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Studies of Hydrolysis Effects Upon Soil Colloids.

Jack Ezelle Simpson
Louisiana State University and Agricultural & Mechanical College

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STUDIES OF HYDROLYSIS EFFECTS UPON SOIL COLLOIDS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

By

Jack Ezelle Simpson

B. S., North Texas State Teachers College, 1933
M. S., Agricultural and Mechanical College of Texas, 1934

1939
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The author also wishes to acknowledge the helpful suggestions offered by Dr. M. B. Sturgis and Dr. A. R. Choppin.
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ABSTRACT

The effects of various saturation-cations in the exchange complex upon the physical and chemical properties of soils have been receiving increasing attention for many years. Gedroiz, De Sigmond, Hissink and other workers have pointed out their importance and have contributed toward solving the problems involved.

The problems of this investigation have been to study various effects of hydrolysis phenomena upon soil colloids. For this study, soil from the A-horizon of a virgin Crowley silt loam was chosen. The colloidal fraction was separated from the other portion of the soil by dispersing with ammonium hydroxide on a rotary shaker, settling for a minimum of 24 hours, and then withdrawing the top 9 cm. Additional ammonium hydroxide was then added, the mixture stirred, allowed to settle again, and the top portion withdrawn as before--this process being repeated ten times for each batch of soil. The colloidal fraction so withdrawn was concentrated by means of coagulation with electrolytes followed by supercentrifuging. This colloidal fraction was divided into three portions; each portion received a different pretreatment prior to subjecting each one of the so-called series to the process of hydrolysis.

The three series were given the following pretreatment: Series I received no pretreatment, and was designated as the natural-state colloid; Series II was given an oxidation treat-
ment to remove the organic matter; Series III had the organic matter removed similarly to Series II, and also had its free oxides removed by a modification of the method proposed by Truog and Drosdoff.

Each series, after it had been given its respective pretreatment, was further divided into five portions. Each portion was then given a base-saturation treatment with a single-kind of cation, the excess cation subsequently removed, and the resulting base-saturated colloid subjected to the hydolytic action of distilled water by shaking on a rotary shaker. The five base-saturating cations employed for this study were calcium, magnesium, hydrogen, potassium and sodium.

At stated time intervals samples were withdrawn and filtered by means of Pasteur-Chamberland filters. The filtrates so obtained had the following determinations made upon them: (1) determination of the saturation-cation used for the particular sample, (2) silica, (3) aluminum and (4) iron. At the same time each sample was withdrawn, the pH of the hydrolyzing mixture was also determined. These five determinations were used as a measure of the hydrolytic effects produced.

The effects of the hydrolytic treatment were compared on the following basis: (1) comparison of the actual effect of continued hydrolysis upon any individual cation-saturated colloid, (2) comparison of the individual members within each single series, (3) comparison of individual members for
all three series, and (4) general comparison of the three series. The interpretation of the results was given in suitable graphs.

As a result of this study, it was found that the general stabilities of base-saturated colloids investigated were in the decreasing order of: calcium-, magnesium-, hydrogen-, potassium- and sodium-saturated complexes. The general trends shown, as well as many of the specific findings, were closely correlated with the modern theories of soil formation and soil genesis. Ample justification was given for the exceptions and outstanding differences in this study as compared with other pertinent work reported in the literature by various workers.
The effects of various cations in the exchange complex upon the physical and chemical properties of soils have been receiving increasing study since Gedroiz, De Sigmond and other workers first pointed out their importance. While such studies have been carried out with various objectives in mind, no comprehensive, quantitative study, insofar as the author is aware, has been made upon the stability to hydrolysis of soil colloids saturated with various cations, nor has a comprehensive investigation been made of the products produced through hydrolytic action under varying conditions. Data obtained from such studies, it is believed, would enable soil workers to explain more adequately various perplexing problems connected with soil genesis and morphology.

It is an accepted fact that the major portion of the physical and chemical phenomena associated with the problems of soils originates in the colloidal complexes. This, plus the fact that usually only a small fraction of a soil is colloidal, provide ample justification and reason for confining this study to the colloidal fraction itself.

A soil fairly high in colloidal content would be a decided advantage in a study of this sort. Also, it was deemed expedient and more logical to attempt to trace and correlate the relationships existing, as results of varying periods of hydrolysis, if a soil were chosen which
had never been cultivated insofar as could be determined. For these reasons, the soil used for this study was taken from the A-horizon of a virgin Crowley silt loam.

The specific purposes and problems of this investigation have been:

1. The preparation of three series of soil colloids. Each series was to receive different chemical treatment prior to the base-saturation process and subsequent hydrolysis. These three series were: (Series I) the colloidal fraction in its natural state, that is, with none of the original constituents such as organic matter and the free oxides removed; (Series II) the colloidal material with the organic matter removed; and, (Series III) the colloidal material with the organic matter and also the free oxides removed.

2. Each of the three series was divided into five portions. Each portion was saturated with a different kind of base-exchange cation, namely, calcium, magnesium, sodium, potassium, and hydrogen. In this manner a total of fifteen different types of soil colloid samples were prepared for the hydrolysis processes.

3. Each of the fifteen different types of soil colloid samples was subjected to the hydrolytic action of distilled water under similar conditions and the effects so produced were followed by means of various physical and chemical determinations. These physical and chemical determinations were:
(a) Determination of change in pH in the liquid mixtures.

(b) Determination of amount of liberated cation used in the base-saturation.

(c) Determination of liberated silica.

(d) Determination of liberated iron.

(e) Determination of liberated aluminum.

(f) Determination of the base-exchange capacities of the different colloidal samples used in the hydrolysis processes.

(g) Determination of the per cent base-saturation in the colloidal material at the beginning of each hydrolysis process.

4. The results of this investigation were correlated under the following general divisions: (2) relationships existing between the individual types within each series; (b) relationships existing between the types of colloids saturated with the same kind of cation but occurring in different series; and, (c) relationships existing between the various series of colloids.
The definition of a soil has been interpreted from several points of view. The geologist has called the soil a deposit of special formation; the agronomist has preferred to call it a medium in which plant-life was fixed and which supplied food to the plants. Such world-recognized agronomists as Dokuchaev (175) and Marbut (180) have given even more specific definitions. Dokuchaev stated that "a soil is the layer of material lying on the surface or near it which has been changed by natural processes under the influence of water, air, and living and dead organic matter." Marbut (180), defining the term soil, stated "a soil consists of the outer layer of the earth's crust, usually unconsolidated, ranging in thickness from a mere film to a maximum of somewhat more than ten feet which differs from the material beneath it, also usually unconsolidated, in color, structure, texture, physical constitution, chemical composition, biological characteristics (probably chemical processes in reaction), and in morphology." From all these considerations, it has been agreed upon that an acceptable definition might be phrased as follows: a soil is a natural body, differentiated into horizons, of mineral and organic constituents usually unconsolidated, of variable depth, which differs from the parent material below in morphology.
physical properties and constitution, chemical properties and composition, and biological characteristics.

A definition, however, no matter how acceptable, does not give the mechanism of what really takes place in the formation of a soil or the changes it is constantly undergoing. It must be borne in mind that all soils are constantly undergoing both physical and chemical changes in an attempt to attain a dynamic equilibrium with their environments; it is never a static condition in the strict sense of the word. There are well-recognized factors which effect and affect these profound changes. The succeeding pages shall be devoted to a review of the contributions of workers in that branch of soil science pertaining to the general processes of soil formation, the constitution of the various subdivisions (the colloidal complexes in particular), the general reactions of the colloidal complexes, the modern theories and suppositions as to the ultimate structure of these complexes, the role played by different cations in the complexes, the various inner-relationships existing between the different colloids themselves, and lastly, the work that has been done on the topic of this dissertation: a study of hydrolysis phenomena in relation to the colloidal constituents.

A. General Processes of Soil Formation

Soils are composed essentially of inorganic mineral
constituents and organic constituents. The parent materials from which these respective constituents arise are, in most cases, substances that are quite resistant to either physical or chemical alterations. However, Antipov-Karataev (6) has shown the break-down of such stable minerals in the soil as nacrite, dickite, mica, limonite and quartz. Evidence that these changes are extremely slow has been published by Hissink (61), in 1938, showing that in the case of Dutch soils virtually no change has taken place in the mineral portion of the absorbing complex in an entire weathering period of over four hundred years. This slowness, in this case, was thought to be due to lack of appreciable quantities of acid humus substances.

Cobb (31) made a comparison in 1927 of the development of soils from acid and basic crystalline rock and found that no constituent of the rock remained constant as development proceeded. He found that SiO₂ was lost in every stage of weathering. In the acid rock series, the K₂O content declined steadily as the material weathered, while in the basic rock series a large initial loss was followed by a steady increase as development proceeded. The Na₂O content declined steadily in both series. CaO and MgO decreased in the basic series but not in the acid one. Basic rocks lost soluble matter much more rapidly in the early stages of weathering but old soils from basic rocks showed less total loss. Gains exhibited in the old soils were principally in the Fe₂O₃ and Al₂O₃.
Mattson and his coworkers (98-105) make a distinction between two fundamental soil-forming processes: (1) anionic solvation and eluviation leading to formation of laterites, red and brown earths, and (2) cationic solvation and eluviation leading to podzolic soils.

G. W. Robinson (181) found that the first product of weathering under humid temperature was a mixture of hydrated silicates of the general formula, \( R_2O_3 \cdot 2SiO_2 \cdot xH_2O \).

It was shown by Palmer (111) that rockweathering processes under Hawaiian climatic conditions has involved the addition of large amounts of water as well as some oxygen.

Robinson and Holmes (181) correlated some of their findings with the hypothesis that the primary product of chemical weathering was a mixture of a hydrated aluminum silicate \( Al_2O_3 \cdot 2SiO_2 \cdot xH_2O \) of the kaolinite type, and a hydrated ferric silicate, \( Fe_2O_3 \cdot 2SiO_2 \cdot xH_2O \). They concluded that in most cases it was necessary to assume the presence of an excess either of silica or sesquioxides. Limonite was found to be the most stable and magnetite the least stable of the iron minerals considered by Fieger and Hammond (41). Feldspars were evidently more stable than iron oxide minerals; potassium feldspar was more stable than sodium feldspar; iron moved through the soil more readily than aluminum.

Orowther (52), in his study of the relation of climatic and geological factors to the composition of soil
clay and the distribution of soil types, stated in 1930 that the ratio of SiO₂: Al₂O₃ in the clay fraction was correlated negatively with the rainfall and positively with the temperature. He further added that leaching is the dominant factor in clay formation. Under comparable climatic conditions the ratio of SiO₂: Al₂O₃ in the clay fraction was lowest in sedentary soils from igneous rocks and highest in young soils from sediments repeatedly subjected to reworking in water. Clays characterized in high SiO₂ content may be formed either by weathering in the presence of soluble silicates in the alkaline soils of arid regions or in immature soils of humid regions where the parent material has been exposed for long periods to the dissolved SiO₂ of river waters.

As a result of these pedogenic processes four main fractions are ordinarily found in soils, that is, according to size-limit definition. These fractions are (1) gravel or small stones, (2) sand, (3) silt, and (4) clay. At the present time there is much controversy concerning the true definition of the clay fraction. It has been proposed (17, 97) that the clay fraction be further subdivided in order that investigations may be put on a comparable basis. It is now largely agreed that the clay fraction shall be divided into a (a) coarse clay fraction and into (b) a fine clay and colloid fraction. Under this new classification the fine clay and colloid fraction is defined as
consisting of those particles having a maximum diameter of 0.001 mm. (1 micron).

Regardless of their origin, it is recognized that this so-called colloidal complex fraction is the real seat of the reactions governing soils—it is the part of the soil that largely defines its true characteristics. It is in these complexes that the base-exchange phenomena takes place; it is these complexes that govern the amount of water held by imbibition; it is these complexes that determine ultimately the texture, color, structure, nutrient qualities—in short, all those characteristics of a true soil.

B. Early Views Concerning the Constitution of Soil Colloids.

Chemical analyses indicated that four chief constituents compose from 90 to 98 per cent of the inorganic colloidal complexes. These constituents are silica, alumina, iron, and combined water. Their relationships to one another, and, in turn, their relationships to the organic constituents, have been the basis for explaining the constitution of soil colloids.

Van Bemmelen (182), one of the earliest workers, considered the weathering complex of the soil consisted of two fractions: (1) a fraction soluble in hot concentrated hydrochloric acid, having a molecular SiO₂/R₂O₃ ratio varying from three to six; (2) a fraction soluble in hot
concentrated sulfuric acid, having a molecular $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio varying from two to three. On the other hand, Stremme (182) distinguished three groups of hydrous aluminum silicates formed by the weathering of mineral silicates: (1) a group considered to be residual products from the decomposition of feldspars and felspathoids, with the approximate composition of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) that do not form gels and yet are not definitely crystalline; (2) a group known as the allaphanoids, with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios varying from less than 2.0 to greater than 2.0, which are typical gels and are formed partly as precipitates and partly as residual products from the decomposition of ferromagnesian minerals; (3) a group which includes the zeolites.

Gedroiz (43), in a study of the ultrachemical composition of soils and its dependence on the kind of cations present in an absorbed condition in soils, concluded that the adsorbed cation changes the ultramechanical composition of the soil. He found that the solubility of humus is greatest when alkali ions are present in the soil and insignificant when only calcium and magnesium are present. These cations also affect the facility with which the humic portion of the soil is washed out. Such washings contained considerable silica, iron and aluminum. Hydrogen ions increased the dispersion of humus more than bivalent and tervalent cations. The influence of the cations present upon the quantity of material left in suspension is the same at the end of seven days as at the end of one day, in other words the effect is continuous, according to this worker (44).
An increase in valence and an increase in atomic weight both tend to increase the size of colloidal aggregates. The affinity force in the combination of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ in the aluminosilicate grain depends on the nature of the cation saturating the aluminosilicate absorbing complex (42, 43, 44).

A criticism of these early views concerning the nature of the fine clay or colloid fraction of soils is given by Robinson (181). "A defect of the earlier theories as to the constitution of the clay or weathering-complex of soils is that they were generally conceived in terms of compounds or complexes built up essentially of silica and alumina, with iron oxides as adventitious constituents. It is now known that iron compounds form essential ingredients in the clay complex, for clays containing notable proportions of iron occur in which the presence of adventitious ferric oxide cannot be assumed. Any theory of the nature of the clay complex must take account of the possible existence of complex ferro- or ferrisilicates and of the possibility of isomorphous replacement of aluminum by iron in complex aluminosilicates.

"The similarity of the base exchange reactions of the soil to those exhibited by zeolites has led certain workers to postulate the presence of these minerals in the weathering complex. The clay complex has, in fact, been termed by some writers the zeolithic (or zeolitic) complex. But since none of the known zeolites has been proved to be present in
soils, it appears better to avoid the use of this term."

C. Modern Theories of Soil Colloid Formation and Structure.

E. J. Russell (182), in his book *Soil Conditions and Plant Growth*, enumerates the following minerals that have been identified in the clay fractions:

1. Not confined to clay
   - Quartz, chiefly in the coarser part of the clay
   - Micas, including glauconite

2. Clay minerals, products of weathering:
   (1) The Kaolin group: Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), Nacite, Dickite, and Halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2-4\text{H}_2\text{O}$). These minerals have only low base exchange capacity, usually less than 10 m. e. per 100 gms. under natural conditions, though Kelly and Jenny have been able to raise it tenfold by grinding in a ball mill. Under natural conditions kaolinite is not very finely dispersed, few particles being smaller than 0.1 micron while halloysite occurs as finer particles. The members of this group have similar X-ray diagrams.

   (2) Montmorillonite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, but sometimes 3 or 5 SiO$_2$, about 5 H$_2$O, some calcium and magnesium but no iron; this occurs in bentonite and in fuller's earth.
Nontronite, $\text{Fe}_2\text{O}_3$. 3 or more $\text{SiO}_2$. about 4 $\text{H}_2\text{O}$.  
Beidellite, $\text{Al}_2\text{O}_3$. with some $\text{Fe}_2\text{O}_3$. 3 or more $\text{SiO}_2$. about 4 $\text{H}_2\text{O}$.
Beidellite consists of isomorphous bodies containing both iron and alumina, intermediate between montmorillonite and nontronite.

All these have high base exchange capacity and similar X-ray spectra. Further they all show a phenomenon characteristic of this group only, that the lattice increases in one dimension as the water content of the mineral increases.

A number of these minerals have been synthesized by heating amorphous silica and alumina with water or sodium hydroxide solution to 300 - 500°C in a hydrothermal bomb.

(3) Other minerals not yet identified, giving X-ray patterns somewhat similar to the montmorillonite group but not showing lattice swelling.

(4) Hydrated ferric, aluminum, titanium and other oxides."

It might be well preface any discussion as to soil colloid formation and structure with the following statement made by G. W. Robinson (181):

"In considering the origin of the clay complex by the chemical weathering of silicate minerals, it is evident that two different types of product are possible. On the one
hand, the secondary products which constitute the clay complex may originate from silicate minerals by the removal of certain elements or groups of elements from their crystalline lattices, the removal being accompanied in some cases by replacement with hydrogen or hydroxyl groups. The products may retain the same general lattice form or, more probably, form modified structures.

"On the other hand, the origin of the clay complex may consist, as supposed by Van Bemmelen and others, in precipitation from the soluble products of silicate hydrolysis. Whilst, according to the precipitation theory, as originally propounded, the products are absorption compounds of indefinite composition, it is equally possible that the precipitates may be definite, though complex, in composition. The difficulty in assigning formulae to the clay complex may be due either to the presence of varying proportions of relatively simple crystalline compounds, or to the complex being built up as a highly complicated lattice whose structure cannot be expressed by any simple formula."

Csiky (33) has agreed with such workers as Mattson and Gustafsson in considering soil particles neither uniform, definite compounds nor simple mixtures of such, but should be considered as gigantic ampholytoid ions which can combine mutually as well as with simple ions. Upon this basis he explained exchange and hydrolytic reactions of the colloidal complexes under acid or alkaline condition. His experimental work was based upon artificial "aluminum silicates", "protein-
lignates", and natural soil colloids. Bradfield (18) prepared colloidal material by supercentrifuging Putnam silt loam and found that by this method he obtained a material that was lower in SiO₂ content and higher in Fe₂O₃ and Al₂O₃ than the original soil. He found evidence that a naturally occurring soil colloid was largely, if not completely, made up of a complex, readily-decomposed aluminosilicate and not made up of a mixture of oxides as some had supposed. According to G. W. Robinson (181), the clay minerals include aluminosilicates and ferri- or ferrosilicates. In addition, minerals may occur in which there is an isomorphous replacement of aluminum by iron. Quartz, hydrated sesquioxides, muscovite mica, talc, glauconite, and chlorite may be present as accessory minerals. Truog and Drosdoff (155) have proposed methods whereby these may be removed or corrected for. They found that the remaining clay mineral is of the type R₂O₃. 4SiO₂. Toth (153) found in 1937 that removal of free iron oxide by the Truog and Drosdoff method did not materially affect the cation-exchange capacity for four diversified soil colloids.

The claim has been made by Ungerer (157) that only by the chemical change of clay ultramicrons to a combination with univalent cations by exchange adsorption is it possible to reach the individual particle structure and put them on a comparable basis. This is necessary as each particular cation exerts its own peculiar influence upon the dispersion of the colloidal material under consideration, which, in
turn, affects its aggregation qualities to such an extent that its real structure is obscured. Csiky (33) believed it quite probable and possible to develop a simple procedure based on equilibrium between the soil complexes and salt solutions, at definite pH values and requiring determinations of their ionic balances so produced, which would completely characterize a soil's colloidal complex, and also enable comparisons to be made between soils of widely varying nature.

A study of base-exchange phenomena was made in 1929 by Magistad (91) using artificial zeolites. He maintained that better control of conditions could be maintained in this manner. From these studies he concluded that cations are held to the zeolite nucleus by primary bonds. Probably only two such bonds exist adjacent to each other inasmuch as substitution of tervalent cations for the exchangeable base in the zeolite has not as yet been obtained. Iron can not take the place of aluminum in the nucleus, but chromium may possibly do so.

It was found by Kelley and Jenny (74), in 1936, that grinding a group of silicate minerals greatly increased their base exchange capacities, changed their pH values from 7.2 to 5.4, and produced a radical change in their surface crystal structure. Their work indicated that base-exchange phenomena results through cations becoming attached to the Si—O— layer, the cations becoming attached to the free valance bond of the oxygen. It was pointed out that the OH group in the lattice is an important source of their
potential cation exchange power. However, they also pointed out that the OH group is not the sole cause of exchange power as some were inclined to believe. Kelley and his co-workers (73, 74, 75) have obtained further evidence that the exchangeable ions are on the outside of the clay particles. They have shown that the base exchange capacity of minerals and clay colloids was increased by grinding in a ball mill provided the crystal structure was one that could hold exchangeable bases. They obtained evidence of two ways in which exchangeable bases could be held by the lattice: either by the net negative charge on an aluminum tetrahedron, i.e., by a group of four closely packed oxygen atoms containing an aluminum ion in the central interstice, or by replacement of a hydrogen from an --OH group on the surface of the lattice—these latter groups may either exist in OH--Al--OH planes or be produced by breaking a Si--O--Si or an Al--O--Al bond, leaving a Si--OH or 2 Al--OH groups. Further, the more finely these minerals are ground, the larger is the proportion of these groups or broken bonds that appear on the surface and the larger the exchange capacity.

One of the early conceptions of clay particles visualized them as spherical bodies. However, it is now definitely established that the particles are laminated, at least in part, and at the same time are variable in respect to their lateral extension. These plates are more or less loosely chemically joined and possess both internal and external surfaces. This internal surface is usually greater
than the external surface.

The minute and heterogeneously dispersed clay particles are electrically active, ordinarily carrying a considerable electrical potential. This is due to an ionic double layer phenomenon. The inner layer or shell is an immovable stratum of negatively charged ions (anions) that are an integral part of the surface of the colloidal particle. The outer shell is made up of certain positive ions (cations) that are, at least in part, readily displaced. The outer shell of the double layer system found in colloidal material contains a large and indefinite amount of water. Part of these water molecules are carried by the swarm cations since all are definitely hydrated. Moreover, water molecules are apparently packed in the interstices and channels between the plates that make up the loosely organized clayey micelle. Even the external faces of the particle may hold water molecules by simple surface attraction. Thus, as the clay particle moves through the dispersive medium, it is accompanied by a swarm of cations and the farther away the more active members of this pulsating throng maintain themselves, the greater is the electrical potential of the particle. Since the charges on the particle itself are normally negative, it functions much like a simple acid radical such as nitrate ion or sulfate ion, and will migrate to the positive pole when subjected to an electrical current.

From all this evidence it may be concluded that the mica-like clay particles are composed of two distinct parts:
(1) the inner and enormously larger insoluble nucleus, or micelle, and (2) the outer and more or less dissociated swarm of cations with variable amounts of water of hydration, i.e., the exchangeable cations.

The work of Casale (26), published in 1921, contained much of the theory that is still accepted today as explaining a part of the phenomena pertaining to the absorbent power of soils and their colloids. Upon the basis of this investigation and closely allied work, Casale pointed out the following: each negative colloid particle by exercising an attraction on the charged ions of opposite sign causes the formation of a zone of concentration of cations around it. The absorption of the cations by the colloid particle takes place when the necessary difference of potential is established between it and the zone of concentration. The greater the number of cations present in the zone, the more easily, of course, is this difference of potential reached. The degree of adsorption and coagulation of a given electrolyte is therefore the greater in proportion to the magnitude of its ionic concentration.

Also, according to Casale, different electrolytes do not have the same coagulating power but with other conditions the same this is the most pronounced the lower the solution tension of the cation of the electrolyte and the greater its relative velocity. Iron and aluminum have the greatest coagulating power, followed by magnesium, calcium, potassium, ammonium and sodium in decreasing order. Sodium is
apparently the exception to the rule because it joins a low relative velocity with a high solution tension and because its salts are feebly dissociated. Not only the cation of the electrolyte added but also the anion apparently influences the coagulating power. Absorption by the colloids is not exerted on each individual cation but on the entire zone of concentration. The complex solutions that moisten the soil yield greater quantities of the swifter cations and the potassium and ammonium are therefore most absorbed, followed by calcium, magnesium and sodium. Since the different cations are held on the colloidal particle by an electrical force, they are deposited in the order in which they arrive on the surface; the last to be neutralized form the outermost layer. Conversely, the ions that form the outermost layer of the colloidal membrane are most easily sent back into solution, as a general rule, and are therefore most easily replaced by other bases. This substitution is not due to the chemical mechanism of metathesis, as maintained by some authorities, but to electrical action, i.e., the potential difference generated between the colloidal particle and the solution moistening it governs and controls the phenomena of absorption and substitution. All of these causes which can cause a variation in the potential difference and the surface tension contribute toward a variation of the composition of the products of absorption.

Further, Casale claimed that organic colloids possess a negative charge less than that of inorganic colloids and
require much greater quantities of electrolytes for their coagulation. They also protect inorganic colloids from coagulation as long as their concentration is below a certain limit; beyond this limit they facilitate coagulation. Their behavior is exactly identical with that of the inorganic colloids when treated with metallic salts of solution tension lower than hydrogen.

Sedlezkii (137) found reason to believe, in 1938, through studies of diffraction diagrams of soil colloid fractions, the existence of an epidermal aluminous material that formed a continuous coating on the individual clay material particles found in various soil colloids. This aluminous material was presumed to be amorphous insofar as X-ray diffraction determinations were concerned. Gordon stated, in 1925, that a colloid gel of SiO₂, Al₂O₃ and Fe₂O₃ lies between the silicate particle and the film of absorbed water. This intermediate film holds salts in its interstices so that they cannot be speedily leached out (52).

The absolute shape of clay particles is not definitely known, though there is much evidence that they are plate-like. Nor is it known for certain whether a clay particle has a permanent size; it is possible that the particles can readily cleave along their cleavage planes, and that treatment such as centrifuging in the Sharples super-centrifuge breaks them up. Mattson has suggested that the size of a clay particle depends on the exchangeable ion in the clay, and is smallest for the sodium and lithium clay and
largest for the calcium (103, 104, 105).

E. J. Russell (182) states in Soil Conditions and Plant Growth:

"The location of the exchangeable ions in the clay particles is still the subject of some controversy. Marshall has argued that the exchangeable ions occupy definite positions in the clay lattice, because he found that the double refraction of suspended clay particles varied with the exchangeable ions on the clay; and he interpreted the result to indicate a change in the optical properties of the lattice itself, and not merely a change in the surface conditions. He considers these ions are situated in the space between successive sandwiches in the clay lattice.

"The alternative view is that the exchangeable ions are on the outer surface of the clay particles. All the exchangeable cations of clay can be replaced rapidly and completely by large cations such as methylene blue and the hexammine cobaltic ion; they must therefore be in some very accessible position. On the other hand these large ions cannot effect exchange with permutites and zeolites: it is assumed that these substances hold their exchangeable ions in pores too narrow for large ions to enter."

X-ray studies have afforded one of the best methods developed up to the present time for revealing the true inner-structure of colloidal particles. Pauling (131) has made X-ray diffraction studies of clay minerals and found that the crystal lattices built up of successive layers of
linked atoms. Two types of layers evidently occur: (1) the silica layer consisting of silicon and oxygen with a tetrahedral arrangement with two unsatisfied valences per unit which may be utilized for the attachment of other layers or cations; and (2) the hydargillite or gibbsite layer, with an aluminum atom at the center of an octahedral arrangement of oxygen atoms. Hofmann, Endell, and Wilm (181) have shown in their study of clay minerals that beidellite and montmorillonite give the same X-ray diffraction pattern, that these minerals have a wide spacing between layers, and that the spacing varies with moisture content. Further, they have shown that the structure in each case was two silica layers for each hydargillite layer. Ross, in X-ray studies of clays, found that clays may be divided into two groups: (1) the kaolin group, which includes kaolinite, \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \), and anauxite, \( \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O} \); (2) the montmorillonite group, which includes montmorillonite, \( \text{(Ca, Mg)O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}^+ \); beidellite, \( \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}^+ \); nontronite, \( \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}^+ \); and crystalline halloysite, \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} \). These minerals exhibit a platy crystalline form analogous to mica, and this structure, involving large surface development and relatively large contact areas between particles, is sufficient to explain the characteristic physical properties of clays. This crystalline nature of clay particles is not inconsistent, either, with their being in the form of a gel structure with the property of imbibing water as the structural elements of many other gels.
are also known to be crystalline. Kelley (72) reviewed, in 1936, the work that has been done up to that time on the crystallinity of soil colloids and reported that studies made with X-ray, optical evidences of all kinds, effects of grinding, dehydration phenomena and spectrographic studies all pointed to the same conclusion reached previously by Hendricks and Fry—that the colloidal material in soils is largely crystalline in structure.

Kelley, Jenny and Brown (73), in reporting on their investigation of the relation of hydration of minerals and soil colloids to crystal structure (1936), declared that soil colloids contain water of crystallization, that is, contain OH ions as parts of the crystal-lattice structure. They considered this to be further independent proof of the crystalline nature of the colloidal particles. They found that soil colloids, unlike other minerals of known structure, lost their lattice water at lower temperatures. This was probably due to both a difference in particle-size and difference in structure. From their findings, at least two major classes of soil colloids appeared to exist: (1) those which resemble in some measure kaolinite and halloysite; (2) those which appear to be related to (but not identical with) beidellite. In all cases, however, the surfaces seem to be Si--O--Si planes, with the possibility that OH planes also exist. They found also that grinding greatly reduces the crystal-lattice water. The following year after this report Kelley and Dore (75), by means of
X-ray diffraction patterns, pointed out that only one type of clay mineral was usually found in the colloid from a single soil series. They claimed there was no definite relation between type of clay mineral and base exchange capacity. Further, exchangeable cations were not located between layers of the crystal lattice. Parent material and the conditions of weathering were considered the important factors in determining the type of clay mineral which would be formed. These same workers declared that the old idea concerning the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios as means of classifying soils finds no correlation for soil colloids (75).

Marshall (94) has made one of the most outstanding contributions in the field of the ultimate structure of clays and colloids derived from soils. His studies have been based upon dividing the clays into two groups: (1) The kaolin group, including kaolinite, dickite, nacrite and silicon layer. Certain nontronites, in which iron has replaced the aluminum, also probably belong to this group. (a) Pyrophyllite and the base-exchange clay group, including pyrophyllite, montmorillonite, beidellite and many nontronites which have iron in place of aluminum. In the latter group the structure consists of one aluminum layer and two silicon layers. In pyrophyllite there are no extensive replacements and the lattice units are stacked very close together—so close as to exclude much possibility for any base exchange capacity. In the base-exchange clays, however, the lattice units are separated by spaces of variable width which contain water and exchangeable cations.
This class forms a single series with the following predominant replacements: aluminum for silicon (beidellite), magnesium for aluminum (montmorillonite), iron for aluminum (nontronite). In the base-exchange clays and colloids, the lattice layers carry negative charges which are balanced by mobile cations held in the wide spaces between the layers themselves. These negative charges arise by the replacement of aluminum for silicon and of magnesium for aluminum in the framework. This total negative charge is balanced partly by cations incorporated in the framework which are non-exchangeable, and partly by the exchangeable cations—the relationship between the two being governed both by electrical and geometrical factors.

In another study made upon the chemical composition and crystal structure of clay minerals, Marshall has found (1935) that chemical evidence interpreted on a layer lattice basis was completely in accord with X-ray evidence pertaining to clay structure (97). His findings are summarized as follows:

In the kaolinite-bhalloysite type clays, the structure is presumably a layer lattice of \( \text{Al}_2(\text{OH})_6 \) alternating with \( \text{SiO}_2\text{O}_3(\text{OH})_2 \) sheets. There is evidence of the existence of three isomers which differ only in the geometric position of the layers. These isomers all have a formula somewhat on the order of \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \) and have little base-exchange capacity.
Clays of the beidellite-montmorillonite type have an aluminum layer and two silicon layers firmly condensed but with wide spaces between these units filled with water molecules. Aluminum can replace silicon, magnesium and iron can replace aluminum; also, phosphorus can replace silicon, and titanium can replace aluminum in these units. For each such replacement one cation is required to balance the charge. When interpreted on this basis, all of these minerals conform to the general formula \( \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O} \), which is further confirmed by X-ray data. The cations which balance the negative charges on the lattice sheets are within the framework and associated with the water molecules in the spaces between the sheets. They tend to hold the sheets together, such as the potassium does in the case of mica, and are the bulk of the replaceable bases. From this experimental work Marshall concluded that the \( \text{SiO}_2/\text{R}_2\text{O}_3 \) ratio is insufficient to define a clay chemically inasmuch as the aluminum apparently has a double function. Therefore, the supposed correlations based on the \( \text{SiO}_2/\text{R}_2\text{O}_3 \) ratio are unreliable. This is in agreement with some of the findings of Kelley and his co-workers (75). Marshall further concludes that both complete chemical and optical analyses are necessary to completely characterize a clay (97).

D. The Role of Different Cations in the Colloidal Complex.

Such phenomena as changes in pH values, penetration of
water molecules, rates of filtration, changes in base-exchange capacities, rates of cationic adsorption and desorption, changes in physical structures, flocculation and deflocculation tendencies, and the causes of gel formation are all affected by the cation or cations present in the colloidal complex as base-exchange cations or as permanently incorporated cations in the stable structure itself.

The general mechanism of base-exchange reactions may be pictured:

\[(\text{clay})\text{--Ca} \rightarrow (\text{clay})\text{--Na} + \text{CaCl}_2 + \text{KCl} \]
\[(\text{micelle})\text{--Na \rightarrow (micelle)--K} \]

and,

\[(\text{clay})\text{--Na} + \text{CaCl}_2 + \text{KCl} \rightarrow (\text{clay})\text{--Ca} \rightarrow (\text{clay})\text{--Na} + \text{CaCl}_2 + \text{KCl} \]

The effects of different cations upon pH has been investigated by a number of workers. Sing and Nijawan (145) found that the nature of the saturating cations affected the pH in the increasing order of manganese, calcium, ammonium, magnesium, potassium and sodium. Cardos and Joffe have shown that calcium complexes have a higher pH value than the magnesium complexes, indicating that the magnesium has a stronger affinity for the silicate than does the calcium—when the samples contain the same amount of SiO₂(25). Lein found that saturating soil complexes with the chloride salts of the respective cations desired in the exchange complex affected the pH in the order: sodium, magnesium, potassium,
calcium, barium, aluminum and iron. He found that their effect upon absorption capacity varied and followed no definite order, but instead depended upon the pH and the state of the colloid (85). According to Aarnio, when clays are treated with very dilute solutions of KCl there may in some cases be a resulting lowering of pH. In such cases, the lowering is probably due to the replacement of aluminum in the complex by the potassium, and the resulting acidity produced through hydrolysis of the liberated aluminum (1). Therefore, according to further work (2) hydrogen and aluminum clays react acidic, whereas most of the others give essentially neutral or alkaline reaction. Further, leaching with neutral salt solutions decreases the acidity of acid soils; univalent salts being more effective in producing this effect than the bivalent ones.

Water movements—penetration, filterability and the like—in soil colloids saturated with different cations is a topic which is receiving increasing attention. It was found by Botkin that penetration of water in clays was retarded the greatest by sodium compounds, with potassium compounds coming next (14). A study of the effect upon rates of filtration produced by different cations used in base-saturation was made by Antipov-Karataev (5). He found that velocity of filtration increased in the order of sodium: ammonium: magnesium: calcium as 1: 6: 33: 46.

Relative stabilities of various soil colloids have been correlated in regard to the respective cations present
in the complex. Baver (10) has given an interesting report of a study he has made upon clays from Putman silt loam which had been saturated with lithium, sodium, potassium, magnesium and calcium. Through specific conductance measurements he was able to show their relative stability and their relative mobilities of the resulting cations. Also, he gave evidence of the effect of valency and hydration of these cations upon their flocculation values. In his study, he pointed out that the relative increasing flocculation values were in the order: lithium: sodium: potassium: calcium: magnesium as 536: 536: 217: 67: 67. He further pointed out that the filtration of calcium colloids was much more rapid than for sodium colloids. Further, hydration of clay aggregates were decreasingly as follows: lithium, sodium, potassium, hydrogen, calcium and magnesium.

Baver made the general concluding statement that the physical-chemical behavior of colloidal clays is a function of those ions dissociated from the particles and of the surfaces involved.

Another investigative work has been made by Sushko and Sushko (151) in which it was shown that different samples of kaolin saturated with calcium, magnesium, and sodium, respectively, displayed different degrees of dispersion. They found that the sodium sample displayed the highest degree of dispersion, with the calcium and magnesium samples differing from each other only slightly. The filtration capacity of these same samples was in the ratio: calcium,
From the study based upon soils saturated with barium, calcium, magnesium, ammonium and sodium, St. Vajna (149) gave evidence, in 1929, of a relationship between the nature of the saturating material and the dispersion of the soil. He claimed that the dispersion of the soil is parallel to the hydration of the cation, and increased in the following order: barium, calcium, magnesium, ammonium and sodium.

A year later, Furi (118), in a study of factors influencing the dispersion of soil colloids in water, showed that the sodium-clayates have the highest dispersion coefficients, i.e., went into suspension the easiest, and that potassium, calcium and barium clayates have a somewhat lower dispersion coefficient. Kotzmann reported in 1932 that dispersity was increased by univalent cations, and coagulation was caused by bivalent cations (78). Also, he found that soils saturated with univalent bases could not form stable aggregates in water, but that those saturated with hydrogen or bivalent cations could form stable aggregates. This work was substantiated by Sing and Nijawan, in 1936, who also found that soils saturated with bivalent bases were less dispersed and formed more resistant aggregates than did soils saturated with univalent bases (145).

About the same time Sing and Nijawan were making their investigation, Myers (108) made a study of the physicochemical reactions between organic and inorganic soil colloids as related to aggregate formation. He found that...
organic colloids saturated with either calcium or hydrogen ions were much more effective in cementing sand particles into water-stable aggregates than were the corresponding inorganic systems. He concluded the favorable effect of organic matter on aggregation was probably associated with a low degree of dispersion after dehydration.

Moiseev (107), in a study of four types of solonetzic soils of Russia, found that sodium gels were evidently more stable than potassium gels. He took thixotropic and viscosity measurements as the criteria for the stability of the gels investigated.

Antipov-Karataev and Sedlitskii (7) gave evidence that in the process of solonetz formation the increase of magnesium in the exchange complex was not the cause of the solonetz properties, but rather the result. They found that soils containing sodium in quantities less than 5 per cent of the total absorbed bases are not solonetzic. Soils containing 5-10 per cent sodium are weakly solonetzic; soils containing 10-20 per cent sodium are solonetzic; and those containing above 20 per cent sodium are genuine solonetz.

On the other hand, Gemmerling (48) gave data in 1930 to show that the process of soil formation in the steppe proceeds in three stages with respect to the influence of cations, namely, sodium, magnesium and calcium. According to Gemmerling, the soil is first affected by the sodium ion, then by the magnesium ion, and finally by the calcium ion—at which stage it reaches maturity.
The various factors affecting the base-exchange capacities of soil colloids is one of the most important lines of investigation in present-day soils work. The roles of the fixed and base-exchangeable cations is receiving more and more attention. For instance, Peterson and Jennings found that the base-exchange capacity of bentonite is less when treated with potassium than when treated with sodium or calcium (114). Magistad has stated (91) that the base exchange capacity of a soil is not a constant, but varies with reaction, moisture and other factors. His interpretation is based on the build-up and break-down of the complexes themselves. The role of uni- and multivalent cations is base-exchange has been investigated by Gieseeking and Jenny (49) who concluded that the behavior of the ions is irregular but that the electric charges and sizes of the ions are two of the major factors which determine the position of an ion in the adsorption and release series. They found that base-exchange equilibrium is not always a true one for different exchange values were found according to whether the approach was from the left-hand or the right-hand side of the equilibrium system:

\[
\text{clay} = \text{Ca} + 2\text{KCl} \rightarrow \text{clay} + \text{CaCl}_2
\]

They found that potassium and ammonium ions are very similar in size and behaved practically alike in the exchange process. In 1936, Chaminade and Drouineau (28) concluded that, among exchangeable cations usually found in soils, the
magnesium, potassium and ammonium may pass into a nonex­
changeable state while the calcium and sodium do not. This
retrogradation was due to the inclusion of the elements in
the crystal nuclei of the soil colloids while the exchange­
able state may become exchangeable again if the crystal
nucleus of the colloids is altered in any way. They found
that energetic grinding was one method of doing this.

Such properties as base-exchange capacity and heat of
wetting of colloids are determined more by the kind and
chemical composition of the colloid surface than its area,
according to the recent claims of Makower, Shaw and
Alexander (93).

The exchangeable cations have, in the past, received
more attention than the fixed cations for the simple reason
that their behavior is generally easier followed. Gedroiz,
one of the earliest investigators, found that sodium, mag­
nesium or potassium come out of the colloidal complex first
and that calcium was the last to be completely replaced
(42). Lichtenwalner, Flenner, and Gordon (86) reported that
both Fe₂O₃ and Al₂O₃ hydrogels adsorbed cations in the order
calcium, magnesium and potassium; the absorption was specific
and the amount of adsorption increased with increase in the
concentration of the salt.

From a study of sodium, potassium and calcium clays
they had made, Joseph and Oakley (67) reported in 1929
that potassium resembles sodium in its chemical relationships as indicated by base exchange, but that it is very different from sodium in physical properties as plasticity and permeability. The relationship between the role of sodium and potassium in colloid was established more clearly by Jenny's work (64) in which he found that potassium is adsorbed better than sodium in the complex and that, correspondingly, the sodium was released easier than the potassium. Also, Kotzmann (79) found that only 4-5 per cent saturation by sodium in the exchange complex produced drastic changes in the properties of the soil, and that saturation as high as 30 per cent had practically the same effect as maximum saturation.

It might be stated in summary that the energies of adsorption of various cations stand in the decreasing order: hydrogen, calcium, magnesium, potassium, sodium (181).

E. General Reactions of the Soil Colloid Complexes.

The general reactions of the soil colloid complexes include an almost inexhaustible number of investigations. No attempt shall be made to enumerate all the types of investigations that have been done; only a review of those pertinent to this dissertation shall be included. As a consequence, the investigations cited herein will, in most cases, be unrelated, isolated topics.
Goletiani (50) reported in his work upon Russian soils that aluminum is the source of the exchange acidity. In the presence of humus the aluminum and the negatively charged humus are mutually coagulated and thereby decrease the exchange acidity. Iron and humus behave in a similar manner. Gels of aluminum hydroxide and aluminum silicate both exhibit lowering of their pH values upon standing for varying periods up to forty days, according to Pugh (117).

Sante Mattson and co-workers (98, 99, 100, 101, 102, 103, 104, 105) have carried on extensive investigations upon soil colloidal behavior and the laws which govern such phenomena. They have found that humus suppresses the solubility of aluminum and iron, and that the humus carries the aluminum and iron in dispersion in the form of an anionic complex; at the same time, aluminum and iron tend to carry humus and silica in dispersion in the form of a cationic complex.

As early as 1918, Gedroiz (42) found evidence that no one cation, whatever its energy of replacement and however large the concentration of the solution of its salt, brought in contact with the soil is capable of completely replacing any soil zeolitic base at once by one single treatment of the soil with a solution of its salt. However, the bases which do not enter into the composition of the salt, a solution of which is used for treatment of the soil, can be completely replaced from the soil by salt solutions of any cation when a large enough number of consecutive treatments
of the soil is made. Any salt, the cation of which is not already present in the zeolotic bases and which does not form an insoluble compound, can be used, according to Gedroiz. However, Hissink claimed, in 1925, that three minutes was sufficient for equilibrium to be established between neutral salts and the exchange complex for any single treatment (58).

It has been found that certain mathematical relationships exist between the adsorptive capacity of colloidal complexes, the solution with which they are in contact, the concentration of cations in the solution, and similar considerations. Although base-exchange mechanism is not the same as the mere adsorption of dyes by such bodies as charcoal, yet is a large measure it does follow some of the same mathematical laws. For instance, the well-known Freundlich equation may be applied quite successfully:

\[ y = (K) (C)^{1/p} \]

in which \( y \) is the concentration of the cation in the soil phase, \( C \) is the concentration in the soil solution phase, and \( K \) and \( p \) are constants. Peterson and Jennings have given data showing the base-exchange reactions also closely approximates the law of mass action in their mechanisms.

Page has pointed out that the absorbing complex of the soil is an insoluble colloidal acid (or acidoid) associated with surface-active basic cations and hydrogen cations. He has questioned the existence of replaceable aluminum ions
in the complex and the possibility of hydroxyl-ion adsorption (110). Clarens (30) reported, in 1937, that saturation and fixation of the silicate radical on clay particles greatly increases the power of fixation for bases.

F. Hydrolysis Phenomena Pertaining to Soil Colloidal Complexes.

Gordon (51), in 1922, advanced the theory that the origin of soil colloids is based largely upon chemical reactions. Many soil particles are hydrated silicates containing aluminum, iron, silicon, sodium, potassium, calcium, magnesium, and others, and are surrounded by a closely-held water film. The salts in the outer layer of the particle are subjected to constant hydrolysis. The hydrolytic products are partly absorbed by the insoluble hydrolytic products of the iron and aluminum salts, forming an insoluble gel-casing for the soil particles. Equilibrium of the soluble salt between the water film and the gel is established. When the colloid is subjected to flooding (or an excess of water) this equilibrium is destroyed and the solution of the soluble absorbed salt continued until most of it is leached from the outer layer of the particle. Upon further leaching, the gel-products of aluminum, silicon and ferric oxide may pass into colloidal solution. The encasing gel is thus removed and disintegration of the silicate particles proceeds. Since the reaction is reversible, the peptized gel, or
hydrosol, may be again deposited as a gel by varying the H-ion concentration.

In a study based upon seven Louisiana coastal prairie soils, Fieger and Hammond (41) found that irrigation of Crowley soil increased the coarse clay and colloidal fractions, decreased the sand and silt in the A and B horizons, increased the percentage of quartz in the A horizon due to hydrolysis and removal of other minerals, and caused deposition of iron- and aluminum-rich concretions to be formed in the B and C horizons.

Wiegner, Gallay and Gessner (1924), in a study of hydration in soils, have made the statement (165) that the presence of electrolytes has much effect on the adsorption of water in soils; further, if hydrated ions are adsorbed, the water of hydration is greater than that adsorbed by the clay alone. Likewise, Wheating, as a result of a study of the influence of hydration on the stability of colloidal solutions of soils (162), concluded that the stability of soil colloids is governed by the quantity of water of hydration held by the particles. This is in agreement with Lutiz (87), who found that hydration of the complexes is an important factor in their dispersion, which in turn was an index to erosiveness. He also found evidence that hydration, rather than charge, was the main factor contributing to the stability of soil suspensions.

The effect of water upon soil complexes was partially demonstrated in 1930 by Wolf and Schlatter (170) who
obtained a stable humus sol by shaking sandy soils with water for 8 days. Yarusov has recently found a correlative relationship existing between the firmness of the binding of the absorbed cation with the complex considered, and also with the hydration of the absorbed cation—the less firm the bond, the greater the degree of hydration (171, 172).

On the other hand, Bouyoucos (15) has stated that when the soil-forming minerals are subjected to the action of water in the ratio of 1 part to 5 of water, whatever solution takes place does so immediately and that apparently little change is noted in this original dissolving and after it has stood 100 days. These rocks do not show a definite solubility as might be expected in the case of pure compounds. He assumed that the basis for practically all the solubility is due to hydrolysis. Bouyoucos has further pointed out (16) that breaking up of the soil particles is caused in a large part by the swelling of the colloids present due to addition of water and thus forcing the particles apart. Again, he has pointed out (17) that shaking dry soils with water causes them to disintegrate into particles of varying sizes. After this first step of disintegration, the smaller particles are extremely stable to further shaking with water. Another investigator, Vilenskii, stated that the stability of soil structure toward water is markedly affected by the nature of the absorbed bases (161).

Goletiani has considered hydrolytic acidity to be the result of OH adsorption which, if penetrating into the
micelle, increases the exchange capacity (50). Sushko has published an article in which he stated that for bog soils and alkaline bog soils the alkalinity decreased with the earlier leachings, but increased as the leaching process continued (150). A survey of the work of Byers and Anderson (23) indicates that the progressive hydrolysis of soil-forming minerals results primarily in an acid complex, probably polybasic, and consists of an aluminosilicic acid radical in which the silica-alumina ratio is greater than 2, and in which, as a soil colloid, the acid hydrogen is replaced partially by bases. As hydrolysis proceeds, the aluminosilicate is converted next to a complex having a silica-alumina ratio of 2 and contains iron as the hydrated oxide. Byers (24) has made a study of the hydrolysis of orthoclase feldspar as a representative of the most important group of soil-forming minerals. According to him, the successive steps in its degradation may be given as:

\[
\begin{align*}
\text{Orthoclase} & \quad \Rightarrow \quad \text{Montmorillonitic acid} & \quad \Rightarrow \quad \text{Pyrophyllitic acid}
\end{align*}
\]
Orthosilicic acid

$\text{H}_4\text{SiO}_4$ orthosilicic acid

$\text{Al(OH)}_3$ aluminum hydroxide

**Halloysitic acid**

**Feldspars, mica, hornblende, and similar minerals** suffer hydrolysis and hydration, while part of the combined iron is oxidized and then hydrated. An example of this (181) is shown in the case of hematite.

$$2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$$

**Hematite**

**Limonite**

Schwartz (133) has made a recent investigation of clayey weathering and kaolinization processes. Among other findings, he brought out these points: although clayey weathering is a process especially of mechanical division and colloid-alization of the parent rock, and the chemical reactions involved are confined to a hydrolytic cleavage under the formation of amorphous alumina-silicic acid gels, the process of kaolinization is a chemical reaction somewhat as represented by the equation

$$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 + 7\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{H}_2\text{SiO}_3 + 2\text{KOH}$$

Two hydrolytic equations, usually found in standard textbooks on the subject, are given below (181, 182). The hydrolysis of a silicate mineral may be pictured as:

$$\text{KAlSi}_3\text{O}_8 + \text{HOH} \rightarrow \text{HAlSi}_3\text{O}_8 + \text{KOH}$$

Another hydrolysis reaction is:

$$3\text{MgFeSiO}_4 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9 + \text{SiO}_2 + 3\text{FeO}$$

**Olivine**

**Serpentine**

**Silica**

**Ferrous oxide**
The following paragraphs shall be devoted to the constituents removed by hydrolysis effects, and their relative amounts. The following relative orders of leaching out are given by Polynov (182):

\[ \text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3; \quad \text{Ca} > \text{Mg}; \quad \text{Na} > \text{K} \]

Smolik (146), by means of a membrane hydrolysis process, separated the colloidal portion of soils into fractions of sols and a crystalloid fraction. The chemical compounds of the colloidal fraction, especially the bases, passed into the dialyzate, but the iron, aluminum and silica did not. The bases were affected in the following decreasing order: sodium, calcium, potassium and magnesium. This work was verified later by dialyzing ultra-filtered clay (less than 0.002 mm. size) and determining that only traces of aluminum, iron or silicon were removed by the process. He did find, however, that of the total base-exchange content of the colloid, the degrees of removal by dialysis were: sodium 90-98 per cent; potassium, 33-52 per cent; magnesium, 16-36 per cent (147). Brown and Byers (21) found that soil colloids represent progressive stages of degradation of complex silicates through hydrolysis, in which might be distinguished the montmorillonitic acid and halloysitic acid stages, and the final or l-teritic stage. The two hypothetical acids were considered amphoteric by them. The colloids themselves were considered to consist of partly neutralized salts of these acids and contain both acidic
and basic radicals, together with organic colloids. In 1928, Belyakova (11) pointed out that component particles of the suspensions from soils usually resemble the soils from which the suspensions originated with the exception of SiO₂. He found that the SiO₂ content of the suspensions decreases with increase in the degree of dispersion. He also pointed out that magnesium is usually one of the most stable constituents of the soil.

Barbier and Chaminade have claimed (9) that the concentration and total quantity of dissolved salts in the aqueous extract of a soil was slightly affected by the absorbing power of the colloidal complex. A given variation in the composition of the colloidal complex, however, always resulted in a large variation in the composition of the solution. In five of the six soils studied, they found the ratio of the concentration of potassium and calcium varied only slightly even with a variation of moisture content between 25 and 50 per cent.

A theory was given by Whitney (163), in 1921, that the ultra-fine clay particles in soils were formed as the result of the bombardment of the small silicate aggregates by water molecules. He believed that calcium, magnesium, sodium and potassium atoms tend to form true solutions; iron, aluminum and silicon go chiefly into a colloidal state. There appeared to be an equilibrium set up between the true solution and the colloidal state; the colloidal state carried much water and the huge molecular aggregates were thought
to be complex hydrates. Bodman (12) found that continuous leaching apparently gradually dispersed the electrolytes and caused subsequent rearrangement of the clay particles. He found that electrolyte decreases in the percolates were rapid, distinct and relatively small. Agitation of soil in water liberates salts through hydrolytic action of the water and through simple solution, Chuen (29) concluded from his work. By this method of extraction there could be no distinction made, he pointed out, between absorbed and non-absorbed salts.

Robinson (124) has made an investigation concerning the chemical composition of soil colloids and, among other data and conclusions, found that the CaO, Na$_2$O, K$_2$O, MgO and SiO$_2$ in the soil colloids are more easily extracted by water than are Al$_2$O$_3$ and Fe$_2$O$_3$, and that the CaO and Na$_2$O are more readily extracted than the MgO and K$_2$O. He further showed that the constituents of the colloidal matter are not present in the proportion to form the commoner hydrated silicates of aluminum and iron, such as kaolinite and nontronite. He concluded, therefore, that the colloidal matter of soils is chiefly composed of the products of the chemical weathering of soil-forming minerals with small and varying amounts of undecomposed fine mineral fragments.

From a study of the hydrolysis of sodium and potassium zeolites, Magistad (90) found that in the cases of artificially prepared sodium and potassium zeolites, the amount of hydrolysis at any dilution is a function of the
number of hydrogen ions present in the total volume of water at the start, and can be mathematically expressed. Sodium zeolite on hydrolysis gives NaOH which in turn reacts with Al₂O₃ to produce NaAlO₂. The amount of Al₂O₃ present in the solution as NaAlO₂ is a logarithmic function of the pH value of the solution. In a similar way, potassium zeolites hydrolyze to form KOH, which in turn reacts to form KAlO₂. Potassium zeolite at equal dilutions hydrolyzes less than does sodium zeolite, according to him.

An empirical equation for calculating the amount of potassium removed by leaching potassium zeolites with distilled water has been given by Magistad (92). He claims the equation may be applied to different types of soil colloids as the constants required in his equation have practically the same value for all colloids obtained in a single soil series. However, there is one constant which must be determined experimentally, and also an exponential factor likewise obtained, before the equation may be applied. However, he claims that once the empirical equation is set up for any soil series, the amount of potassium liberated by a leaching process may be calculated for any length of time.

Magistad’s equation is:

$$\log \frac{A}{(A-Y)} = K V^p$$

where A is the absorptive capacity in milliequivalents, Y is the loss in milliequivalents, K is a constant, V is the
volume in liters, and \( p \) a factor which may vary for different zeolite materials.

In addition to the above findings, Magistad (91) found that sodium and potassium zeolites hydrolyze according to a definite law, and that the amounts removed by leaching can also be expressed by a mathematical equation.

Breazeale found (20) that the amount of potassium dissolved from orthoclase when subjected to water, depended upon such factors as origin of the sample, fineness of subdivision, and the ratio of the solid to the water. He stated that a small amount of the potassium hydrolyzes to form KOH, which in turn reacts with the \( \text{Al}_2\text{O}_3 \) to form \( \text{AlK}_2\text{O}_2 \). The role of calcium was shown by Sokovolskii (148) in that elimination of calcium from soils by replacement brings about a condition whereby extraction of such soils with distilled water brings into pseudo solution some of the soil colloids. By such a treatment the structure of the soil is destroyed. The behavior of sodium, as indicated by Peterson and Jennings (114) in a study of the chemical equilibrium existing between soluble salts and base-exchange compounds, is that all replaceable sodium in calcareous soils may be replaced by a continued leaching with distilled water. Thomas (152) claims that for alkali soils leached with water there was a nearly constant solubility of the sodium on a high level of concentration as compared with the other exchange bases. These alkali soils also contained appreciable amounts of soluble silicates. In 1936, Dhar and Mukerji (36) stated
that the washing away of a normal soil by rain water, or 
even good irrigation water, removed more calcium than sodium, 
and hence lead to the formation of alkali soils from normal 
one.

Scharrer (131) in a study of the migration and washing 
out of plant foods in soil, concluded that the decreasing 
order of cations to be washed out of soils was calcium, mag­ 
nesium, sodium, potassium and ammonium, which agrees with 
numerous other worker's findings. However, Metzger (106) 
found in his study of a Clarksville silt loam soil that the 
effect of submerging this soil up to a period of 75 days af­ 
fected the replaceable cations as follows: sodium and potas­ 
sium were not significantly influenced by the water content 
of the soil, calcium was slightly decreased by the flooding 
process, and magnesium, aluminum, iron, manganese and am­
monium cations were greatly increased.
EXPERIMENTAL WORK

The soil colloid used in the experimental work of this dissertation was obtained from the A-horizon of a virgin Crowley silt loam. About one hundred pounds of soil was brought to the laboratory at a time in order to assure uniformity of sample.

A. Separation of the Colloidal Fraction.

The choice of a method for separating the soil in order to study any particular fraction, i.e., fraction according to particle size, several considerations must be understood. The actual diameter of the particles themselves cannot be used as the real basis for separating them into their respective fractions, but instead, it is their effective diameters which actually must be considered. The effective diameters of a colloidal particle is governed largely by the cation with which it is saturated. For instance, a sodium cation is hydrated to a much greater extent than is a hydrogen cation, thus causing a difference in their effective diameters. This is pointed out to show that application of any specific mathematical formulas defining the particle-size must necessarily be based upon assumptions which it is doubtful could be rigidly established. Notwithstanding this inherent point, application of Stoke's Law relative to
settling velocities perhaps more closely approximates a true
definition of the particle-size.

For reasons just outlined, the colloidal fraction used in this study was separated by utilizing the settling velocities of the soil particles through application of Stokes' Law. To insure that the upper size limit was well below that required of a soil colloid and fine clay fraction, the time allowed for settling was always more than the calculated value. The general procedure for separating the colloidal fraction from the other portion of the soil was done according to the method given below.

The soil was sieved to remove stones, gravel, roots and other material. It was then dispersed on a rotary shaker for 24 hours with 0.8 molar ammonium hydroxide solution and the mixture then put into large stone crocks. The upper 9 cm. of the solution was withdrawn after a minimum settling time of 24 hours, sufficient 0.8 molar ammonium hydroxide solution added to bring the level back to the original mark, the mixture thoroughly stirred, and the settling process repeated. Ten such settlings and withdrawals were made before each batch was discarded. In this way a representative colloidal fraction was obtained whose particles for the most part were smaller than one micron (0.001 μm) in maximum diameter. Under these conditions the fraction so collected satisfied the requirements for a true colloidal and fine clay material (95, 97, 157).

The colloidal solution was neutralized with dilute
hydrochloric acid, calcium chloride was added, the mixture allowed to stand for several hours to permit the colloidal fraction to coagulate and settle to the bottom of the vessels employed, and the top portion of the clear liquid siphoned off. The colloidal fraction remaining in the vessels was further concentrated by centrifuging with a Sharples super-centrifuge at 36,000 r.p.m. All the colloid was then combined, dispersed in the smallest quantity of water convenient to work with, and thoroughly mixed in one vessel to assure uniformity.

B. Preparation of Colloids for Hydrolysis.

The colloidal fraction obtained as previously described was divided into three portions as the purpose of the experimental work was to make a comparison of the effects of hydrolysis upon three different series of colloids—that is, each colloid series was to receive a different chemical treatment prior to saturation with a particular kind of cation. These chemical pre-treatments and the subsequent cation-saturation is described below.


This series of the colloid did not receive any chemical pretreatment after the colloid was actually separated and concentrated for use. In other words, the organic matter and the free oxides were left intact; it consisted of the
colloidal complex in the same condition as it occurred in the natural state in the soil.

The colloid for this series was divided into five portions and each portion saturated with a different kind of cation, namely, calcium, magnesium, sodium, potassium and hydrogen. The saturation process was as follows: each portion was dispersed for one hour in a one normal chloride solution of the respective cation desired, the mixture then supercentrifuged to separate the solid from the filtrate, and the process repeated until three such saturations had been made. This method was employed for preparing the calcium-, magnesium-, sodium- and potassium-saturated colloids but in the case of hydrogen colloid 0.03 normal hydrochloric acid was used instead of one normal so that the colloidal complexes would not be affected by too high concentration of acid.

After the third saturation process, the excess electrolytes were washed out with water by dispersing in water for fifteen minutes, supercentrifuging, and re-dispersing the solid in water as before. Each colloidal sample was washed three times; in each case the filtrate from the last washing gave a negative test for chloride, which was taken as proper criterion for assuming removal of the excess cations.

2. Series II. Colloids free of organic matter.

The colloid for this series was dispersed in the smallest amount of water possible, 30 per cent hydrogen peroxide added, and oxidation of the organic matter carried out at room temperature until action ceased, whereupon the mixture was placed in a water-bath and oxidation continued at a temperature not
exceeding 80°C. Oxidation was continued by further additions of hydrogen peroxide until all the organic matter was removed. At the end of this process the colloid was gray in color and silky in appearance.

After the organic matter was removed, the colloidal mass was divided into five separate portions; each portion was saturated with the same cations employed for Series I—calcium, magnesium, sodium, potassium and hydrogen. However, in this case the saturation and washing out of excess electrolytes was done in a somewhat different manner than for Series I. The procedure employed for Series II is given below.

One normal chloride solutions of calcium, magnesium, sodium and potassium were used for saturating the colloid samples, but each particular colloid sample was treated a different number of times with the respective salt. The calcium and magnesium colloids were saturated three times, the sodium colloid five times, and the potassium colloid four times. The hydrogen colloid was prepared by saturating five times with 0.03 normal hydrochloric acid.

After the final saturation in each case, the excess electrolytes were removed by washing with 85 per cent alcohol. The purpose of the alcohol was to remove the excess electrolytes with a minimum amount of hydrolysis. It was observed in all cases that the excess electrolytes had been removed by the time any appreciable turbidity had appeared in the filtrates. And since the relative turbidity of the
filtrates may be used as an approximate measure of the hydrolysis produced by this operation, it was reasonable to assume that this method of removing the excess electrolytes minimized to a negligible degree any hydrolysis that occurred prior to the actual time of beginning each hydrolysis study. Each alcohol-washing treatment consisted of dispersing for thirty minutes in the 85 per cent ethyl alcohol, supercentrifuging, and redispersing in alcohol again—the process being repeated until no chloride test was given by the filtrate. The different colloid samples required different numbers of times of washing as follows: calcium, magnesium and potassium colloids each required four washings, the hydrogen colloid two washings, and the sodium colloid five washings.


The colloid for Series III was treated with hydrogen peroxide for removal of organic matter similar to that described for Series II. After removal of the organic matter, the free oxides of aluminum, iron and silicon were removed according to a modification of the method of Truog and Drosdoff (154, 155). This modified method consisted of the following treatment:

(1) Approximately one hundred grams of colloid was dispersed in two liters of water, placed in a four-liter beaker, and heated to 80° to 90° C.

(2) One ml. of 20 per cent Na₂S·9H₂O was added
for each gram of colloid and the solution gently boiled for five minutes. Two grams of ammonium chloride was added for each gram of colloid, the temperature being maintained by means of an electric hot plate at 80° to 90°C. At this higher pH the free SiO₂ coating on the colloidal particles is dissolved.

(3) The mixture was brought rapidly to pH 7 by means of a two normal hydrochloric acid solution; 30 ml. was added from a graduated cylinder and the remainder by a burette mounted on the hot plate. Additional hydrochloric acid was added slowly, using bromothymal blue as an external indicator, until pH 6 was reached. Nascent hydrogen sulfide was liberated at this point and accomplished the reduction of the iron to the ferrous state. An air-driven stirrer was used throughout this and subsequent operations to facilitate the reduction process.

(4) Another portion of the 20 per cent sodium sulfide solution was added in the ratio of one ml. to one gram of colloid, the mixture stirred vigorously, two normal hydrochloric acid added rapidly until pH 7 was reached, and the addition of the hydrochloric acid continued very slowly until pH 6 was again reached.

(5) After pH 6 was reached, more two normal hydrochloric acid was added until pH 3 was attained, using bromophenol blue as an external indicator, and the solution then allowed to stand ten minutes or until the color was a very light gray. During this ten minute period tests were made
every two or three minutes to see that pH 3 was maintained.

(6) The solution was brought back to pH 7 with two normal ammonium hydroxide.

(7) Two normal hydrochloric acid was added slowly until pH 6 was reached, then added rapidly until pH 3 was again reached, allowed to digest five to ten minutes until a light gray color developed and until coagulation had definitely occurred. The mixture was then supercentrifuged to separate the liquid from the colloidal solid.

At the completion of this process for the removal of the organic matter and the free oxides, the colloidal material was almost white in color and exceedingly silky in appearance.

After the removal of the organic matter and the free oxides, the colloidal material was divided into five separate portions; each portion was saturated with a single kind of base-exchange cation corresponding to those used for Series I and II, namely, calcium, magnesium, sodium, potassium and hydrogen. The general methods of procedure were the same as employed for Series II. One normal chloride solutions were used for all except the hydrogen colloid. The hydrogen colloid was given five saturation treatments with 0.03 normal hydrochloric acid. The calcium, magnesium and potassium colloids each received four saturation treatments, and the sodium colloid received five saturation treatments with their respective chloride salts.

Each of the base-saturated colloidal samples was washed with 85 per cent ethyl alcohol in the same manner as the colloids in Series II. The hydrogen colloid was washed
three times, the calcium, sodium and magnesium colloids each were washed four times, and the potassium colloid was washed five times. In all cases the filtrates from the last washings gave negative chloride tests.

G. The Process of Hydrolysis.

The process of hydrolysis, withdrawing of samples, filtering the samples after withdrawal, and the subsequent analysis were carried out in the same general manner for all three series of colloids. Series II and Series III were carried through identical operations; Series I had a slight difference from the other two in the matter of time intervals for taking samples. In Series I there were no 18-hour samples or 72 hour samples; also, there was a 144-hour sample taken in Series I for which there were no corresponding samples in either Series II or Series III. These differences in time intervals, however, did not materially affect the general trend of the results.

Pure distilled water was used in all three series for the hydrolysis processes. The colloids, which had been previously prepared and base-saturated as described in the preceding parts, were dispersed in water, made up to the proper concentration of approximately twenty parts of water to one part of colloid, put into five shaking-bottles, and subjected to continuous shaking on an end-over-end rotary shaker which revolved at fourteen revolutions per minute.
A thirty-minute period of dispersion was necessary for Series I prior to starting the hydrolysis proper; fifteen minutes dispersion periods were sufficient for Series II and III.

D. Sampling and Filtering.

At the stipulated time intervals 250 ml. samples were withdrawn in the case of Series I, and 350 ml. samples withdrawn for Series II and III. The time intervals for withdrawing samples for Series I were: zero, six, twelve, twenty-four, thirty-six, forty-eight, ninety-six and one hundred forty-four hours. The time intervals for taking samples for Series II and III were: zero, six, twelve, eighteen, twenty-four, thirty-six, forty-eight, seventy-two and ninety-six hours.

Pasteur-Chamberland filters were used to separate the colloidal solid from the solution. Prior to filtering the first sample of any particular cation-saturated colloid, the filters to be used were prepared by filtering some of the colloidal mixture through them. This was done so that base-exchange phenomena which might take place between the filter and the colloidal mixture would have reached equilibrium before actually filtering one of the samples. Any excess electrolytes left in the filters by this pretreatment was removed by filtering pure water through them after the colloid had been washed off the outside of the filters. The
same filters were used throughout a hydrolysis run. Thus, it was necessary to impregnate the filters only at the beginning of each hydrolysis process as the variation between samples saturated with the same cation was not enough to present difficulties on this point.

In all cases the samples were filtered immediately after taking off the shaker in order to stop the hydrolysis as soon as possible after withdrawal. Test tubes measuring 32 x 200 mm. were used as containers for the filters, the Pasteur-Chamberland filters being placed inside of these and the filtering process accomplished by suction from a water-pump. In this manner the full surface of the filters could be utilized almost throughout the filtering process as the free-space between the filter and the wall of the vessel was at its most practical minimum. After the last portion of the liquid had been removed by the filtering process, the filters were inverted to allow the filtrate to drain from them, the filters replaced in the test tubes, the test tubes filled with water, and this water filtered through the filters. Thus about 25 ml. of water was used to wash the colloid on each filter and to displace the filtrate left in the walls of the filter. When the last portion of wash-water had filtered through, the filters were again inverted and this wash-liquid allowed to run into the receiving vessel together with the first part of the filtrate.

The colloid on the filters was removed by means of distilled water and gentle rubbing with the fingers after
the suction had been released. It was found that this method was the simplest and easiest way to remove the colloids and at the same time minimize the errors involved in handling the filtrates.

The filtrates thus obtained were evaporated to a small volume (but not allowed to go to dryness), subsequently made up to 200 ml., and placed in glass-stoppered bottles. These solutions were later analyzed for various constituents to trace the effects of hydrolysis upon the different colloidal samples. The constituents determined on these filtrates were: (1) the cation with which each respective colloid sample had been previously saturated with, (2) aluminum, (3) silica, and (4) iron.

The solid colloidal material itself was dried and stored in glass-stoppered bottles. Two specific determinations were made upon the solid-material samples obtained from the zero-time interval: (1) the base-exchange capacity and (2) the per cent base-saturation actually present. It was necessary to know this on each hydrolysis process measured so as to determine if the colloids were on a comparable basis at the beginning.

Each time a sample was withdrawn during the hydrolytic period another portion was taken for the purpose of determining the pH value of the mixture undergoing hydrolysis. The pH values were determined with a Beckmann pH meter using a glass electrode.
The analytical results for all the colloidal samples used in this investigation are recorded in Tables I to V inclusive.

E. Methods of Analysis upon the Filtrates.

1. Determination of calcium (base-saturation cation).

The method used was that given by Kolthoff and Sandell (178). Fifty ml. samples were withdrawn, evaporated to about 25 ml. on the hot plate, two drops of methyl red added, the solution acidified with hydrochloric acid, and then 3 ml. excess of concentrated hydrochloric acid added. Ten ml. of a solution containing 0.6 gram ammonium oxalate was added, the solution heated on a hot plate to 70° to 80° C., and then 1:1 ammonium hydroxide added dropwise by means of a burette until the color changed to a distinct yellow. The solution was set aside for two to four hours at room temperature, and then maintained at 5° C. for twelve hours. The calcium oxalate thus precipitated was filtered on Whatman No. 42 ashless filter paper and the precipitate washed three times with 2 ml. portions of water, or until free of excess oxalate ions. The precipitate was then dissolved with hot 1:8 sulfuric acid and titrated while hot (around 60° C.) with 0.0480 normal potassium permanganate solution. At the end of the titration the filter paper was added to the beaker and the titration completed to the first color permanent for approximately ten seconds. A microburette
was employed.

2. Determination of magnesium (base-saturation cation).

The method used was that given by Kolthoff and Sandell (178). Fifty ml. samples were used for all determinations. Five ml. of concentrated hydrochloric acid, 10 ml. of a solution containing 25 grams di-ammonium hydrogen phosphate per 100 ml. water, and four drops of methyl red indicator were added to each determination. Concentrated ammonium hydroxide was added with constant stirring until the indicator turned distinctly yellow, an additional 5 ml. of ammonium hydroxide added, and the stirring continued for several minutes. All of these operations were carried out at room temperature. The magnesium ammonium phosphate precipitate thus formed was allowed to digest at room temperature for one to two hours and then maintained at 5°C for twelve hours. The precipitate was then filtered on Whatman No. 42 filter paper, washed, then the paper gently charred over a gas burner, and finally ignited in a muffle furnace at 1100°C. This last operation converted the magnesium ammonium phosphate to magnesium pyrophosphate, the form in which it was finally weighed. From the weight of the magnesium pyrophosphate it was possible to calculate the weight of magnesium.

3. Determination of total acidity (base-saturation cation).

Fifty ml. samples were used in this determination.
Each sample was titrated with 0.0118 normal sodium hydroxide solution by means of a micro-burette and using phenolphthalein as the indicator—the same indicator used in the standardization of the sodium hydroxide.

4. Determination of sodium (base-saturation cation).

The sodium determinations were made according to the method outlined by Piper (115) which consists of precipitating the sodium as the triple salt, sodium uranyl magnesium acetate. Modifications for preparing the reagent may be found in Soil Analysis, page 96, by C. H. Wright. Fifty ml. samples were withdrawn, evaporated to 6 ml. on a hot plate, and 30 ml. of the reagent added to the cold solution. The precipitate thus formed was permitted to digest for twelve hours at 5° C. and filtered in Gooch crucibles. The precipitate was washed five times with 2 ml. portions of the reagent, followed by five times with 2 ml. portions of ethyl alcohol, and finally twice with 5 ml. portions of ethyl ether. The crucibles were then brought to constant weight in a desiccator without heating. The weight of the precipitate multiplied by the factor 0.015 gives the weight of sodium.

5. Determination of potassium (base-saturation cation).

The method proposed by Van Rysselberghe (160) was used for this determination. Fifty ml. samples were treated with
30 ml. of the cobaltinitrite reagent, the potassium cobaltinitrite precipitate allowed to digest and settle for twenty-four hours. The precipitate was transferred to Gooch crucibles with the smallest volume possible of water acidified with acetic acid, the precipitate then washed three times with 2 ml. portions of this acidified water, and finally washed with two 2 ml. portions of ethyl alcohol. The precipitate was dried at 105°C to constant weight. The amount of potassium in the precipitate was determined from analysis of known potassium samples precipitated at the same time and handled under the same conditions as the unknown samples.


The aluminum determinations were made according to the method of Hemmett and Sottery (54). Twenty-five ml. samples were used. Each sample was made faintly acid with hydrochloric acid, 1 ml. of 5 normal hydrochloric acid, 5 ml. of 3 normal ammonium acetate, and 5 ml. of aluminon reagent (0.1 per cent solution of the ammonium salt of aurin tricarboxylic acid) added. The solution was then thoroughly mixed and allowed to stand approximately five minutes or until the lake had formed. Two ml. of concentrated ammonium hydroxide and 10 ml. of 5 normal ammonium carbonate solution were next added, the total volume made to 50 ml., mixed thoroughly, and after standing twenty-five minutes the colors so developed compared with standards prepared at the same time from known amounts of aluminum solutions. Comparison
was made in 50 ml. Nessler tubes.

\[ \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \] was used as the aluminum standard.

Two standard solutions were employed. One contained 0.1 mg. aluminum per ml. and the other contained 0.01 mg. aluminum per ml.

7. Determination of silica.

Silica was determined according to a modification of the method proposed by Schwartz (134). The method depends upon the intensity of the yellow color produced by the formation of ammonium silicomolybdate. The reagent used was a 10 per cent ammonium molybdate solution containing sufficient sulfuric acid to give the solution a pH of one. Three ml. of the reagent was added to 25 ml. samples and after standing fifteen minutes compared with standards prepared at the same time with known amounts of silica solutions. Comparison was made in 50 ml. Nessler tubes.

The silica standards were prepared from meta sodium silicate, \( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} \), and containing 0.01 mg. silica per ml., 0.1 mg. silica per ml., and 1.0 mg. silica per ml., respectively.

8. Determination of iron.

Iron was determined according to a modification of the method first proposed by McFarlane (39), and depends upon the intensity of the red color developed by the reaction of ferrous iron with alpha,alpha bypyridine.
All the iron was reduced to the ferrous state by means of titanic chloride solution. This reagent was prepared by adding 5 ml. of a 20 per cent titanic chloride solution to 100 ml. of boiling one normal hydrochloric acid solution. The alpha, alpha bipyridine reagent was prepared by dissolving 0.632 gram in 90 ml. water plus 10 ml. of one normal hydrochloric acid. Sodium acetate buffer solution, also used in the determination, was prepared by adding equal volumes of 0.2 normal solutions of acetic acid and sodium hydroxide. The pH of the buffer solution was approximately 4.7.

The actual determination was carried out as follows: 2 ml. of alpha, alpha bipyridine reagent was added to 10 ml. of solution to be tested, 1 ml. of titanic chloride then added, and finally 7.5 ml. of sodium acetate buffer solution added. The intensity of the red color so developed was compared in Nessler tubes with standard iron solutions treated in a similar manner and prepared simultaneously with the unknowns.

The iron standards were prepared by dissolving 4.3 grams FeK$_4$(SO$_4$)$_2$·12H$_2$O in one liter of solution. This standard No. 1 contained 0.5 mg. iron per ml. From Standard No. 1 other standards were prepared so that one ml. contained, respectively, 0.05 mg., 0.005 mg. and 0.0005 mg. iron per ml. A small amount of sulfuric acid was added to each standard solution to prevent hydrolysis of the salt and to stabilize the solution.
F. Methods of Analysis for the Solid Colloids.

1. Determination of total base-exchange capacity.

The total base-exchange capacity was determined by modifications of the methods proposed by Parker (112), and by Schollenberger and Dreibelbis (132). Two grams of the very finely ground colloidal material (dried at 108° C.) was allowed to soak in water overnight and then dispersed with a high-speed disperser for thirty minutes. As soon as the colloidal material was dispersed, sufficient concentrated ammonium acetate solution was added to make the final concentration one normal with respect to ammonium acetate. The dispersion was continued for another thirty minutes, and the colloidal mixture filtered through Pasteur-Chamberland filters which had been previously saturated with ammonium acetate solution and the excess ammonium acetate washed out by means of distilled water. The colloidal material thus stuck to the filter was given a continuous leaching process with one normal ammonium acetate until a total of 250 ml. had been used. Immediately after the leaching process, the excess ammonium acetate was removed by washing with three portions of water and six portions of 95 per cent ethyl alcohol. Each washing process consisted of filling the 32 x 200 mm. test tubes (which were used as containing vessels for the filters during the filtering processes) with the wash-solution, applying suction until all the wash-solution was drawn through the filters, inverting the filters to
empty them, and repeating the process until all the washings had been done. In each case the last washing gave a negative test for ammonia with Nessler's reagent.

The ammonium acetate served two purposes: (1) to displace all the cations with which the colloid may have been saturated and (2) to saturate the colloid with ammonium ions to the full extent of its respective base-exchange capacity. The filtrate from the leaching process, plus the wash-solutions used to wash out the excess ammonium acetate, contained all the unaffected ammonium acetate and also all the base-exchange cations removed from the colloid by the ammonium acetate.

The total base-exchange capacity for all except the hydrogen colloid was determined by the Kjeldahl method for determining ammonia. This consisted of distilling off the ammonia from the ammonium-saturated colloidal material after adding an excess of sodium hydroxide, catching the ammonia in standard sulfuric acid solution, and titrating the excess sulfuric acid by means of standard sodium hydroxide solution with methyl red as the indicator. From this data the milliequivalents of ammonium-ion present, which represents the true number of milliequivalents of base-exchange capacity, may be calculated.

In the case of the hydrogen-saturated colloid a different procedure had to be employed to obtain consistent results. The hydrogen-saturated colloid was put through a similar dispersion and leaching process as just described
for the other colloids, but barium acetate was used instead of ammonium acetate. The base-exchange capacity of the hydrogen colloid was determined by removing with 0.05 normal hydrochloric acid the barium it was thus saturated with, precipitating the barium as the sulfate, and igniting to constant weight as barium sulfate. From this the total base-exchange capacity was calculated.

2. Determination of per cent base-saturation.

The base-exchange cations removed by the ammonium acetate treatment were determined after destroying the ammonium salts by adding nitric acid and evaporating to dryness, and then determining each particular kind of cation by the same methods described previously. Thus, the amount of calcium, magnesium, sodium and potassium in each respectively saturated colloid was determined.

The base-saturation for the hydrogen colloid was determined from the leachate and washings obtained from the barium acetate leaching process discussed under the determination of total base-exchange capacity. The entire leachate and washings was titrated with standard barium hydroxide solution to the same end-point as that of an equal volume of the original barium acetate. Cresol red was the indicator used. From this data the amount of hydrogen-ion originally present in the colloid as base-exchangeable hydrogen was calculated.

The per cent base-saturation was calculated in all cases
by the equation:

\[
\frac{\text{m. e. of respective cation as exchangeable material}}{\text{m. e. of total base-exchange capacity}} \times 100 = \text{per cent base-saturation}
\]
DISCUSSION OF RESULTS

The discussion of the results obtained in this investigation of the effects of hydrolysis upon soil colloids shall be presented according to the outline given below.

(A) pH of the liquid mixture during the entire period of hydrolysis.

The amount of the following liberated by the hydrolytic process:

(B) Base-saturation cation
(C) Silica
(D) Iron
(E) Aluminum

Each discussion shall be treated according to: (1) actual effect of continued hydrolysis upon any individual cation-saturated colloid, (2) comparison of the individual members within a single series, (3) comparison of individual members for all three series, and (4) general comparison of the three series upon the basis of one kind of determination.

The analytical results for all the determinations made in this investigation are presented in Tables I to V inclusive; the graphs showing the interpretation of the results obtained are shown in Figures 1 to 20 inclusive.
A. The Effect of Hydrolysis upon pH of Soil Colloids.

Acid reactions and alkaline reactions of soil colloids may be explained by such general reactions as:

\[ \text{Clay} + X + H^+ + OH^- \rightarrow \text{Clay} + X^- + OH^- \text{ (alkaline)} \]
and, \[ \text{Clay} + Y + H^+ + OH^- \rightarrow \text{Clay} + OH^- + Y^- + H^+ \text{ (acid)} \]

wherein \( X \) and \( Y \) may represent positive and negative ions or groups.

In all the different cation-saturated colloids studies, it was found that the organic matter caused more fluctuation in the pH values than in the other colloids. Apparently, instead of exhibiting a stabilizing influence, it did not have the same buffering effect as those without organic matter or without the free oxides. The effects evidenced by the variously-saturated colloids is given below.

1. Calcium colloids.

The pH of the three calcium-saturated colloids, Figure 1, behaved as follows: Series I showed an increase the first 24 hours, and then gradually decreased, but not to the initial value; Series II was considered as of constant value and was less in absolute value than Series I; Series III was also considered as of constant value. Series I had the highest pH, Series II next, and Series III the lowest—the magnitude of differences between the three series was about the same.

2. Magnesium colloids.

The magnesium-saturated colloids, Figure 2, gave the
following results: Series I showed an increase the first 24 hours, then decreased slightly and maintained a constant value after 36 hours; Series II was practically of constant value; Series III was likewise practically of constant value throughout the hydrolysis process. Series I had a slightly higher pH than did Series II, while Series III was considerably less than the other two.

3. Hydrogen colloids.

Figure 3 shows the behavior of the hydrogen-saturated colloids. Series I showed erratic fluctuations the first 24 hours and then gradually increased in pH; Series II showed a decrease at first and then became constant after 18 hours; Series III was almost of constant value throughout the experiment, showing a very gradual decrease. All three series were fairly close together in pH values with Series III having the highest, Series I the next highest, and Series II the lowest values.

4. Potassium colloids.

The potassium-saturated colloids, Figure 4, evidenced: Series I gave an initial lowering, increased almost to the original value, and then showed a very slight decrease; Series II showed a rather steady decrease in pH for the first 48 hours and then became almost constant; Series III exhibited a marked decrease the first 48 hours and then decreased only slightly. Series II had the highest pH value, Series I was next and not far from the values of Series II, and Series III was much less than either of the other two.
5. Sodium colloids.

The sodium-saturated colloids, shown in Figure 5, reacted as follows: Series I had the highest initial pH of any, showed a distinct decrease the first 24 hours, and increased slightly until at 36 hours it became almost constant; Series II had a very slight, steady decrease, standing as an average between the beginning and end of the values obtained for Series I; Series III behaved similar to Series II in that it was almost a constant value—it showed a slight decrease and then practically a constant value. The pH of Series III was considerably less than either of the other two series.

General Statements of Results

It was found that the general trends for pH were almost identical for calcium and magnesium. In each case the Series I colloid had an initial increase and then a decrease—but did not decrease to the original value—and then became almost constant. Also, it was found that the relative values for each series in these two were comparable. In both the calcium and the magnesium colloids, Series I had the highest pH, while Series II and Series III had the lowest pH and considerably less than the other Series. It may be pointed out, in general, that these two types of colloids—calcium and magnesium—were very comparable in the manner in which their pH values were affected under these conditions.

There were some similarities between the sodium- and potassium-saturated colloids. Series I was not very comparable with the others, but Series II and Series III were
very similar. Series II and III had almost identical curves and had about the same initial and final values.

The hydrogen-saturated colloid did not show marked similarity to the other four colloids.

It may be noted that the different pretreatments each series underwent prior to base-saturation had marked effects upon their respective pH values. The effect of removing organic matter (Series II) was usually to lower the pH; in all cases except the hydrogen-saturated colloid the effect of removing both organic matter and the free oxides (Series III) was to materially lower the pH. However, in the case of the hydrogen colloid the effect was exactly opposite. It may also be stated that the natural-state colloid (Series I) in all cases showed more erratic results, the removal of organic matter (Series II) tended to give smoother curves and less abrupt fluctuations, and the removal of both organic matter and the free oxides (Series III) resulted in very smooth curves which were for the most part straight lines.

The hydrogen colloids had the lowest pH of any studied; sodium colloids had the highest pH, closely followed by the potassium ones; magnesium and calcium colloids gave pH values in between these, with the magnesium somewhat higher than the calcium ones. This agrees largely with the findings of Sing and Nijawan (145). Cardos and Joffe (25), however, reported according to the soils they investigated that magnesium complexes gave lower pH values than calcium, which is not in agreement with this study. Nor do the findings of Lein (85)
altogether agree with this. However, discrepancies of this nature are found throughout the literature, as too many other factors often enter into the particular investigations to put them on a comparable basis.

The natural-state sodium- and potassium-colloids behaved very similar to work reported by Sushko (150) in that for alkaline soils the pH is lowered by the first leachings. It must be noted that most of the equations, given by various investigators (133, 179, 181, 182) for what takes place when a soil mineral undergoes hydrolytic cleavage, indicate the liberation of some sort of hydroxide. This should increase the pH. However, the findings of this investigation do not seem to altogether justify such assumptions as the most alkaline soils (sodium and potassium) gave a decrease in pH as hydrolysis proceeded. Evidently, from this, the products indicated by various authorities must undergo an immediate secondary reaction if given an opportunity, or else their equations are incorrect. In the conditions of this experiment, however, there was an opportunity for further reactions as the hydrolytic processes were not done under leaching conditions, but rather, in closed systems.

The equations given by Byers (24) seem quite plausible as an explanation of what may happen. In these, silicic acid and aluminum hydroxide may be the products when certain minerals hydrolyze. This could be a reasonable explanation of the changes in pH found in this investigation. Also, what may actually happen to the hydroxide compounds initially liberated by hydrolysis has been explained by Magnusd (90)
as the subsequent formation of such compounds as aluminates. If these aluminates so formed are relatively stable to further hydrolysis, then this could be used as an explanation of the pH effects noted in this study.

B. The Effect of Hydrolysis upon Liberation of the Base-saturation Cation.

The general mechanism for the liberation of the base-saturation cation may be depicted by such a reaction as:

\[ \text{Ca-clay} + 2^+ H \quad \text{(from } H_2O) \xrightarrow{\text{---}} \text{H-clay} + \text{Ca}^{++} \]

The actual effects, which may include hydration and molecular rearrangements, are not shown, for these mechanisms, up to the present time, are quite obscure. But whatever the mechanism involved, it can be shown that the results of the effects of hydrolysis, as evidenced by the material found in the hydrolyzate itself, may be quantitatively determined.

All the data obtained from the determinations of the respective base-saturation cation liberated was calculated upon a milliequivalent basis in order to have a comparative basis for graphing the data. The data is given in the Tables, and the graphic interpretations are shown in Figures 6 to 10 inclusive.

The results of the effects of hydrolysis upon the liberation of the respective cation with which the colloids were saturated may be summarized, according to the particular cation involved, as follows:
1. Calcium colloids.

In Figure 6 is shown the hydrolytic liberation of calcium from the calcium-saturated soil colloids. Series I displayed a small, erratic increase with time of hydrolysis; Series II maintained an almost constant value; and Series III was quite similar in showing practically a constant value. It is seen that Series II and III responded to hydrolysis in the same general way, and Series I was not far different. It may also be stated that hydrolytic action affected Series II the most, affected Series I next, and affected Series III the least. However, there was not a wide divergence in the effects, as shown by the graph.

Series I showed the smallest amount of soluble calcium of the three series, but this series increased about three times the initial value as hydrolysis proceeded. Series II yielded the largest amount of calcium, but increased only about 10 per cent during the entire 96 hours. Series III had an increase of 18 per cent during the hydrolysis.

2. Magnesium colloids.

Figure 7 shows that the rate of liberation of magnesium from the magnesium-saturated colloids was most pronounced in Series I, which gave a fairly steady increase during the entire time of hydrolysis. Series II yielded the most magnesium of any of the series; it increased slightly at first and then decreased about a corresponding amount to finally give apparently a constant value. Series III gave what might be considered a constant value, and gave up the smallest
amount of magnesium of the three series.

Magnesium was freed in Series I more than in any of the others. It increased about seven times the beginning value. On the other hand, Series II increased only about 23 per cent, and Series III, which gave on an average the least magnesium of any during the period, showed a relative increase of about 60 per cent.

3. Hydrogen colloids.

The hydrolytic liberation of hydrogen-ions from the hydrogen-saturated colloid is graphically shown in Figure 8. On a milliequivalent basis, it may be seen that all three series gave values for the liberated hydrogen-ion which should be considered rather constant. The three lines are practically parallel and, too, are not far apart in absolute values. Series III gave the highest amounts, Series II the next, and Series I gave the lowest amounts for these determinations.

Hydrogen-ion liberation was too erratic in Series I for calculation of mathematical relationships; it contained the least amount of titratable acid of the three series. Series II just about doubled in titratable acid in 96 hours, whereas Series III had the most of all, and almost trebled in the same period of hydrolysis.

4. Potassium colloids.

Series II yielded by far the most potassium from the potassium-saturated colloids. The first 48 hours it gave a slight increase and an equal decrease, and then increased
again slightly. On the other hand, Series III gave a decided, steady increase the first 15 hours and then became constant. Series I evidenced a steady increase for 48 hours and then decreased slightly. However, it may be stated that this slight lowering may have been due to experimental error. It may also be pointed out that Series I and III approximated each other, and were considerably below Series II in this phase of the study. These results are shown in Figure 9.

Series I increased almost three times, Series II increased about 12 per cent, and Series III showed an increase of over fifty times that for its zero sample. Series II had by far the most potassium in the hydrolyzate—having over three times that for either of the other two series.

5. Sodium colloids.

In the sodium-saturated colloids, the hydrolytic liberation of sodium was most affected in Series II. There was a slight increase for 24 hours, then a decrease during the next 24 hours, and then a steady increase until the end of the experiment. Series I did not yield as much sodium as did Series II. The amounts liberated varied somewhat but were almost constant. Series III gave increasing amounts of sodium. Series I and III closely approached each other insofar as their relative equivalents liberated were concerned; however, this pair yielded much less sodium than Series II.

Series III had the smallest initial value but had about the same amount at the end of the hydrolytic process as did Series I. Series III yielded a gain of almost ten times its
starting value, whereas Series I yielded a gain of less than 25 per cent. Series II, which was quite comparable in amount with that for the same series for potassium colloids, contained an average amount in the hydrolysate of over four or five times either Series I or III; it showed a net increase of 25 per cent—about the same per cent gain as for Series I.

General Statements of Results

As a whole, the hydrogen-saturated colloids were affected the least by hydrolysis; the calcium-saturated ones were next to the hydrogen colloids in this respect. Magnesium colloid occupied a middle position, and the sodium- and potassium-saturated colloids were the most affected insofar as liberation of their saturated-cation. Again, there was a similarity between sodium- and potassium-saturated colloids as the general trends obtained in all three series were quite alike both as to the respective rate of liberation and as to absolute values. The magnesium colloid was between the calcium and hydrogen pair, and the sodium and potassium pair previously mentioned. These findings are in agreement with Bayer (10), Casale (26), Vilenskii (161) and a part of Puri's work (118) wherein they reported upon the relative ease of dispersion produced by various cations. Likewise, Kotzmann (78), Sing and Nijawan (145), and Moseev (107) have all contributed work which bear a positive relation to this study of the effects produced by the saturation-cation.
Gedroiz (42), Jenny (64) and Joseph (67) all have reported work which would indicate that the order of effect of hydrolysis upon the respective cation-saturated complexes would be as found in this dissertation. The release of saturation-cation is also consistent with the relative energies of adsorption given by Getman and Daniels (174). Smolik (146) confirms the author's findings in reporting the relative release of base-cations—sodium being released the easiest of all. In a study of leaching effects, Bodman (12) found that electrolyte decreases in the percolates were rapid, distinct, and relatively small—all of which is consistent with this work. The order of removal of cations by washing effects, reported by Scharrer (131) was apparently opposite to the conclusions reached in this work. He gave the decreasing order of removal as calcium, magnesium, sodium and potassium—a finding almost opposite to this study. Also, the author does not agree with Metzger (106) in his claims that a period as long as 75 days of subjecting soils to water submergence does not significantly affect the sodium and potassium content.

In all cases except for the hydrogen-saturated colloids, those with only the organic matter removed (Series II) gave the largest amounts of saturation-cation in the hydrolyzate, and even in the case of the hydrogen colloid this one was only slightly exceeded by Series III. Myers (108) reported practically the same thing in his comparison of organic and inorganic complexes with respect to their effects upon aggre-
In all but the magnesium-saturated colloids the effects were very similar in each case in that Series I and Series III gave values not far apart. Series III gave the most consistent values, whether the particular case gave constant values or a change in values as hydrolysis proceeded. Series III for calcium, magnesium and hydrogen colloids gave constant values; Series III gave in the cases of sodium and potassium a steady increase at the beginning and then became constant. This is to be expected as the complicating factors of organic matter and the free oxides were not present in this series.

C. The Effect of Hydrolysis upon Liberation of Silica.

The first product formed in the hydrolytic liberation of silica is not definitely known. It is reasonable to suppose, however, that it may split out of the parent aggregate as some form of silicic acid or a hydrated form of silicon dioxide. It may first form a simpler compound than the original material, and this new product, due to its increased solubility, yield the silica by subsequent hydrolysis. It was not possible to trace the intermediary products which may have been formed; it was possible only to determine the concentration of the silica as the time of hydrolytic action proceeded.
1. Calcium colloids.

Reference to Figure 11 reveals that the silica liberated from calcium-saturated colloids was practically constant in amount as time proceeded for hydrolysis of both Series I and II. In the case of Series III there was a marked increase in liberated silica the first 48 hours and then apparently reached an equilibrium. Series I and II were closely parallel, with Series II liberating a slight amount more than Series I. The initial amounts were about the same for all three series.

2. Magnesium colloids.

Figure 12 shows that for magnesium-saturated colloids, Series I and II closely approximated each other, with Series II liberating somewhat more than Series I. Series I and II each gave practically constant amounts of silica throughout their respective hydrolytic period. Series III gave a steady, marked increase for 48 hours and then reached equilibrium. The amounts at the start of the hydrolytic period were almost the same.

3. Hydrogen colloids.

The hydrogen-saturated colloids liberated silica as shown in Figure 13. Series I gave a slight, unsteady increase; Series II showed a more marked, irregular increase the first 48 hours and then approached a constant rate very slowly; Series III gave very erratic results, and although the curve is drawn to show an increase in liberated silica it should be regarded more as the author's interpretation of the erratic
data at hand and not as what was shown to have occurred.

It should be noted that the initial amount in Series II was more than either of the other two series, which initially had about the same amounts.

4. Potassium colloids.

The potassium-saturated colloids, graphically shown in Figure 14, gave rather consistent results. Series I gave a slight, steady increase as time proceeded; Series II slightly increased for 24 hours and then gave just about a constant value; Series III gave a marked, steady increase for 24 hours and then maintained a constant amount. Series I and II were quite alike. They diverged slightly the first 24 hours and then presented a constant parallel. They had practically the same initial value, which was somewhat lower than that for Series III.

5. Sodium colloids.

Figure 15 depicts the amounts of silica liberated from sodium-saturated colloids. All three series had almost the same initial values, then diverged somewhat, but after 30 hours all were about constant. Series I was constant throughout, Series II increased slightly for 12 hours and then became constant, and Series III gave an increase for 36 hours and then was constant.

General Statements of Results

The curves for the calcium-saturated colloids and for the magnesium-saturated colloids were almost identical; also,
their absolute values were almost the same. The potassium- and sodium-saturated colloids also gave curves very similar to those for calcium and magnesium colloids. The sodium and potassium colloids resembled each other, also; in neither case did the Series III colloid respond as much to hydrolysis as was evidenced in the calcium and magnesium colloids. In a general way, the curves for the hydrogen colloid were similar to the others but not so marked. There was not a great difference in the initial values of all the fifteen colloidal samples considered. In all cases the Series III colloids responded the most to hydrolysis, the Series II colloids responded somewhat less, and the Series I colloids were affected the least. It may be pointed out that Series I and II closely resembled one another in their response to hydrolytic action but the Series III colloids yielded considerably more silica than either Series I or II. It was shown conclusively that Smolik (146) had no justification for an early statement attributed to him in which he stated that hydrolysis would not affect soil complexes to the extent of liberating silica. However, in some later work, Smolik (147) admitted that there might be a possibility for such a phenomenon to occur to a limited degree.

The author has substantiated Thomas' work (152) wherein alkali soils were found to contain appreciable amounts of silica; this investigation has also agreed with the views expressed by Gedroiz (43).
D. The Effect of Hydrolysis upon Liberation of Iron.

The results obtained in determining the iron liberated by hydrolysis were so erratic they are not given in graph form. The relative experimental error in this sort of determination is necessarily high as iron is such a common impurity in all substances. However, some information was obtained which gives valuable insight as to the relative stability of the iron compounds in certain types of soil colloids appearing in the same series, and comparative values between the different series themselves.

1. Calcium colloids.

The calcium-saturated colloids evidently exert a stabilizing influence upon the iron content as in all three series there was either no iron liberated or the amount was so small as to be considered negligible. The amount obtained in the few cases was probably due to experimental error.

2. Magnesium colloids.

Magnesium-saturated colloids behaved as follows: Series I gave too many zero values to give any credence to the three isolated values found. Series II showed an almost constant amount of iron being liberated; Series III behaved similarly. Although the amounts for both Series II and III were quite small, Series II yielded six or eight times as much iron as did Series III. This is quite logical, as Series III had the free iron oxides removed prior to being subjected to hydrolytic action.
3. Hydrogen colloids.

In the case of hydrogen-saturated colloids the evidence pointed to the conclusion that Series I did not give up its iron in sufficient quantities to be considered as positive values. Series II, however, evidenced a steady increase in liberated iron as long as hydrolysis continued. Series III showed iron present throughout the hydrolysis but the amounts fluctuated. However, there were decidedly no zero values in either Series II or III. An explanation for all this behavior may be as follows: the humus and the protective coatings of the free oxides, in the case of Series I, prevented the iron from being affected by hydrolysis in such a way as to yield water-soluble iron; the removal of the organic matter in Series II gave the hydrolyzing medium an opportunity to liberate the iron from its complexes in increasing amounts as time continued; in Series III the removal of the free oxides of iron and silicon, as well as the organic matter, gave the hydrogen ions an opportunity to react with the iron complexes themselves. The liberation must have been due to the hydrogen ion as similar behavior was not found in the case of either magnesium or calcium.

4. Potassium colloids.

The potassium-saturated colloids gave, in general, the same reaction as the sodium-saturated ones insofar as the iron content was concerned. It was noted that in Series I the potassium colloid evidenced more iron, and in Series II and III perhaps a little less iron than for the sodium ones. At any rate, it was found that, as in the case of the sodium
5. Sodium colloids.

Definite statements can be made concerning the sodium-saturated soil colloids. In Series I and Series III there was some iron present, and in comparable amounts, although no definite trends were ascertained. In Series II, however, there was a relatively large amount of iron present in the hydrolyzate—at least five times as much as found in either of the other series. This may be accounted for easily enough. As shown before, the humus exerts a profound stabilizing influence which accounts for the lack of much iron from Series I. The free iron oxides have been removed from Series III and accounts for its low values as evidently the iron at the operating pH of these systems (between 6.39 and 7.53) cannot be liberated by the hydrogen ions, a fact relevant with the liberation found in the case of hydrogen-saturated colloids. Thus, the iron that did respond to hydrolysis was found in Series II, wherein the soil complexes were not protected by organic matter, thus permitting its iron complexes (and the oxides themselves no doubt) to be subjected to the hydrolyzing medium.

General Statements of Results

For the most part, sodium-saturated colloids contained more iron in their hydrolyzates than the other colloids. Potassium colloids closely followed the sodium ones in this respect. The apparent ability of the base-saturating cations
to yield soluble iron as a result of the hydrolytic process stood in the following decreasing order: sodium, potassium, hydrogen, and the calcium and magnesium about the same.

These findings are consistent with Robinson’s comparison (124) of the ease which characterizes the extraction of basic oxides and such oxides as aluminum oxide and ferric oxide from soil minerals. He found that aluminum and iron oxides were very stable to extraction, whereas the others were relatively easy to extract.

E. The Effect of Hydrolysis upon Liberation of Aluminum.

The aluminum is another constituent that appears in soil colloids in various forms. It is found as aluminates, as certain aluminum salts, as a part of complex crystalline aggregates occupying definite positions in the crystal-lattices, and as aluminum oxide. The fact that all of these forms of aluminum may or may not be hydrated lends further complexity to the questions that may be asked concerning the role it plays in soil colloids. Aluminum is affected by humus matter somewhat like iron is affected; however, owing to its amphoteric nature it may be affected by a great many conditions to which iron is quite resistant. Consequently, the liberation of aluminum may be effected in several ways; by hydration, by an excess hydrogen ions, by an excess hydroxyl ions, by changes in solubility induced through salt effects, or by hydrolysis processes. This study
was made under as nearly comparable conditions as feasible, and the aluminum liberated in the hydrolyzing medium, in which the various colloids were placed, determined. It is pointed out that the author does not claim the aluminum so liberated was due to hydrolysis phenomena alone but that it was liberated in the hydrolyzing medium as the final results of one or more subsequent reactions.

1. Calcium colloids.

Figure 16 shows that in Series I of the calcium-saturated colloids there was a sharp increase for 6 hours and then a rather sharp decrease the next 30 hours, after which the amount present was constant. Series II gave constant values throughout the hydrolysis. Series III steadily decreased for 12 hours and then became constant. Organic matter evidently did not stabilize the aluminum, as it did the iron, for more aluminum was found in the case of Series I than for either of the other series. After the initial 12 hours, Series II and III gave practically the same amounts of aluminum.

2. Magnesium colloids.

The magnesium-saturated colloids have amounts of aluminum as graphed in Figure 17. The aluminum content in Series I increased for 6 hours and then more or less became constant; Series II had the highest initial value of any of the three, showed a steady decrease for 24 hours, and then gave a constant amount; Series III, after a somewhat variable beginning, was practically constant all the way through the hydrolytic period and had the least aluminum of any three
series considered. After 12 hours Series II and III were quite alike in the amounts of aluminum present in their respective hydrolyzates.

3. Hydrogen colloids.

The behavior of hydrogen-saturated colloids was quite erratic in respect to the aluminum content found in the hydrolyzate. The curves do not represent the absolute values; rather, they represent the author's interpretation of their probable shapes considering the most logical values after allowing for inherent experimental errors. There seemed justification for the decrease and subsequent increase depicted for the Series I colloid. Likewise, it seemed more probable that the curve for Series III should show an increase until, at about 36 hours, it reached a constant value. On this basis, six of the nine points fall well along the curve drawn. Series II gave an actual line as drawn; it indicated a steady increase for 18 hours and then was constant. It can be said, regardless of the question of the correct curvatures for the three lines, that Series I definitely had the most aluminum liberated, Series II was next, and Series III had the least liberated. These results are shown in Figure 1d.

4. Potassium colloids.

The results for the liberation of aluminum by the potassium-saturated colloids are illustrated in Figure 19. Apparently, Series I had an increase of aluminum content yielded by hydrolysis as the length of time increased. Series
II displayed two successive decreases and finally increased to the value of that found for the 12 to 36 hour period. If two points (the 49 hour and the 72 hour) had been disregarded this curve would have shown a decrease for 12 hours and then a steady value. This has more probability than the one shown, but from the general experimental evidence the author did not feel justified in drawing the curve as mentioned. Series III showed a steady decrease for 24 hours and then became constant in amount.

5. Sodium colloids.

Figure 20 shows the interpretation for the liberated aluminum from sodium-saturated colloids. Series I gave fluctuating amounts but it seemed most likely that the real phenomena consisted of the aluminum first showing an increase and then a decrease below the initial value. The Series II hydrolyzate increased in aluminum slightly, and on the average contained more than did Series I and III. Series III had about the same initial value as Series II but showed a decrease for 48 hours, after which it was constant.

General Statements of Results

The sodium and potassium colloids just mentioned were somewhat comparable in several respects. The relative amounts of liberated aluminum in the different series were in the same order—Series II the most, Series I was next, and Series III the least. Series III gave almost identical curves for both sodium and potassium colloids.
Calcium-, magnesium- and hydrogen-saturated colloids all had more aluminum in the hydrolyzates from Series I samples. After the first 12 hours, Series II and III of the calcium- and magnesium-saturated colloids were about the same value.

The most predictable values were obtained for Series III, with Series II, for the most part, likewise giving fairly consistent results.

It was found that the Series III colloids, on an average, gave the least amount of aluminum of all the colloid samples studied. It may be said, too, that the natural-state colloids (Series I) liberated the most aluminum of the average. These findings do not agree with the work reported by Mattson and his co-workers (98-105) in which they reported the suppression of the solubility of aluminum by humus. However, Gordon's theory (51) concerning leaching effects, and also the views of Gedroiz (43), correlates well with the results of this dissertation. Fieger and Hammond's work (41) also indicated that aluminum was moved through a soil profile as a result of leaching effect—a statement in keeping with this work.

However, it should be pointed out that no definite statement is justified, from the results of this study, as to which exchange-cation exerts the most profound influence upon the aluminum content of soil colloids.
General Correlations Between this Study and Modern Theories of Soil Genesis

The modern conception of soil development has stressed the importance of the kind of cation which is predominantly present adsorbed upon the colloidal complex. It has been assumed that variations in the type of cation present determined the type of soil developed. On such a basis, it was considered that a predominance of Ca-ion caused the development of a chernozem or related soil, Na-ion the development finally of a solodi, while H-ion was the predominating ion causing podsol formation. Recent work of Rost at Minnesota and Ellis at Manitoba has suggested that Mg-ion may be instrumental in solodi formation, acting, according to their data and interpretation, similarly to Na-ions. This modern concept further assumes that calcium-saturated soils are relatively quite stable, the sodium- and hydrogen-saturated soils quite unstable, with magnesium-saturated soils somewhat less stable than the calcium soils. It should be further noted that the theory considers the changes produced during soil development as occurring mainly in the finer fractions, chiefly the colloidal complex, and that the soil-forming processes, particularly hydrolysis, cause a breakdown of the complexes with the formation of water-soluble, water-dispersed and water-insoluble products— the movement or precipitation of these products causing or inducing the final characteristics of the mature soil.
The data reported in this dissertation in general substantiates this theory. However, it should be noted that magnesium colloids are relatively quite stable and produce less soluble iron and silica than sodium colloids, indicating that the formation of a solodi by magnesium ions would be a much slower process than with sodium ions, or that the soils investigated by Rost and Ellis had magnesium replacing sodium after solodi development had taken place.

Recent work has indicated that podsol development in nature takes place quite rapidly, a typical black earth prairie changing within a relatively short period of time to podsolic in character, which may be ascertained by a study of the characteristics of the profile.

The hydrogen colloids studied and the results reported in this dissertation seem to indicate a rather high degree of stability. However, if stability is considered from the point of view of liberated silica then the hydrogen colloids, in comparison with the others studied, were by no means the most stable. The fairly large amount of water-soluble silica from hydrolysis of the hydrogen colloids indicate that during podsol development in nature, some reaction proceeds which causes deposition of some of the soluble silica as silicon dioxide which results in the development of the A₂-horizon. This shows that hydrolysis is not the only factor of importance influencing podsol development. The presence of carbon dioxide and of rapidly decaying organic matter, particularly leaves and needles of trees, may be mentioned.
as probably important factors.

A general summary may be stated:

The calcium colloids in general showed the greatest stability, with magnesium and hydrogen somewhat less stable, while the potassium and sodium colloids were the least stable. This order of stability is in agreement with the findings of other workers, and fits quite well with the modern concept of soil development. The theory of solodi development through the influence of sodium ions agrees quite well with the data presented herein, and the rapid changes induced by sodium as observed under field conditions is borne out. This also confirms the findings of Fieger and Sturgis, who reported rapid solution effects due to flooding with sodium-containing water.
CONCLUSIONS

As a result of this study of the effects of hydrolysis upon soil colloids, the following conclusions may be given.

A. The effect of hydrolysis upon the pH of soil colloids.

The different pretreatments each series underwent prior to base-saturation had marked effects upon their respective pH values. The effect of removing organic matter (Series II) was usually to lower the pH; in all cases except the hydrogen-saturated colloid the effect of removing both organic matter and the free oxides (Series III) was to materially lower the pH. In the case of the hydrogen colloid the effect was exactly opposite. The natural-state colloid (Series I) in all cases showed more erratic results, the removal of organic matter (Series II) tended to give smoother curves and less abrupt fluctuations, and the removal of both organic matter and the free oxides (Series III) resulted in very smooth curves which were for the most part straight lines.

The hydrogen colloids had the lowest pH of any studied; sodium colloids had the highest pH, closely followed by the potassium ones; magnesium and calcium colloids gave pH values in between these, with the magnesium somewhat higher than the calcium ones.

It was found that the general trends for pH were almost
identical for calcium and magnesium. In each case the Series I colloid had an initial increase and then a decrease—but did not decrease to the original value—and then became almost constant. It was found that the relative values for each series in these two were comparable. In both the calcium and the magnesium colloids, Series I had the highest pH, while Series II and Series III had the lowest pH and considerably less than the other series. In general, these two types of colloids—calcium and magnesium—were very comparable in the manner in which their pH values were affected under these conditions.

There were some similarities between the sodium- and potassium-saturated colloids. Series I was not very comparable with the others, but Series II and Series III were very similar. Series II and III had almost identical curves and had about the same initial and final values.

The hydrogen-saturated colloid did not show marked similarity to the other four colloids.

B. The effect of hydrolysis upon liberation of the base-saturation cation.

As a whole, the hydrogen-saturated colloids were affected the least by hydrolysis insofar as liberation of the base-saturation cation; the calcium-saturated ones were next to the hydrogen colloids in this respect. Magnesium colloid occupied a middle position, and the sodium- and potassium-
saturated colloids were the most affected in this respect. Again, there was a similarity between sodium- and potassium-saturated colloids as the general trends obtained in all three series were quite alike both as to the respective rate of liberation and as to absolute values. The magnesium colloid was between the calcium and hydrogen pair, and the sodium and potassium pair previously mentioned.

In all cases except for the hydrogen-saturated colloids, those with only the organic matter removed (Series II) gave the largest amounts of saturation-cation in the hydrolyzate, and even in the case of the hydrogen colloid this one was only slightly exceeded by Series III.

In all but the magnesium-saturated colloids the effects were very similar in each case in that Series I and Series III gave values not far apart. Series III gave the most consistent values, whether the particular case gave constant values or a change in values as hydrolysis proceeded—the calcium, magnesium and hydrogen colloids gave constant values and the sodium and potassium gave a steady increase from the beginning and then became constant.

C. The effect of hydrolysis upon liberation of silica.

The curves for the calcium-saturated colloids and for the magnesium-saturated colloids were almost identical; also, their absolute values were almost the same. The potassium- and sodium-saturated colloids also gave curves very similar
to those for calcium and magnesium colloids. The sodium and potassium colloids closely resembled each other, also. In a general way, the curves for the hydrogen colloids were similar to the others. There was not a great difference in the initial amounts of all the fifteen colloidal samples considered.

In all cases the Series III colloids responded the most to hydrolysis—all five colloidal samples showing an increase in liberated silica the first 24 to 48 hours and then being practically constant. The Series II colloids responded somewhat less. In all cases, except the hydrogen-saturated colloid, the amount of silica liberated by the Series II colloids were quite alike. They displayed a very slight increase at the beginning of the hydrolytic process and then became constant. The shape of the curve obtained even in the case of the hydrogen colloid was quite similar to the other four; however, its absolute value was somewhat higher. The Series I colloids were affected the least by the hydrolysis process. In all cases the natural-state colloid did not show an increase of silica in the hydrolyzate with increase in time of hydrolysis, except for a slight change in the case of the hydrogen colloid. Not only did none of these samples show an increase in silica as hydrolysis proceeded, but there was very little difference in the initial amounts liberated in any of the five differently-saturated colloids—calcium, magnesium, hydrogen, potassium and sodium.

It may be pointed out that Series I and II closely
resembled one another in their response to hydrolytic action, but the Series III colloids yielded considerably more silica than either Series I or II.

D. The effect of hydrolysis upon liberation of iron.

For the most part, sodium-saturated colloids contained more iron in their hydrolyzates than the other colloids. Potassium colloids closely followed the sodium ones in this respect. The apparent ability of the base-saturating cations to yield soluble iron as a result of the hydrolytic process stood in the following decreasing order: sodium, potassium, hydrogen, and the calcium and magnesium about the same.

E. The effect of hydrolysis upon liberation of aluminum.

The sodium and potassium colloids were somewhat comparable in several respects. The relative amounts of liberated aluminum in the different series were in the same order—Series II the most, Series I was next, and Series III the least. Series III gave almost identical curves for both sodium and potassium colloids.

Calcium-, magnesium- and hydrogen-saturated colloids all had more aluminum in the hydrolyzates from Series I samples. After the first 12 hours, Series II and III of the calcium- and magnesium-saturated colloids were about the
same value.

The most predictable values were obtained for Series III, with Series II, for the most part, likewise giving fairly consistent results.

It was found that the Series III colloids, on an average, gave the least amount of aluminum of all the colloid samples studied. It may be said, too, that the natural-state colloids (Series I) liberated the most aluminum on the average.

It should be pointed out that no definite statement is justified, from the results of this study, as to which exchange-cation exerts the most profound influence upon the aluminum content of soil colloids.

F. General Statements concerning the effects of hydrolysis.

It was found for all the colloids studied, with the exception of the hydrogen-ion-saturated colloids, that the pH was materially lowered by removal of organic matter and the free oxides. The hydrogen-ion-saturated colloids showed exactly opposite this effect; the removal of the organic matter and free oxides materially raised the pH values, i.e., decreased the acidity.

Of the three constituents—silica, iron and aluminum—determined in the hydrolyzates from all fifteen colloidal samples studied, respective hydrolytic liberation was found to be: the iron content was the least affected, the aluminum content was next least affected, and the silica was affected the most.
## TABLE I

CALCIUM SATURATED COLLOIDS

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<th>Time in Hours</th>
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<th>Milligrams in Hydrolyzate from 100 grams Colloid</th>
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Milligrams of Silica, Iron, and Aluminum in Hydrolyzate.
### TABLE II

**MAGNESIUM SATURATED COLLOIDS**

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<th>Time (Hours)</th>
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### Table IV

**POTASSIUM SATURATED COLLOIDS**

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>pH</th>
<th>Milliequiv. Potassium in Hydrolyzate</th>
<th>Milligrams in Hydrolyzate from 100 grams Colloid</th>
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<tbody>
<tr>
<td><strong>Series I. Natural-state Colloid</strong></td>
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<tr>
<td>0</td>
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<tr>
<td>Time (Hours)</td>
<td>pH</td>
<td>Milliequiv.</td>
<td>Milligrams in Hydrolyzate from 100 grams Colloid</td>
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<td>--------------------------------------------------</td>
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<td>Sodium in Hydrolyzate from 100 grams Colloid</td>
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</table>
Figure 1 Effect of hydrolysis upon the pH of Calcium-saturated soil colloids.
Figure 2. Effect of hydrolysis upon the pH of magnesium-saturated soil colloids.
Figure 5. Effect of hydrolysis upon the pH of hydrogen-saturated soil colloids.
Figure 5. Effect of hydrolysis upon the pH of sodium-saturated soil colloids.
Figure 6. Hydrolytic liberation of calcium from calcium-saturated soil colloids.
Figure 7. Hydrolytic liberation of magnesium from magnesium-saturated soil colloids.
Figure 8. Hydrolytic liberation of hydrogen-ion from hydrogen-saturated soil colloids.
The graph illustrates the liberation of potassium from potassium-saturated soil colloids. The x-axis represents time in hours, ranging from 0 to 96. The y-axis shows the liberation of potassium. Three different types of colloids are compared:

- Natural-state Colloid
- Colloid free of Organic Matter
- Colloid with Organic Matter and Free Oxides Removed

The graph shows that the liberation of potassium varies with different conditions, with the natural-state colloid showing the highest liberation, followed by the colloid with organic matter and free oxides removed, and the colloid free of organic matter showing the least liberation.
Figure 3. Alkaline liberation of sodium from sodium-saturated soil colloids.
Figure 11. Hydrolytic liberation of silica from calcium-saturated soil colloids.
The graph illustrates the tempo liberation of silica from magnesium-saturated soil colloids.

- **Natural-state Colloid**
- **Colloid free of Organic Matter**
- **Colloid with Organic Matter and Free Oxides Removed**

*Time in Hours: 0, 12, 24, 36, 48, 72, 96*
liberation of silicon from aggregation-ion-sorbed soil colloids.
Figure 14. Hydrolytic liberation of silica from potassium-saturated soil colloids.
Figure 15. Hydrolytic liberation of silica from sodium-saturated soil colloids.
The graph illustrates the analytic liberation of aluminum from calcium-saturated soil colloids over time. The x-axis represents time in hours, ranging from 0 to 96, while the y-axis shows the milligrams of aluminum in hydrolyzate from 100 grams colloid, ranging from 0.0 to 6.0.

The graph includes three distinct lines, each corresponding to a different type of colloid:
- Natural-state Colloid
- Colloid free of Organic Matter
- Colloid with Organic Matter and Free Oxides Removed

The data points and curves indicate varying rates of aluminum liberation with time, reflecting the differences in the colloidal characteristics and their organic and inorganic content.
Figure 17. Hydrolytic liberation of aluminum from magnesium-saturated soil colloids.
Catalytic liberation of aluminum from hydrogen-ion-saturated soil colloids.
The figure shows the hydrolytic liberation of aluminum from sodium-saturated soil colloids over time.

- **Natural-state colloids**
- **Colloid free of organic matter**
- **With organic matter**

The graph plots the milligrams of aluminum in hydrolyzate from 100 grams of colloid against time in hours. The data points and curves indicate the release of aluminum over time, with different lines representing colloids with and without organic matter.

**Figure 30.** Hydrolytic liberation of aluminum from sodium-saturated soil colloids.
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Jack Ezelle Simpson was born in Denton County, Texas, April 8, 1910. He attended Denton public schools, and was graduated from Denton Senior High School in 1927. He attended North Texas State Teachers College in 1927-8 and in 1928-9, was out of school for the next two years while working for a construction company, and re-enrolled at the same college in September, 1931. In August, 1933, he received a bachelor of science degree at North Texas State Teachers College with a major in chemistry and minors in mathematics and physics. The last twelve months he was at this college he served as under-graduate assistant in the Department of Chemistry.

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In 1934-35 he was principal of a high school in Texas. The following year he accepted a position as a state chemist at the Texas Agricultural Experiment Station located at the Agricultural and Mechanical College of Texas, College Station. He worked as a state chemist from September, 1935, to September, 1936, and resigned this position to attend Louisiana State University to continue work toward a doctor
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EXAMINATION AND THESIS REPORT

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Major Field:  Chemistry

Title of Thesis:  Studies of Hydrolysis Effects upon Soil Colloids

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

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July 19, 1939