from past fertilizer practices. The measurement of the exchangeable cations of the soil under optimum moisture conditions becomes highly desirable and may be more closely approached by the method proposed.

Type of Clay Mineral and Concentration of the Hydrogen Clay Suspension. Marshall and McLean (18) have recently presented data showing the effects of the clay concentration upon the activities of adsorbed potassium and calcium. Their work indicates that these activities may vary with changes in the concentration of the clay. This variation in cation activity due to clay concentration does not become a disturbing influence in the studies reported here since the ionic exchange is relatively small and since the clay concentration could be maintained constant for all treatments.

For high cation-hydrogen ion ratios no real effect should be apparent in the resulting suite of cations exchanged due to the type of clay mineral comprising the hydrogen clay. This assumption is made in view of the fact that in using a high cation:hydrogen ratio only a relatively small exchange of cations is being made from the soil. Since there is some evidence to indicate that the exchange capacities of plant roots may vary decidedly, the selection of different cation exchange materials with varied exchange properties may make possible the reproduction of the exchange properties of varied types of plant roots. The exchange capacity of barley roots has been shown to be of the same order as that of the kaolinitic clay, and that of certain legumes comparable to that of montmorillonitic clay (6).

The Membrane. The collodion membrane was used to separate the soil and hydrogen clay systems without disturbing the cation exchange. The membrane should not be excessively permeable to water, nor so impermeable that ionic movement is retarded. It should not be excessively thick, yet sufficiently strong to hold the soil sample. The exact size of the pores need not be controlled precisely so long as they are standardized and also sufficiently large to permit ready movement of the exchangeable cations. Also the required cation exchange properties for these membranes should be reproducible under moderately rigid conditions of temperature and relative humidity.

EXPERIMENTAL PROCEDURE

The investigation included: (a) the preparation of a collodion membrane for separating the soil from the standardized hydrogen clay, (b) the measurement of the various suites of cations exchanged from the soil to the electrodyalized hydrogen clay, (c) the measurement of the effects of varying ratios of exchangeable cations of the soil to the exchangeable hydrogen ions of the electrodyalized acid clay, and (d) the measurement of the effects of the time intervals of soil acid clay contact on the suite of cations exchanged from the soil.

Preparation of the Membrane. The collodion membranes were cast on the inside of pyrex glass tubes, 20 by 150 mm. A stock solution of collodion (24 per cent alcohol) adjusted to 5.0 per cent with a 1:1 solution of absolute alcohol and ether was used. The tube was filled one third with collodion; it was then tilted down to an angle of 45°, and the excess collodion allowed to drain away while the tube was rotated rapidly for 20-30 seconds to insure a uniform layering of the collodion. The tube was then placed on a horizontal axle and rotated at 24 r.p.m., while drying for three minutes. The ether and alcohol vapors were drawn from the bottom of the tube by inserting a suction tube, for 15 seconds. The tubes with membranes were placed in cooled distilled water. After several hours, the membranes were removed from the tubes, washed thoroughly, and kept in distilled water until ready for use.

Since slight leaks in the membrane might go unnoticed, it was necessary to test each one. This was done by filling it with .01N potassium chloride solution and suspending it in 75 milliliters of distilled water. The resistance of the potassium chloride solution was measured after a ten-minute interval. This served to tell whether the membrane contained any breaks or excessively large pores. Following the testing of the membrane, it was thoroughly washed, returned to the test tube and kept in distilled water until used. No attempt was made to preserve these membranes over a prolonged period of time since they could be freshly made in a relatively short time.

Measuring the Exchange Reaction. In order to measure the exchange of actions from the soil by use of electrodyalized hydrogen clay, ten milliliters of distilled water were placed in a freshly prepared collodion tube, and the desired aliquot of soil added by means of a large stemmed funnel. Sufficient water was then added to just saturate the soil, resulting in an approximately 1:1 soil:water ratio. The collodion tube of soil was then immersed in the required aliquot of freshly electrodyalized hydrogen clay suspension (8 per cent) contained in a 100 milliliter glass tube. By this procedure the exchange of hydrogen ions from the electrodyalized clay for the cations of the soil under test was allowed to take place. The extent of cation exchange was readily followed by measurement of the pH of the clay suspension at regular time intervals during its rise from an initial pH value of 3.2 to that desired at the close of the reaction period. At the end of the specified time interval the membrane and its soil sample were taken out of the clay, and the cations adsorbed by the clay removed from it by

alternate washing and centrifuging with neutral normal ammonium acetate. Quantitative determinations of calcium, magnesium, potassium, and sodium accepted by it from the soil under test were made by standard analytical procedures. Sodium and potassium were determined by use of the Elmer Perkins flame photometer; calcium was precipitated as calcium oxalate and titrated with potassium permanganate; while magnesium was determined by the Lundegardh flame photometer (7). The pH of the electrodyalized hydrogen clay was measured by use of a pH machine equipped with large glass electrodes, which were conveniently immersed into the clay suspension without pouring the clay from its glass tube container.

Variation in the results due to the differences in membrane characteristics was ascertained through the random selection of ten membranes from a group which was cast under variations of 4° C. and 10 per cent in temperature and relative humidity, respectively. Twenty grams of soil were placed in each of these membranes and each immersed into equal quantities of electrodyalized hydrogen clay. After a time interval of 96 hours the exchanged cations were determined. From these replications, the variations in cation exchange due to variable characteristics of the membrane were established.

The electrodyalized hydrogen clay as used was prepared from the colloidal clay fraction (0.2 μ) of Putnam subsoil clay (beidellite) and subsequently electrodyalized (1). After electrolysis its pH value was 3.2, and its exchange capacity, 68.10 M.E./100 grams clay. It was prepared for use by adjustment to a concentration of 8 per cent. The desired aliquots of clay were obtained by weighing. The milliequivalents of hydrogen desired determined the grams of clay used.

The Establishment of Cation:Hydrogen Ion Ratios. Using Gila (adobe) clay, treatments were established to give eight cation:hydrogen ion ratios varying from 0.97 to 19.45. These ratios were made possible by varying the amount of soil and hydrogen clay used so that the total exchangeable cations in the soil divided by the total exchangeable hydrogen of the electrodyalized clay gave the cation:hydrogen ion ratios shown in Table 1. The total milliequivalents of exchangeable hydrogen were calculated from the exchange capacity of the clay and the grams of clay used. In the case of Gila clay the total exchangeable cations of the soil were based on the exchangeable, water soluble, and sparingly soluble carbonates. These were included in the calculation of the cation:hydrogen ion ratio because they were considered as being in equilibrium with the exchangeable cations of the soil and as constituting a source of exchangeable calcium and magnesium. One cannot readily ascertain the relative amounts of calcium and magnesium obtained from either the exchangeable or the carbonate forms. These eight ratios were used to study the effect of the cation:hydrogen ion ratio upon the suite of cations exchanged from Gila (adobe) soil.

The Stage of Cation Exchange. The rate of cation exchange between the hydrogen clay and the soil was readily followed by noting the progressive changes in the pH of the hydrogen clay. This value increased from an initial pH of 3.2 to near 7.0 as the exchange approached a steady state.

Eight treatments were established in which the cation exchange was terminated when the pH of the acid clay had changed from an initial value of 3.2 to the following: 4.3, 4.8, 5.3, 5.8, 6.0, 6.3, 6.8, and 7.0. Thus, by removing the collodion tube of soil from the clay suspensions when the pH of the latter had changed to the desired extent the suite of ions removed from the soil during this time interval was measured quantitatively. The cation:hydrogen ion ratio of 15.0 was selected for all these treatments.

The soils used in these studies included (a) Gila (adobe) clay, a calcareous soil described previously (3), containing 6 per cent of free calcium carbonate, and (b) Marshall silt loam, a prairie soil of the sub-humid region. The results reported are for the most part those obtained from the Gila clay. In general, the results obtained for Marshall silt loam agreed in principle with those for the Gila soil.

TABLE 1.--DATA USED IN THE ESTABLISHMENT OF DIFFERENT CATION:HYDROGEN ION RATIOS

Treat- ment	Total Exchangeable Cations in Soil*	Grams of Soil	Total M.E. Exchangeable H+ Ions in Acid Clay	Cation: Hydrogen Ion Ratios
1	4.52	2.5	4.67	0.97
2	9.03	5.0	4.67	1.93
3	18.64	10.0	4.67	3.86
4	27.06	15.0	4.67	5.80
5	32.47	18.0	4.67	6.95
6	32.47	18.0	3.34	9.72
7	32.47	18.0	2.66	12.21
8	32.47	18.0	1.67	19.45

* Exchangeable, water soluble, and carbonates of Gila (adobe) clay.

RESULTS AND DISCUSSION

Characteristics of the Membrane Affecting Cation Exchange. Membranes that had been dried for different periods showed that their permeability to the exchanging cations decreased significantly for increased drying periods ranging between one and one half to six minutes. The equivalent conductance values of hydrogen clay systems were determined after their four-hour equilibrium period with sodium clay in the collodion tube. The results indicated that for a three-minute drying period a variation of 10 to 15 seconds in the casting time did not measurably affect cation exchange. That this type of membrane could be reproduced with uniform characteristics for cation exchange was demonstrated through the random selection of ten membranes taken from several lots prepared under moderately rigid conditions. The results of these measurements indicated excellent uniformity of the membranes as far as cation exchange was concerned. No differences in the rate or the amounts of cations exchanged exceeding that of analytical errors were apparent. The probable error was ± 0.089 milliequivalents for calcium. This included variations in the analytical procedure as well as in the membranes. No measureable differences

were obtained for sodium and potassium as determined by the use of an Elmer Perkins flame photometer. In general, the variations in the temperature over a range of 4° C had little effect on the ionic exchange properties of the membranes. Casting of the membranes at temperatures between 24° C. and 28° C. was found satisfactory. At temperatures below and above this, there was a tendency to form uneven folds at the lower, or bubbles at the higher, temperatures which resulted in defective membranes. These data showed that the membranes can be prepared under moderately rigid conditions to give sufficient uniformity of the pore size and thereby no significant irregularity in the rate or the quantity of ions exchanging.

The Effect of the Cation:Hydrogen Ion Ratio on Cation Exchange. The rate of cation exchange increased with increasing cation:hydrogen ion ratios. The pH values of the clay suspensions for the eight different cation:hydrogen ion ratios for an equilibrium period of 96 hours are plotted against the cation:hydrogen ion ratios in Figure 6. These data show an increase in the rate of cation exchange as the ratio increased for both the Gila clay and the Marshall silt loam. In the case of Gila clay, the effects of the soluble salts and free carbonates upon the rate of cation exchange are quite significant when compared with that of Marshall silt loam, containing no free salts or carbonates. The final pH of the acid clay undergoing cation exchange with the Gila soil was 7.0 after 96 hours; that of Marshall silt

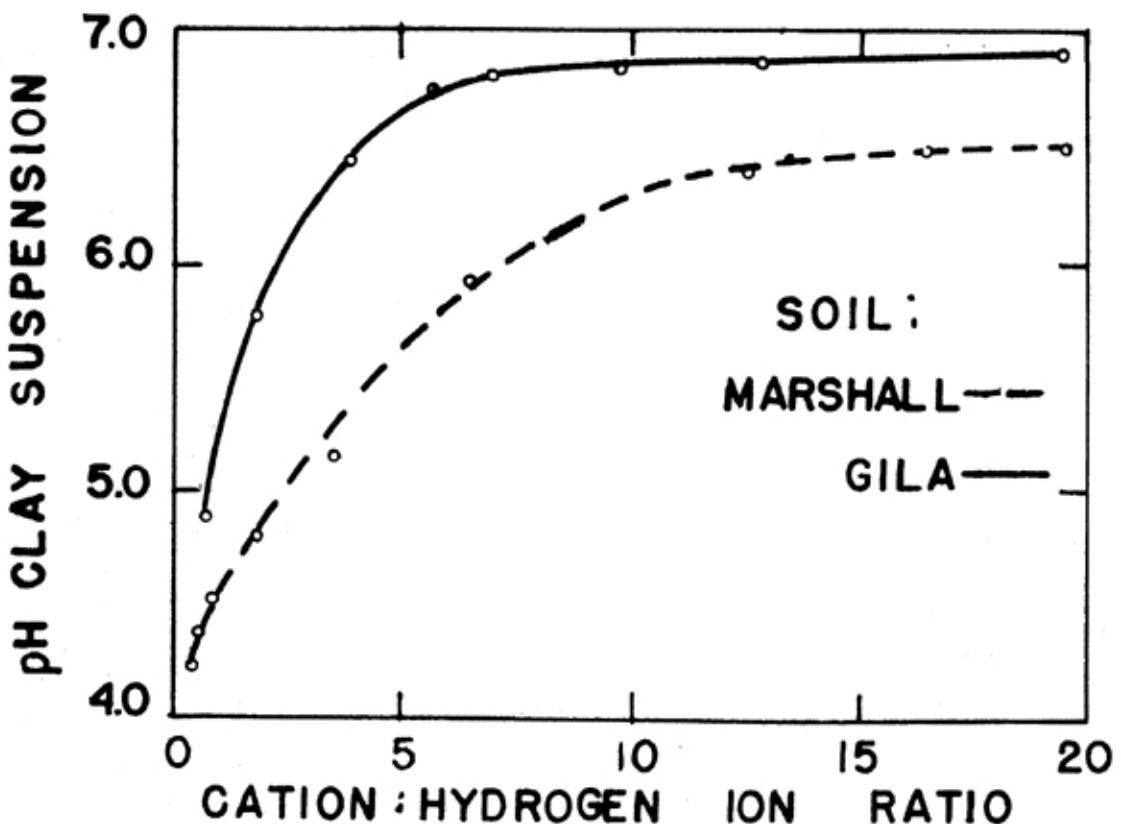


Figure 6. The effect of the cation:hydrogen ion ratio upon the rate of cation exchange between the soil colloid and the hydrogen clay. Time interval 96 hours.

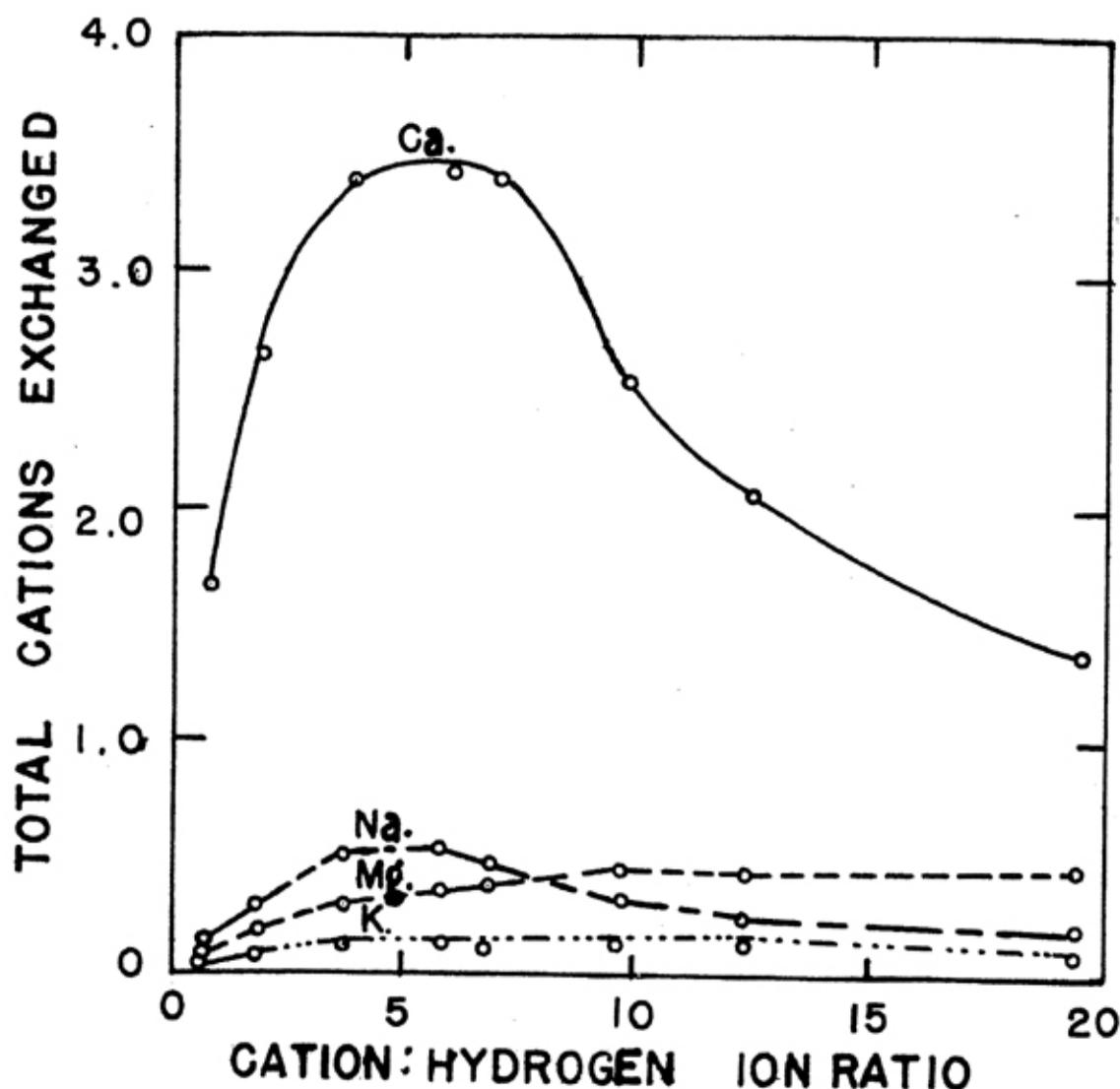


Figure 7. The effects of the cation:hydrogen ion ratio upon the M.E. of cations exchanged from the soil.

loam was 6.5. The cation:hydrogen ion ratio above a value of 6.95 for the Gila soil and 12.0 for the Marshall soil had little effect upon the rate of cation exchange.

The Fraction of the Total Cations in the Soil Exchanged. The total cations exchanged from Gila clay under different cation:hydrogen ion ratios are shown in Figure 7. The amount of each cation available for exchange from the soil and that amount actually exchanged for hydrogen ions was known. From these values the fraction of the total cations present in the soil which was exchanged was calculated. This represents a measure of the fraction of each cation's total in the soil that was removed. The data resulting from such calculations are given in Figure 8. The fraction of each cation exchanged represents that portion of its total in the soil which is most readily exchangeable. The fraction exchanged has been computed and plotted on the basis of the total cations in the soil, including exchangeable, soluble, and sparingly soluble carbonates. The time of equilibrium allowed was that required to change the pH of the clay suspension from 3.2 to 7.0, or to a constant pH value in cases where there were insufficient

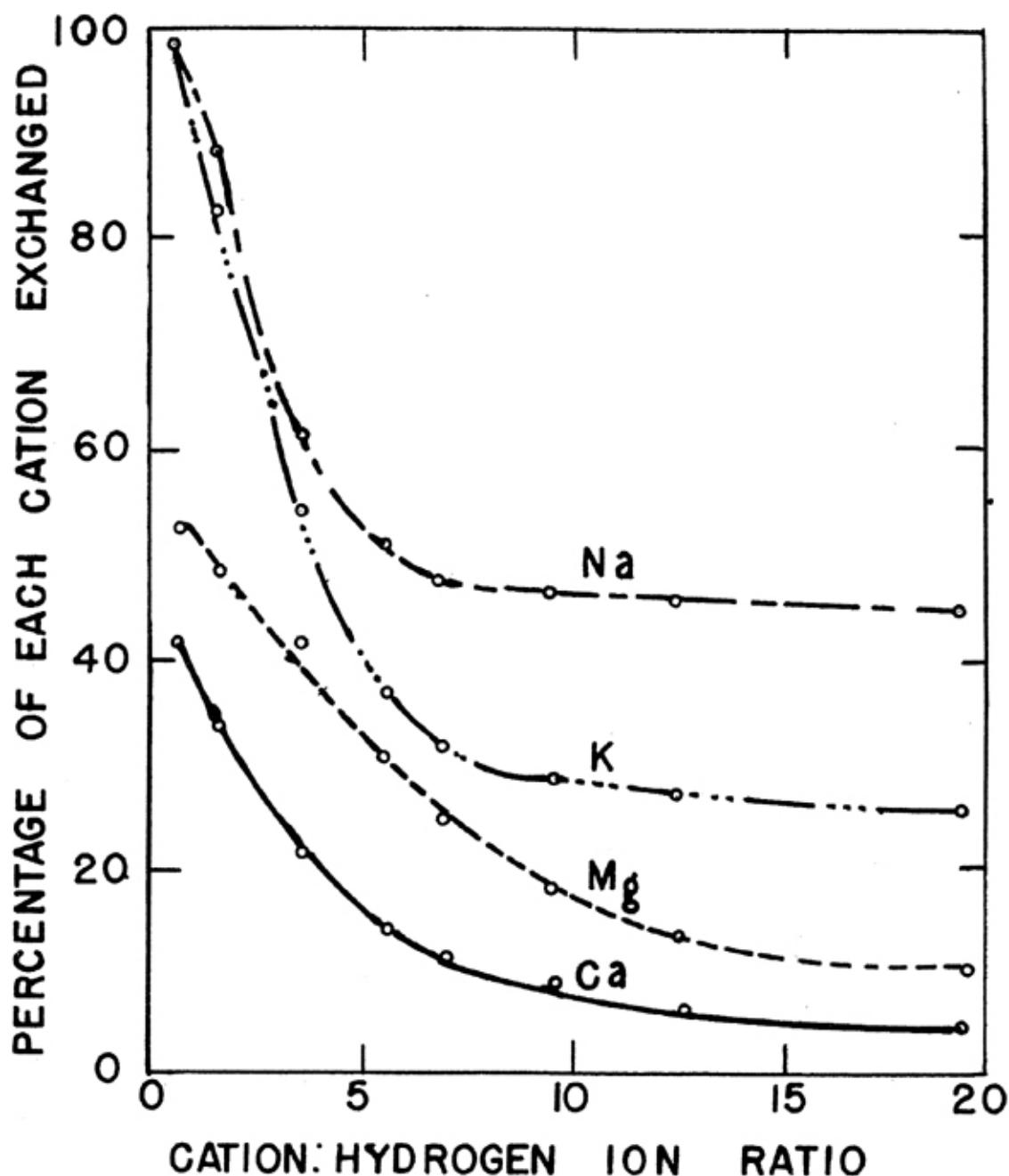


Figure 8. The effect of the cation:hydrogen ion ratio upon the percentage exchange of each cation's total in the soil.

cations to change the pH of the clay to 7.0. As expected, the lowest ratios gave the highest fractions of cations exchanged. These were of the order of 100 per cent for sodium and potassium, 52 for magnesium, and 42 for calcium. At the highest ratios the fractions of sodium and potassium exchanged were only 48 and 28 per cent, respectively, while the fractions of calcium and magnesium were 5 to 11 per cent, respectively.

The relative ease of exchange for the different cations is clearly demonstrated by a comparison of these values. While the percentages for the lower ratios approach those obtained by leaching experiments, it is evident that the potential for cation exchange was not sufficient to remove all of the calcium and magnesium. The values of sodium and potassium indicate their relative ease of removal, particularly in the presence of free carbonates

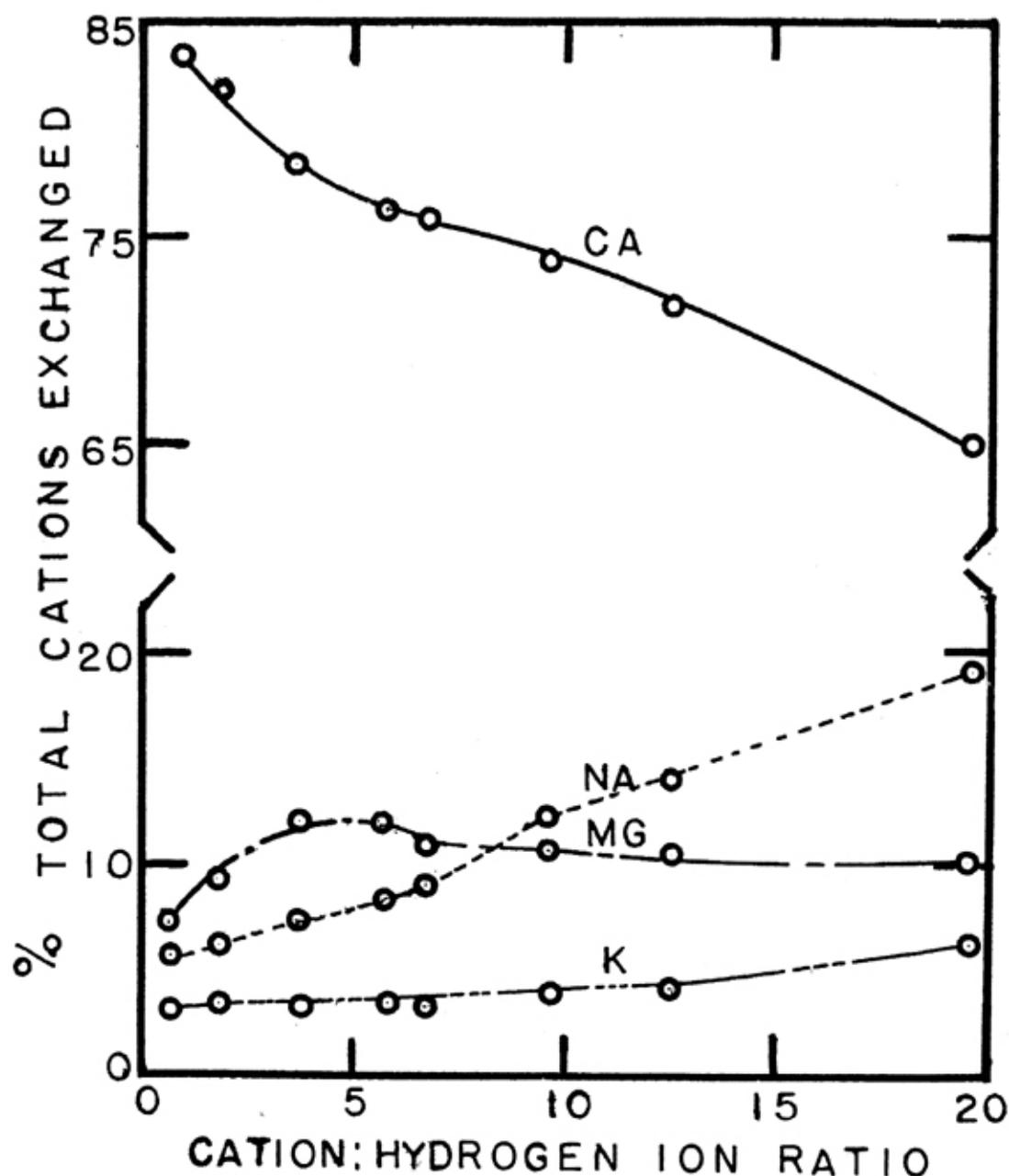


Figure 9. The effect of the cation:hydrogen ion ratio upon the suite of cations exchanged.

of calcium and magnesium. The fraction of the total cations exchanged from the soil decreased from 46 per cent at the lowest ratio to 7 per cent at the highest ratio. The data indicate clearly that the altering of the cation:hydrogen ion ratio has decided effects on the size of the fraction of the exchangeable cations removed.

It is of interest to note that the values obtained from moderately high ratios approached those values of "fractions active" for calcium and potassium as determined by the clay membrane technique (19). Their values are of the order of 3 per cent for calcium and 64 per cent for potassium, for a 1.5 per cent suspension of Wyoming Bentonite with 5 per cent potassium and 95 per cent calcium saturation. The values reported in this investigation represent actual cation exchange values using the hydrogen ion,

while the values for the fraction active as determined by the clay membrane technique are based upon the measured activities of these cations. This, according to Marshall (17) implies an infinitesimal removal of cations, and although the method does not involve actual removal by cation exchange, a comparison of the data indicates the close relationship between cation activity and cation exchange. These two methods of measuring the active fractions of ions in the soil differ in their approach, but it should be apparent from these data that by utilizing a high cation:hydrogen ion ratio that fraction of the readily exchangeable cations which is exchanged may be adjusted to give values of the same order as those obtained by the measurements of cationic activity. The agronomic implications become apparent in view of the fact that the ionic environment of the plant root is represented chiefly by the relative activities of the cations and their dissociation from the soil colloid. They further substantiate the belief that the availability of cations can be predicted from the cation activities.

The Suite of Cations Exchanged. The suite of cations exchanged is more significant than the fractions of their totals exchanged from the soil.

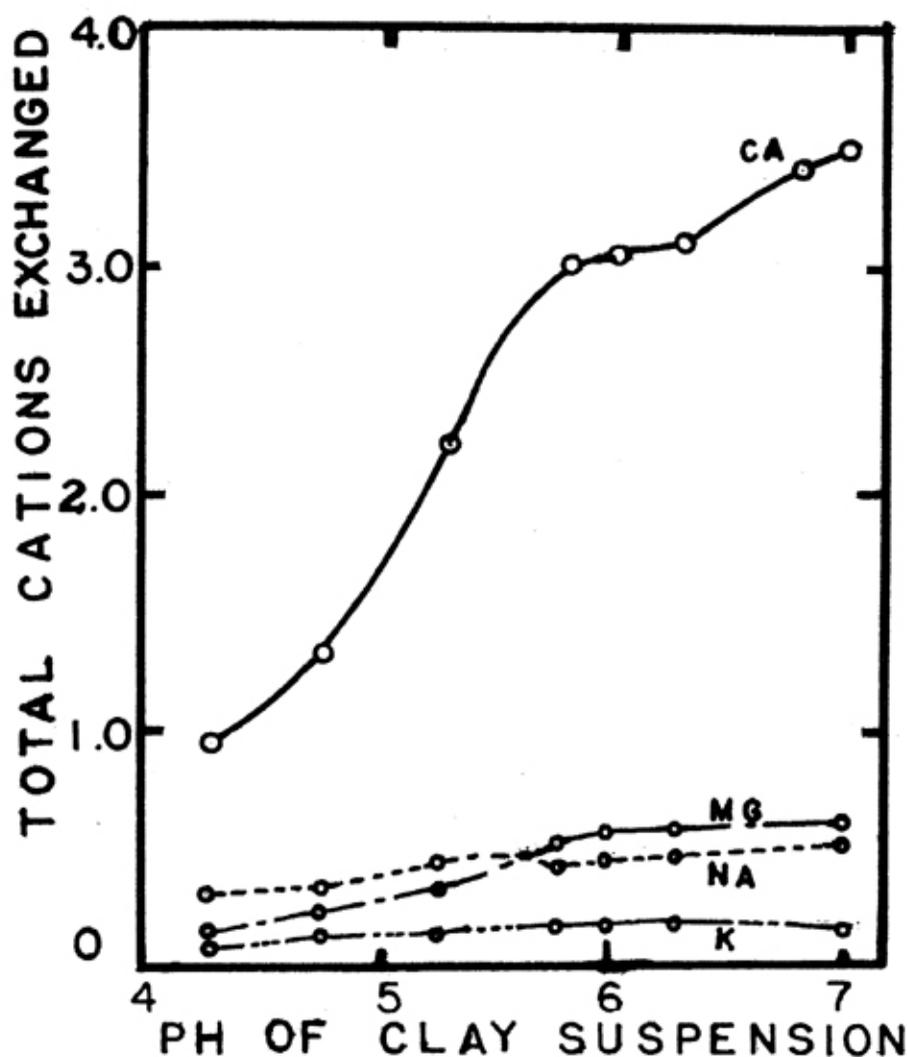


Figure 10. The total cations exchanged from the soil as the pH of the hydrogen clay progressed from an initial pH of 3.2 to a final pH of 7.0. Cation:H ratio = 15.0.

The relative portions of the four cations making up this suite were greatly altered with increasing cation:hydrogen ion ratios. These relationships are shown graphically in Figure 9. Calcium constituted 83 per cent of the suite of the total cations exchanged at the low ratio, while at the higher ratio this percentage was only 64. The percentages of sodium and magnesium in the suite increased from 6 and 7 per cent, respectively, at the lowest ratio to 19 and 10 per cent at the highest ratios. Potassium increased from 3 per cent to 6 per cent in the suite of exchanged cations.

At the higher cation:hydrogen ion ratio the suite of cations removed was relatively richer in the monovalent ones, while at the lower ratios it is relatively higher in the divalent ones. This suggests that exchange reactions between the plant root and soil colloid should be affected similarly by variations in the cation:hydrogen ion ratio. As a result, the suite of cations exchanged to the plant root should vary greatly. These data indicate that the suite of ions exchanged from the soil becomes of greater significance in plant nutrition than the total of exchangeable cations present on the clay colloid. This has been further substantiated in a study of the complementary ion effects of calcium and sodium upon the suite of most available cations in soils (4). The measurement of the suite of ions exchanged by this technique includes those influences which are dominant under field conditions, such as the type of clay mineral, the organic matter, the exchange capacity, the percentage saturation with cations, and the complementary ion effects.

Fractional Cation Exchange. The degree to which any cation exchange reaction will approach a steady state is dependent upon the effective concentration of each of the ions involved and the time interval allowed for the reaction to proceed. In ordinary base exchange measurements involving the displacement of cations, the reactions are pushed to completion by use of an excess of a displacing cation. Attempts to study the exchange reaction at any one given stage present many obvious complications. Fractional electro dialysis has provided a method for studying the step-by-step removal of cations from the soil. However, the chemical and physical artificialities to which the soil is subjected during electro dialysis make the interpretation of such data in terms of plant responses very difficult. Since the plant root may enter into exchange reactions with the soil colloid for variable lengths of time, it therefore must obtain variable suites of cations. In view of the ionization of the cations from the soil colloid, a plant root coming into contact with them should exchange not only a greater quantity of cations from the soil, but also an entirely different suite of ions as the time interval of increased. The following data were obtained through the removal of the exchangeable cations from the soil over varied time intervals of exchange between the soil and the hydrogen clay.

Total Cations Exchanged. The total cations exchanged from Gila soil under various time intervals are shown graphically in Figure 10. The differences in the relative ease of exchange for calcium, magnesium, sodium, and potassium, are quite evident from these data. Stopping the exchange reaction when the clay suspension had increased in pH from 3.2 to 5.3

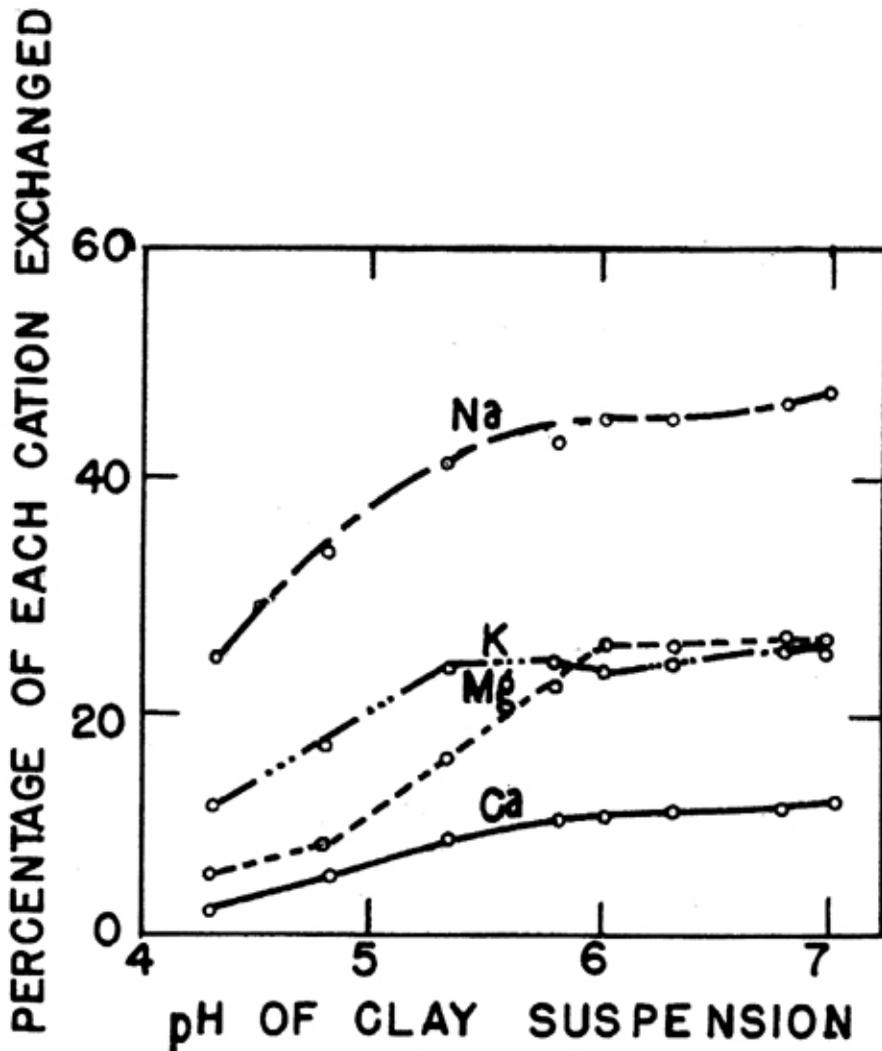


Figure 11. The percentage exchange of each cation of its total in the soil as the pH of the hydrogen clay progressed from a pH of 3.2 to 7.0.

showed that 90 and 88 per cent of the totals for sodium and potassium, respectively, had been exchanged as compared to only 60 and 66 per cent of the magnesium and calcium, respectively. Thus, over a relatively short exchange period the reaction is dominated by almost complete exchange of monovalent ions, while the divalent ions are more prominent in the later stages of exchange.

Fraction Exchanged of Cation's Total in Soil. The fraction exchanged of each cation's total in the soil is illustrated graphically in Figure 11. The fractions of sodium and potassium increased from 24 and 11 per cent, to 47 and 26 per cent, respectively, for the maximum period of exchange. The fractions of calcium and magnesium exchanged at the shorter periods were 3 and 12 per cent, and increased to 5 and 26 per cent, respectively, for the longer periods of exchange.

It is of interest to note that the fraction of magnesium exchanged increased markedly after the fractions of potassium and sodium had reached a relatively constant value. This indicates the degree to which sodium may repress the exchange of calcium and magnesium. This effect has been shown more recently to be even more pronounced than indicated by these

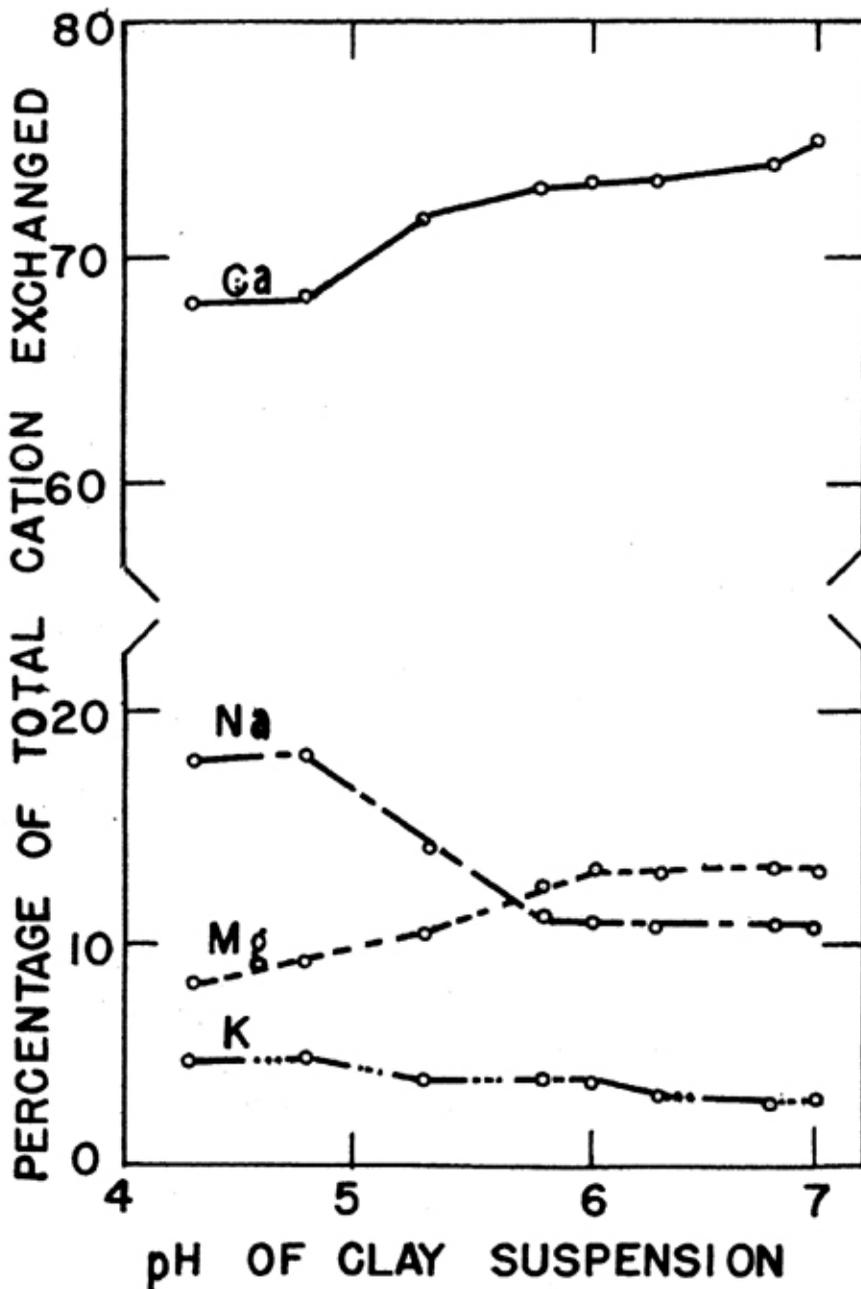


Figure 12. The suite of cations exchanged from the soil as the pH of the hydrogen clay progressed from a pH of 3.2 to 7.0.

data (4). These data indicate that if the period of exchange between the plant root and the cations of the soil is relatively short, then the suite of ions exchanged will be higher in potassium and sodium but lower in magnesium and calcium. It appears that in soils high in exchangeable sodium, the plant root must reach a somewhat steady state of equilibrium with sodium before appreciable quantities of other cations are exchanged from the soil colloid.

The Suite of Cations Exchanged. The importance of these relationships becomes more apparent through an expression of the suite of exchanged cations. This is represented by the fraction which each cation constitutes of the total cations exchanged for any given time interval. Figure 12 indicates the effects of varying the time interval of cation ex-

change upon the suite of cations removed from the soil. These data show a decrease from 18 to 11 per cent for sodium in the exchanged suite of ions, while potassium decreased from 5 to 3 per cent for the longer time intervals. The fractions of calcium and magnesium, however, increased from 68 and 8 per cent to 75 and 12 per cent, respectively, for the longer time interval of soil-clay contact.

It should be stressed again that the most significant feature in the exchange of ions from the soil to the plant root lies not so much in the total quantity available for exchange, but rather in the suite (the respective percentage of each cation in the total exchanged) of cations presented to the root. It is this suite of ions from which the plant root must obtain those ions required for growth. The variable time interval of cation exchange, as well as the cation:hydrogen ratio, between the plant root and the soil colloid represents one of the reasons why soil fertility may not always alter plant composition as one would predict. This may be particularly significant in explaining differences between the chemical composition of perennial legumes and annual cereal crops, when the former have a longer and more effective time interval of soil colloid-root contact for cation exchange than the latter type of crop. The cation:hydrogen ratio may also be expected to vary greatly between annual and perennial crops as well as those crops which vary decidedly in the percentage of active roots.

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