

ABSTRACT OF THESIS

by

Charles O. Scott

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ABSTRACT

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Although investigations of many kinds have been made in the fields of soil chemistry and soil physics, there still remain countless problems to be solved. Each soil, in itself, presents a whole series of investigations. The results of the investigations from any particular soil do not necessarily correlate with or parallel the results of the investigations of a like nature made on another soil.

The soil from certain sections in the Grand Junction, Colorado area has presented problems in management and reclamation which at the present time have not been solved completely by either laboratory or field studies. Consequently it has been surmised that the comparison of some fundamental properties of a sample of soil from the Grand Junction area with a productive soil from another area would yield some useful data. The comparison of both of the soils with samples of identified clay should give some enlightenment as to physical and chemical properties.

The problem

The problem of this thesis is to determine the relationship of ionic exchange capacity to specific surface, particle size, and type of clay minerals present in

certain soils and clays.

Problem analysis.---A solution of the problem depends first upon the measurement of the following variables, and then the determination of the effect of these variables on ionic exchange capacity:

1. Particle size fractions in the soils and clays.
2. Total ionic exchange capacity and distribution of exchange capacity in fractions of soils and clays.
3. Relative specific surface of the colloidal fraction of the soils and clays.
4. Clay minerals in the soils.

Delimitation.---This study was limited to two soils of considerable variance in properties and two identified clays. These soils and clays were selected as follows:

Materials

One soil sample was taken from the Agronomy farm at Fort Collins. This is a productive soil of the Fort Collins loam series. The second soil sample was collected in the Grand Junction area in 1946 as a part of the soil survey of that area and was classified as a saline-alkali soil. The immediate area was barren ground, which was not cultivated. The texture was described as silty clay loam to heavy silt loam surface with a lighter texture below 20 inches. The clay samples consisted of bentonite from

Wyoming, kaolinite from the J. T. Baker Chemical Co., and a limited supply of illite.

Methods

The particle size fractions were determined essentially by the standard pipette method of Olmstead et al. A modification of the method was introduced wherein a 50 ml., Lowy automatic pipette was used to withdraw the samples from the sedimentation cylinder. This procedure gave samples which were of sufficient size to make determinations of ionic exchange capacity directly. Each of the soil and clay samples in triplicate were subjected to the mechanical analysis after being washed with distilled water while a second set of triplicate samples were subjected to acid and peroxide treatment before dispersion for the mechanical analysis.

The fractions obtained from the mechanical analysis were employed directly in the determination of ionic exchange capacity. The method developed for this determination was essentially a semi-micro adaptation of the ammonium acetate method. The total ionic exchange capacity of the natural unfractionated soils and clays was obtained using separate samples and following the procedure as used for each individual fraction.

The procedure followed in determining the relative specific surface of the colloidal fraction of soils and clays was taken directly from a research report from

the laboratories of the U. S. Department of Agriculture, Beltsville, Maryland. The less than 2 micron fraction of the soil or clay was separated by sedimentation and leached with dilute hydrochloric acid to make it essentially a H-clay. After the clays were dried over P_2O_5 they were saturated with ethylene glycol at the rate of one gram of glycol to one gram of clay. One gram samples of clay plus one gram of ethylene glycol were placed in vacuum desiccators containing anhydrous $CaCl_2$. The samples were weighed at 16 hours and 24 hours after being under a vacuum of less than 0.1 millimeters of mercury. The same procedure was applied to natural unfractionated soils, silt plus clay fractions, and to samples heated to 600 degrees centigrade. Heating destroys the crystal lattice of the montmorillonite clays and thus prevents swelling or internal adsorption of the ethylene glycol.

Kelley's dehydration method for the identification of clay minerals in the soils was followed. The colloidal portion of the soil was heated at progressively higher temperatures and the weight obtained after each temperature change. The loss in weight of the colloidal materials was established over a range of 20 to 800 degrees centigrade. The characteristic curves of the soil colloids were then compared with those of identified clays.

Results

The percentage of sand, silt, and clay in each of the samples is compared with the percentage of the total

ionic exchange capacity contributed by each of these fractions in Figure 1. Values for the less than 2 micron clay for ionic exchange capacity and retention of ethylene glycol are presented in Figure 2. The dehydration curves for the colloidal fractions are shown in Figures 3 and 4, and another interpretation of these curves is presented in Figures 7 and 8. In all the figures the Grand Junction soil is referred to as soil 57-A.

Discussion

In establishing the identity of the clay minerals of the soils the geologic origin of the Grand Junction soil, 57-A, gives definite support to the clay mineral as being illite, however neither of the other two recognized groups of clay minerals, montmorillonite and kaolinite could be excluded. For the Fort Collins soil the geologic studies might indicate a mixture of montmorillonitic and illitic materials.

In a review of clay mineral concepts Grim indicates that kaolinite is seldom found in sizes smaller than 0.2 microns in diameter. He states that montmorillonitic materials are commonly found in large amounts in sizes of less than 0.2 microns in diameter and that some illitic materials breakdown to this size group while others do not. Both the Fort Collins and Grand Junction soils contain significant amounts of material falling in the less than 0.2 micron diameter group.

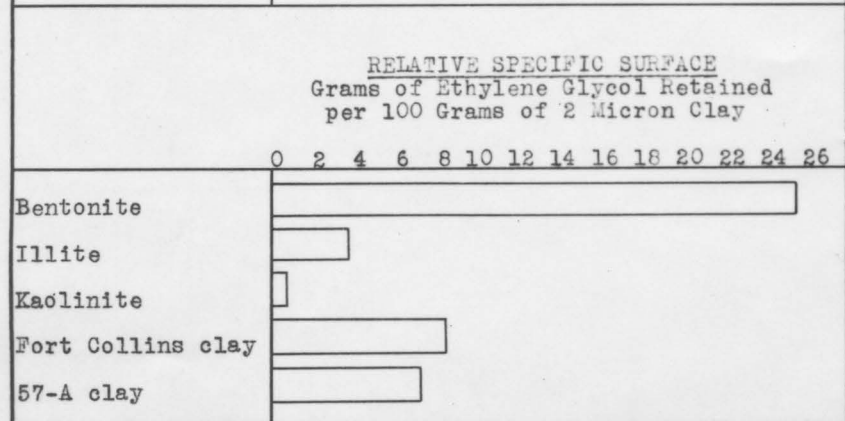
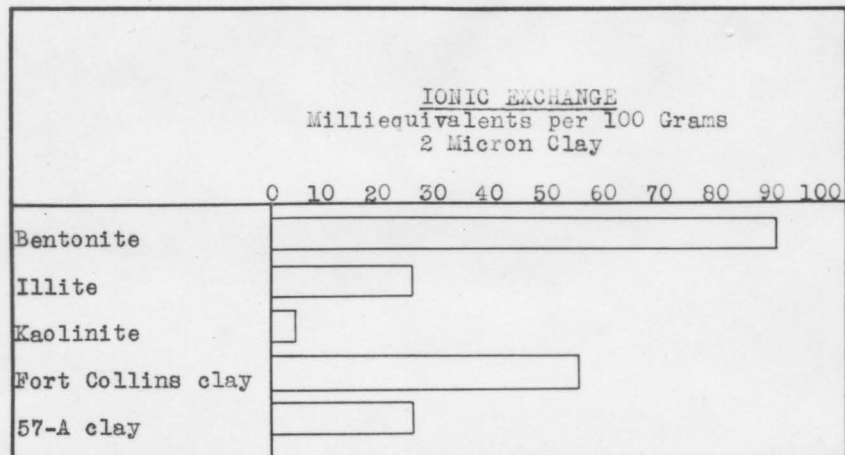


Fig. 2.--Ionic exchange in relation to relative specific surface.

Values for relative specific surface after 24 hours under vacuum are used.

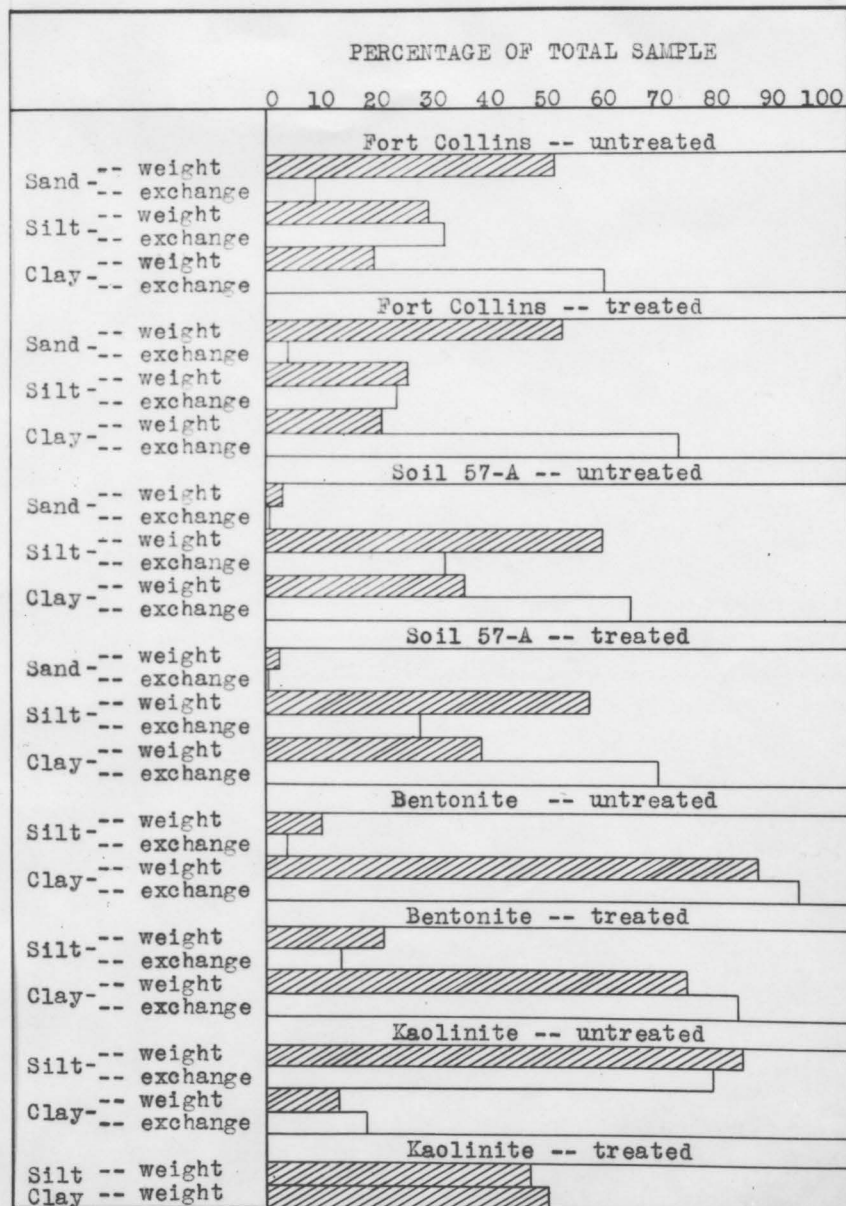


Fig. 1.--Ionic exchange in relation to particle size.

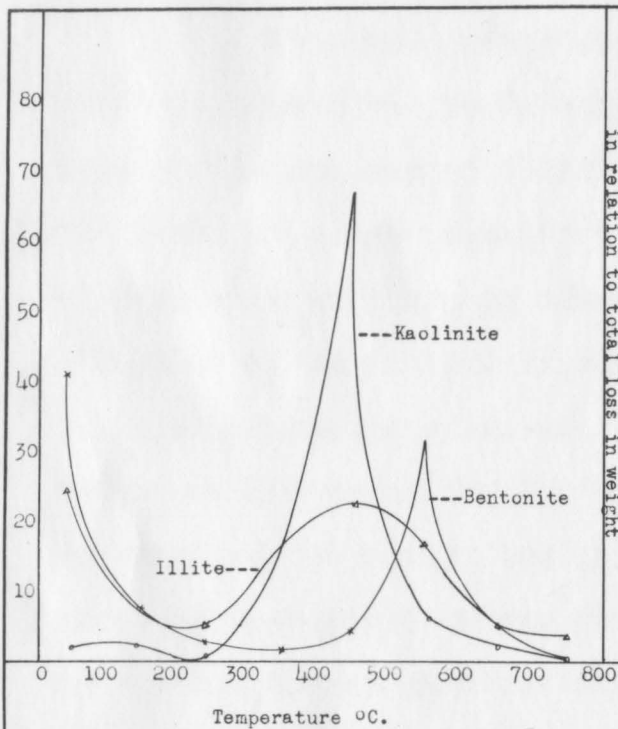


Fig. 7.--Rate of water loss from dehydration of Bentonite, Illite, and Kaolinite.

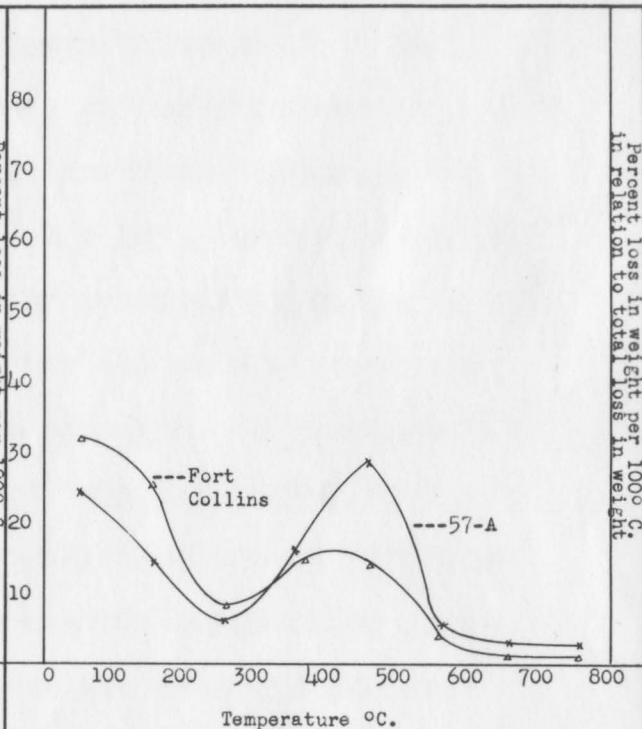


Fig. 8.--Rate of water loss from dehydration of Fort Collins and 57-A colloids.

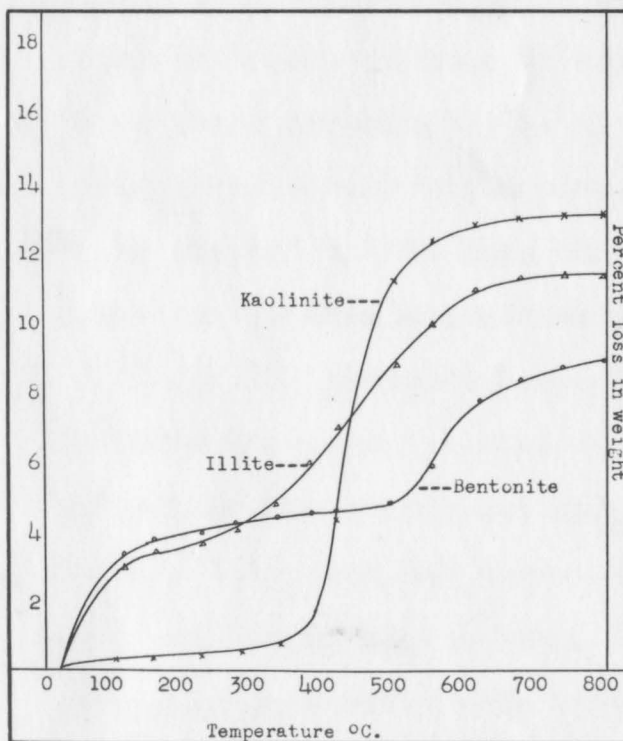


Fig. 3.--Dehydration of clay colloids; Bentonite, Illite, and Kaolinite.

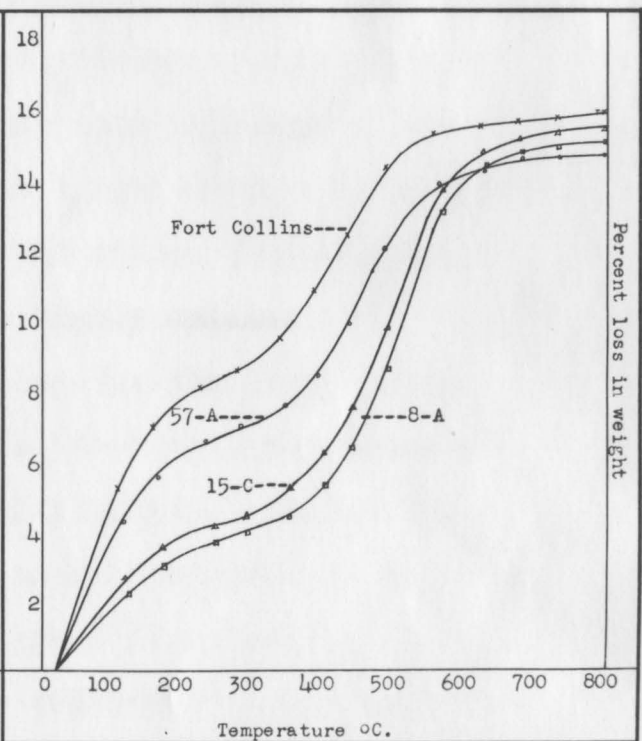


Fig. 4.--Dehydration of soil colloids; Fort Collins, 57-A, 15-C, and 8-A.

The actual ionic exchange capacities of the soil colloids give strong support of the presence of appreciable amounts of illite in the Grand Junction soil. The ionic exchange capacity of this soil for the fraction of 2 microns and less in diameter practically coincides with that of the illite sample for the same size group. The ionic exchange value of approximately 40 milliequivalents per 100 grams for the less than 0.2 micron diameter material of the Grand Junction clay is close to the upper limit of recognized values for illitic material as given by several investigators. The values of ionic exchange for known illitic materials fall between the higher values for montmorillonite and the lower values for kaolinite. However, if the value for the Grand Junction soil were obtained from a mixture of montmorillonite and kaolinite there would necessarily be a near equal mixture of the two. This in turn would cause a large amount of kaolinite to be present in the less than 0.2 micron fraction which according to Grim and others is highly unlikely.

The ionic exchange value for the Fort Collins 2 micron and less material falls about half way between the values for illite and montmorillonite. The value for the less than 0.2 micron diameter material is close to 70 milliequivalents per 100 grams of material. Kelley indicates that while pure montmorillonite materials probably range from 90 to 110 milliequivalents per 100 grams

for their ionic exchange values, soils with a high percentage of montmorillonite in the clay fraction may not have an ionic exchange value of more than 75 milliequivalents per 100 grams.

The studies of retention of ethylene glycol indicate that the Fort Collins clay falls above the limits for known illitic material, but not high enough to come into the range of montmorillonitic material alone. This would indicate the presence of a mixture of those minerals in the Fort Collins clay. The Grand Junction clay falls just within the upper limit of known illitic material. This would suggest the presence of illite and possibly a small amount of montmorillonite. Characteristics of kaolinite do not appear in either of the soil colloids. Conclusions drawn from the values for retention of ethylene glycol after the samples were heated to destroy the expanding crystal lattice are in agreement with the conclusions from the values for the unheated samples.

Evidence from the thermal curves appears to exclude kaolinite and probably favors a mixture of montmorillonite and illite for the Fort Collins soil colloid. A comparison of the curves as interpreted by Kelley and others indicates that the total loss in weight is not significant, but the rate of loss at a particular temperature indicated by breaks or long linear portions is of chief value in interpreting the curves.

The shape of a calculated curve of 50 per cent illite and 50 per cent bentonite strongly resembles the curve of the lower horizon of the Fort Collins clay. The resemblance of the Grand Junction curve to that of a 75 per cent illite and 25 per cent bentonite mixture is substantiated by a breakdown of the curve into percentages over specific temperature ranges. Kaolinite appears to be excluded by a comparison of the curves. The kaolinite gives a distinctive breakdown which does not appear in any of the other samples.

Tabulated evidence in establishing the identity of the clay minerals in the Fort Collins soil show that:

1. Particle size distribution favors montmorillonite and possibly illite.

2. Ionic exchange capacity for the less than 2 micron diameter material falls between illite and montmorillonite values. Ionic exchange values for the less than 0.2 micron diameter material strongly favor the presence of montmorillonite. The same evidence would make the presence of kaolinite in appreciable amounts impossible.

3. Retention of ethylene glycol by the 2 micron and less material of both the heated and unheated samples indicate a mixture of illite and montmorillonite with the values tending to fall closer to the illite grouping.

4. Dehydration studies favor the presence of a near equal mixture of illitic and montmorillonitic

material.

Evidence in establishing the identity of the clay minerals in the Grand Junction soil show that:

1. Particle size distribution favors montmorillonite and possibly illite.

2. Ionic exchange capacity for the less than 2 micron diameter material coincides with that of the illite. The value for the less than 0.2 micron diameter fraction is near the upper limit for illite. This evidence would practically eliminate the presence of kaolinite since kaolinite would need to be present in large quantities if the ionic exchange value is due to a mixture of montmorillonite and kaolinite rather than illite. Kaolinite does not occur in appreciable amounts in this size group.

3. Retention of ethylene glycol by both the heated and unheated samples compares favorably with the upper limits for illite as established by Grim.

4. Dehydration studies compare favorably with values of chiefly illitic material with montmorillonite present in a smaller amount.

Perhaps the most profound implication of the entire study is a realization of the possibilities of the method offered for continued and allied studies, and the need for such studies.

The procedures as used in this investigation

could be applied to good advantage, almost without change, to known samples of illite, and other materials of the kaolinite and montmorillonite groups. Data for definite mixtures of known clays and for soil colloids of identified clays would be significant for use in comparing with unknown samples. It seems very probable that a classification of soils could thus be established and relationships set up so that a soil colloid might be quite readily classified.

Especially is this method promising in obtaining ionic exchange relationships relative to specific surface by the ethylene glycol method. The relationships should be investigated for clay fractions and sub-fractions as well as larger particles. The pipette method of obtaining samples offers a means of studying the relationships within a soil far better than obtaining fractions by centrifugation and drawing generalities which may be extremely biased.

The importance of the silt fraction in the total soil is demonstrated. In nearly all of the literature the activity of the soil is placed directly upon the clay or colloidal portion. It is readily acknowledged that the activity of the clay is high in comparison with the activity of the silt or sand. However, it is shown that even in soils with relatively high clay fractions the exchange capacity contributed by the silt and sand is seldom less

than one-fourth of the total and in other soils may be at least one-half.

It seems logical to propose then, that the silt fraction should be the object of as much investigation as has been placed upon the clay fraction. To a certain extent the silt fraction should be more easily investigated owing to the visibility of the particles by ordinary means. Although complete separation of silt fractions is tedious, a modification of the sedimentation and pipette method might afford a means of obtaining fractions of soil large enough to actually test by plant growth the significance of the various fractions in supplying nutrient elements. A correlation of this with ionic exchange capacities and relative specific surface would provide a fascinating possibility for further research.

Numerous other possibilities are evident for continued research with more than reasonable expectations of obtaining significant results.

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T H E S I S

IONIC EXCHANGE CAPACITY
AS RELATED TO
RELATIVE SPECIFIC SURFACE, PARTICLE SIZE, AND TYPES OF
CLAY MINERALS PRESENT IN CERTAIN SOILS AND CLAYS

Submitted by
Charles O. Scott

In partial fulfillment of the requirements
for the Degree of Master of Science
Colorado
Agricultural and Mechanical College
Fort Collins, Colorado

March, 1949

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR
SUPERVISION BY CHARLES O. SCOTT
ENTITLED IONIC EXCHANGE CAPACITY AS RELATED TO RELATIVE
SPECIFIC SURFACE, PARTICLE SIZE, AND TYPES OF
CLAY MINERALS PRESENT IN CERTAIN SOILS AND CLAYS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE.

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Chapter I

INTRODUCTION

Although investigations of many kinds have been made in the fields of soil chemistry and soil physics, there still remain countless problems to be solved. Each soil, in itself, presents a whole series of investigations. The results of the investigations from any particular soil do not necessarily correlate with or parallel the results of the investigations of a like nature made on another soil.

If a soil could be placed in a definite category, such as a pure salt in a chemical sense, there would be few problems which could not be investigated almost to completeness. However, the soil is a heterogeneous mass of numerous organic and inorganic compounds, which contribute to the basic properties and behavior of a soil. In general it is accepted that the very fine (colloidal) fraction of these compounds is the most active, chemically and physically. The amount of the organic colloidal portion in most soils is small compared with the inorganic fraction and is a complex substance fairly resistant to decay. The inorganic colloidal fraction has

been found to be largely made-up of the clay minerals plus a certain amount of primary minerals and less weathered secondary minerals.

The clay minerals, in general, have been classified in to three rather broad groups, kaolinite, montmorillonite, and illite or mica-like minerals. Each group has specific characteristics which in turn lend certain properties to a soil in which they may be found.

The colloidal fraction actually may be a very small part of the total soil and therefore will not influence the soil activity as much as it might if present in larger than usual amounts. For this reason the remainder of the soil may be of almost equal interest and importance, especially in a study of the physical nature of the soil.

The soil from certain sections in the Grand Junction, Colorado, area has presented problems in reclamation which at the present time have not been solved completely by either laboratory or field studies. Consequently it has been surmised that the comparison of some fundamental properties of a sample of soil from the Grand Junction area with a productive soil from another area would yield some useful data. The comparison of both of the soils with samples of identified clays should give some enlightenment as to physical and chemical properties.

The problem

The problem of this thesis is to determine the relationship of ionic exchange capacity to specific surface, particle size, and type of minerals present in certain soils and clays.

Problem analysis.--A solution of the problem depends first upon the measurement of the following variables, and then the determination of the effect of these variables on ionic exchange capacity:

1. Particle size fractions in the soils and clays.
2. Total ionic exchange capacity and distribution of exchange capacity in fractions of soils and clays.
3. Relative specific surface of the colloidal fraction of the soils and clays.
4. Clay minerals in the soils.

Delimitation.--This study is limited to two soils of considerable variance in properties and two identified clays. These soils and clays are described in more detail in chapter III.

Chapter II

REVIEW OF LITERATURE

This problem is concerned with certain physical and chemical relations of two soils having varied properties. Identified clays have been used to make a more complete and accurate comparison with the colloidal portion of the soils. A review of literature is especially pertinent to this problem since some of the relations of soils and clays established by other investigators may be directly comparable. The literature review is of importance, too, in the development of techniques and procedures used in the investigations.

Mechanical soil analysis

In nearly all mechanical soil analyses and separations the determinations are based on the fact that the smaller particles in water suspensions fall more slowly than larger ones. In the development of a satisfactory method discussion arose concerning the degree of dispersion. Hilgard (21) objected to the use of acids to disintegrate compound particles, particularly in calcareous soils. Bouyoucos (4) believed the sample should have less rigorous treatment than the international

practical method proposes.

Olmstead, Alexander, and Middleton (35) in 1930 examined the more important contributions and compiled a report of their findings. As a result of their study and applications they presented a method of mechanical soil analysis.

The method which they developed included these important points: In pretreatment the organic matter was removed with hydrogen peroxide, but the hydrochloric acid treatment, used in the international method, ordinarily was omitted. A method of removing organic matter in the presence of manganese dioxide by leaching with acetic acid was used for certain soils. Soluble matter was removed by washing and filtering with Pasteur-Chamberland suction filters. The sample was dried and weighed, and this weight was the basis of calculation of percentages of material in each size class when the results were for use in textural classification. In all operations up to dispersion the sample remained in an extra-tall form beaker. The sample was deflocculated by shaking in a dilute sodium oxalate solution. The clay and silt were separated from the sand by means of a 300-mesh sieve. The clay fractions were determined by sedimentation using the pipette method. An investigation of dispersion aids, incidental to this method, disclosed the fact that acid

treatment introduced undesirable solution losses and was not necessary for dispersion, even in calcareous soils, particularly if sodium oxalate was used as the dispersing agent.

A second review, of an entirely different nature, was presented by Keen (25) in 1931. His discussion included largely the theories upon which the methods were based and how they were applied.

Fry (15) in 1933 presented a method for making complete mechanical separations for use with petrographic study.

A more recent and detailed procedure for complete separations for petrographic study was presented by Truog et al., (45,46) in 1936.

Baver (3) in 1948 included recent developments, which were not extensive, and in general substantiated the more important methods mentioned above.

Ionic exchange relations

The power of the soil for exchanging cations with solutions was no doubt observed in the remote past when it was noted that liquid manures became decolorized and deodorized upon filtration through the soil. However, the phenomenon as such was not recognized until 1850 by Way (47) and independently about the the same time by Thompson (44).

Since that time numerous investigators have been interested in the processes involved in ionic exchange in soils and other materials until at the present time several concepts have been developed to account for the phenomenon. Critical reviews of the literature covering this subject were published by Melsted and Bray (33) in 1947 and by Kelley (26) in 1948.

In the preface to his monograph on ionic exchange phenomena Kelley stated

It is not necessary to review all of the numerous papers on cation exchange in this monograph. Only those of chief historic interest and those which reveal the evolutionary developments of the subject will be discussed. Literally hundreds of papers have been published, all but a few of which have been read by the author, and these are probably of little importance. Many of the published papers are of purely local interest and throw no light on general principles. At most, they have served merely to confirm the conclusions already drawn by others. The reader who is interested in a more comprehensive biographical review of the subject is referred to sections in Blanck's "Handbuch der Bodenlehre" Volume VIII by Gehring and Kappen (26:xi).

In view of the fact that such excellent and exhaustive reviews of the subject are readily available there will be no attempt to repeat the work, but rather mention will be made of only a limited number of experiments which treat specifically with the more narrow subject of ionic exchange in relation to particle size and specific surface.

Kelley and Jenny (30) in 1936 related crystal structure to base exchange and its bearing on base exchange in soils. Somewhat incidental to their investigations they included the base exchange capacities of certain materials in relation to particle size. Their data included the following comparisons of 100-mesh material with finely ground material of indefinite size.

Table 1.--BASE EXCHANGE AS RELATED TO PARTICLE SIZE_a

Material	Base Exchange in Milliequivalents/100g.	
	100 mesh	ground
Quartz	0	0
Talc	9.8	219.0
Kaolinite	8.0	100.5
Bentonite	126.0	238.0
Cecil soil colloid	17.0	151.0

_a Table from Kelley and Jenny (30:375)

Bray (6), in conducting investigations on some Illinois soils in 1937, fractionated into three size groups the colloid (less than 1 micron in diameter) extracted from various horizons of several soils from the Peorian loess region and studied their chemical differences. His data indicated that the exchange capacity of the finer fractions increased markedly with decreasing particle size. Particles smaller than 0.06 micron possessed exchange capacities from 30 to 325 per cent larger than 1.0 to 0.1 micron particles, depending upon the nature of the colloid.

Variations from 46 to 88 milliequivalents per 100 grams of 0.06 micron colloid were reported. By repeated fractionations and working of the colloid from the Hartburg silt loam profile (18 to 24 inches), the exchange capacity of the 1.0 to 0.1 micron colloid was reduced from 62 to 41 milliequivalents per 100 grams. This was attributed to the physical breaking down of the larger colloidal complexes which released the smaller and much more surface-active beidellitic material from a less active micaceous nucleus.

Bray assigned the regular increase in base exchange capacity with the decrease in particle size to a variation in the minerals which make up the colloids and accompany the size variations rather than to the decreased particle size itself.

Whitt and Bayer (49) in 1937 reported some relations of particle size to base exchange and hydration properties of Putnam clay. Their separations were made with the use of the super centrifuge. They reported that the property of swelling was not present in particles greater than 1 micron in diameter and the maximum toluene adsorption took place in the same particle size range. The wide break in exchange capacity was also reported to be very near this point.

Data presented by Whitt and Bayer for the Putnam clay are as follows:

Table 2.--PARTICLE SIZE OF PUTNAM CLAY AS RELATED TO
HYDRATION AND BASE EXCHANGE VALUES_b

Particle size in microns	Milliequivalents per 100 grams	Hydration in cc/gram		
		Water	Toluene	Swelling
20 -5	2.9	0.499	0.593	-0.094
5 -2	6.6	0.830	1.009	-0.179
2 -1	21.7	1.197	1.518	-0.321
1 -0.5	35.0	1.620	1.470	+0.150
0.5-0.2	52.5	1.876	1.272	+0.604
0.1-0.05	56.5	1.874	1.067	+0.807
<0.05	62.2	1.956	0.976	+0.980

_b Table from Whitt and Bayer (49:910)

In a study of the chemical composition of mechanical separates in the soil profile Joffe and Kunin (23) in 1942 indicated that, in agreement with Whitt and Bayer, it is possible for a coarse fraction to hold a finer fraction so tenaciously that ordinary dispersion methods are of little value. They divided the soil into one sand, two silt, and three clay groups by sedimentation and centrifugation and carried on a complete chemical analysis.

In a second study in 1943 by Joffe and Kunin (24) the same soil and separates as used in the chemical analysis were submitted to examinations for cation exchange properties with special reference to pedogenic implications. In sand fractions of different horizons of Montaldo silt loam the base exchange capacities varied

from 0.380 milliequivalents per gram in the C horizon to 0.056 milliequivalents per gram in the B₁ Horizon. No claim was made that the sand or silt fractions were entirely free from clay, but it was demonstrated that an extraordinarily large amount of clay must be present if the base exchange capacity was due to clay only. The silt fractions are reported to have base exchange values which were only slightly less than those of the clay. The base exchange value of the sand in the C horizon, 0.380 milliequivalents per gram was greater than that for the silt or clay fractions of that horizon. Only the less than 0.3 micron clay of the A₁ and A₂ horizons had larger values, 0.463 and 0.394 milliequivalents per gram respectively. It was suggested that the differences were directly related to the degree of weathering.

Joffe and Kunin suggested the following reasoning to account for the interference of organic matter.

The high (exchange) capacity in the fractions (of the soils) of the A horizon is due to the organo-mineral gels---and to the organic matter mixed with the clay mechanically. One would expect the mechanically mixed organic matter to be less rigidly held by the sand and silts. This means that in the final separation of the different fractions, the fine clay would have more organic matter than the silt or sand. In treating the fine clay fractions with hydrogen peroxide the residual organic matter adhering mechanically is attacked more readily than the organo-mineral gels. The latter are complex chemical entities, such as humates of bases of higher valence. For that reason it is not possible to free all the

organic matter from the fine fractions by ordinary means of hydrogen peroxide treatment (24:385).

Joffe and Kunin further reported that the increase in exchange capacity of kaolinite with decrease in particle size was not proportional to the calculated increase in surface, which was given as fivefold and thirtyfold respectively. Base exchange values given for kaolinite varied from 0.0218 milliequivalents per gram for 5 micron material to 0.0972 milliequivalents per gram for the less than 0.3 micron fraction of kaolinite.

In attempting to compare the base exchange capacity of bentonite with that of kaolinite, Joffe and Kunin dispersed the bentonite clay material and allowed it to stand several days for impurities, which might have been present in the form of large particles, to settle out. The suspended material was then arbitrarily divided into three size groups with the super centrifuge, and the base exchange capacities determined. The values ranged from 0.882 to 0.913 milliequivalents per gram, and were not consistent in variation with particle size. It was concluded that there was no increase in exchange with decrease in particle size with the bentonite material.

It is reported by Joffe and Kunin that according to Ardenne, Endell, and Hoffman (2) who examined clays with the aid of the electron microscope, the ratio of

thickness of a montmorillonite platelet to its length varied from 100-1 to 300-1, whereas in kaolinite the ratio was only about 5-1, or at most 25-1. They further reported that upon grinding, these surfaces in kaolinite were increased and the exchange capacity likewise increased, while in the montmorillonite the expansion along the C-axis simply gave the cations a chance to enter between the lattice layers and to exchange the cations present.

In the same report Joffe and Kunin indicated that on Colt's Neck loam fractions the sand and silt accounted for approximately 40 to 50 per cent of the exchange.

The fractionation and properties of clays from the surface soils of the Pearman and Maury series were studied by Seay and Weeks (43) in 1947. The soils were treated to remove readily soluble phosphorous, replaceable bases, and organic matter. Part of the Pearman soil was treated in addition to remove free iron and aluminum oxides. The soils were then saturated with sodium ions, dispersed in water at pH 8.0, and the sand and silt (greater than 2 microns) separated from the clay by gravity sedimentation. The clay was further separated by use of gravity sedimentation and the Sharples' super centrifuge into five fractions of various particle sizes.

The actual sizes of the clay fractions were

checked by means of the electron microscope and found to agree quite closely with calculated sizes. Chemical and physical properties of the separates were studied. It was found that base and anion exchange capacities increased directly with decrease in size of particles of the clay.

Limited studies with x-ray diffraction and the electron microscope indicated that the clays contained a mixture of 1:1 and 2:1 type of clay minerals with the 2:1 type in greater proportion where the particle size was smallest.

Measurement of specific surface

Until recently, methods for measurement of specific surface or relative specific surface have been much more widely applied to materials outside the field of soils than to soil materials.

Brunauer and Emmett (7,8,13) in 1937 and 1938 described a method for measuring the surface of iron synthetic ammonia catalysts whereby a point was determined on adsorption isotherms for nitrogen at -195.8 degrees Centigrade, and at -183 degrees Centigrade which corresponded to the completion of a monomolecular layer of adsorbed molecules. A multiplication of the number of molecules in such a layer by the average cross-sectional area of each molecule gave an estimation of the absolute

area of the catalyst, subject only to the uncertainties in values for molecular diameters and in the closeness of packing of the adsorbed molecules.

In 1938 Emmett, Brunauer, and Love (14), on the basis that van der Waals' adsorption depended but little on the chemical nature of the adsorbing substance, applied the method to soil colloids. Barnes and Cecil soil colloids were used for the investigations. Although they believed the data insufficient to warrant extended correlations with other known physical and chemical properties of these soil samples, they indicated that no insurmountable difficulties were inherent in the application of the method to soils and soil colloids.

They concluded that the similarity between the isotherms for soils and those for iron catalysts substantiated the possibility of the direct application of the method to soils. They further concluded the use of low temperature isotherms of such gases as nitrogen and argon involved no specific chemical adsorption between the gas and the soil, while this was not true of adsorption measurements using water vapor, and possibly was not true of those using ammonia or carbon dioxide.

Nelson and Hendricks (34) in 1943 reported results of investigations using essentially the method developed by Brunauer and Emmett. They found that for ad-

sorption of the gas the samples must be completely desiccated, and with the sample in this condition the gas could not penetrate to the internal surfaces of montmorillonitic materials. The specific surface in square meters per gram of material was given as follows: less than 0.3 micron kaolinite, 15.5; less than 0.3 micron illite 97.1; and montmorillonite 15.5.

From the investigations they concluded that:

1. Average particle sizes determined in this manner are in essential agreement with values obtained from electron micrographs.
2. Clay minerals upon heating lose their water of constitution without essential change in particle size.
3. Amounts of colloid in soils can be determined from gas sorption on the soils and a portion of the separated colloids. This method is of particular value when adequate dispersion for particle analysis by sedimentation cannot be attained.
4. Average particle sizes in colloids from surface horizons of five soils of widely different types are greater than those of the B and C horizons.

Hendricks (18) early in 1948 described in a preliminary report the use of ethylene glycol retention on clays and soil colloids as a method for obtaining relative specific surface.

Later in 1948 Dyal (12), in a complete report of

the ethylene glycol method, gave background, procedure, and results for the method. The procedure is given in detail in the chapter covering materials and methods so will not be repeated here. A portion from the introduction to Dyal's work should clarify the basis of the method. Since it appears only in mimeograph form it seems justifiable to quote and elaborate at some length.

Montmorillonite and endellite, the hydrated form of halloysite, are the only clay minerals which form definite solvates with polar molecules between the structural layers. Layer hydrates of montmorillonite contain one to possibly four layers of water molecules and conditions cannot necessarily be established for formation of a definite hydrate to the exclusion of others. Ethylene glycol, glycerol, and other polyhydroxylic aliphatic compounds have been shown by Bradley (5) and MacEwan (32) to form two layer solvates in the presence of excess solvent. These solvates are relatively stable under desiccation or exposure to moist air. Their stabilities and the fact that the separation of the layers is in the region of 17.0 angstrom units makes the solvates ideal for identification of montmorillonite by x-ray diffraction. It might be expected that a definite amount of a compound would be required for formation of the solvate and that direct estimation of this amount could serve as the basis for an analytical method.

Presence in clays and soils of mixed layer minerals having in part the swelling and base exchange properties of montmorillonite raise some question as to the type of analysis desired. These minerals cannot readily be identified by x-ray diffraction methods and their poorly defined character has limited complete mineralogical descriptions of finely divided fractions of soils. An analytical method is needed to measure the interlayer swelling irrespective of mineral type. One is proposed here depending upon direct gravimetric determination of ethylene glycol sorption of a sample.

Solvation of clay minerals takes place not only between structural layers where possible, but also upon external surfaces. Measurement of total solvation, therefore, can afford a measure of total surface in polar systems. If the internal surface alone is to be determined then some estimate must be made of external surface. ----In the end, however, greatest interest for soils work might be in the total surface for polar systems since this would give a measure of interaction with water. The base exchange capacities of clay minerals also appear to be approximately determined by the total surface in polar systems. (12:1-2)

For a basis of comparison Dyal used clay minerals of the montmorillonite, illite, and kaolin groups, and fractions having apparent diameters of less than two microns were separated from all samples by sedimentation. In the application of the method soil colloids separated in the same way as the clay minerals were used. The procedure for the standards and soils was the same and is given in detail in the following chapter.

Retention of ethylene glycol in grams per gram of clay after 24 hours evacuation, as reported by Dyal, assigned a value of 0.014 for two samples of kaolinite; Illite was reported to have a range from 0.036 to 0.074; while montmorillonite values were from 0.226 to 0.273. After heating the samples to 600 degrees centigrade the retention for kaolinite was 0.007 to 0.012; for illite 0.024 to 0.058; and for montmorillonite 0.006 to 0.027. Soil colloid samples were found to fall in nearly all of the above classes.

In his discussion of the method Dyal points out that

Base exchange of clays is a surface property and is due to lack of complete balance of charge within the lattice. This can be a result either of the termination of the lattice or of presence of ions having various charges in certain lattice positions. Apparently only side faces of kaolinite give rise to exchangeable cations while in the mica-like minerals of clays both side faces and the more extensive flat layer surfaces are important. Montmorillonite has both the external surface features of a mica-like clay mineral as well as external cations accessible by layer separation in polar solvents. For these reasons the base exchange capacities are in the order, (for decreasing values) montmorillonite, mica-like, and kaolins.

An approximate parallelism might be expected between the surface for retention of polar solvents and base exchange. This is due to the tendency of montmorillonites and mica-like clay minerals to have the same silicate surface for an exchangeable cation. The parallelism can only be approximately, however, for montmorillonite can vary in exchange capacity, as shown for instance when ferric ions are reduced in the lattice, and part of the surface of kaolin minerals is probably neutral. The degree of parallelism should be studied in detail. (12:10)

Thermal and related studies

Formerly it was believed that the so-called clay of soils was amorphous and that the exchangeable ions were held on the surface of the colloidal particles by a vaguely defined force called "adsorption". However, since about 1930 both of these concepts have been found to be not entirely sound. In fact, the evidence is conclusively in favor of assigning a crystal structure to soil clays with

definite bonds which hold exchangeable ions.

Methods for the estimation and identification of soil clays have been based upon x-ray diffraction, chemical analysis for characteristic constituents, cation exchange, dehydration, and differential thermal analysis. None of these has been found to be entirely adequate, but combined use of several methods is rather reliable even though time consuming. Although the purely chemical analysis probably outdates the others, none of them have developed entirely independent of the others. The literature obviously then cannot be separated into precise categories, but the thermal studies will be considered of prime importance at the moment with other methods incidental to them.

Hendricks and Fry (20) in 1930 as a result of microscopical examination and x-ray powder diffraction photographs of the finely divided materials separated from soils by suspension methods show that these fractions contain crystalline substances. Their studies indicated that a specific sample gives a characteristic powder diffraction pattern that can be identified as arising from one of the clay minerals, and by comparison with the powder diffraction patterns of known clay minerals, it was shown that montmorillonite-beidellite, Ordovician bentonite (or a mixture of montmorillonite and quartz),

and halloysite were the common mineral constituents of the soil colloids observed.

Further investigations indicated that fine fractions from a specific type of soil obtained from widely different localities gave the same type of diffraction pattern.

In 1931 Kelley, Dore, and Brown (27) also used x-ray analysis and chemical methods to study soil colloids. They concluded that from their data it was justifiable to say that the substances composing the colloidal material of the soils, that were investigated, was not amorphous, but chiefly crystalline.

They found that the replaceable bases occurred not only on the surface of colloidal particles but also on the interior of the crystals. Since the x-ray analysis indicated an orderly arrangement of the atoms within the particles, and since the exchange of bases was stoichiometric, they concluded that the base exchange substances were true chemical compounds. The replaceable bases, therefore, were not merely adsorbed on the surface of the particles, but rather, they believed, the bases were an integral part of the chemical constitution of the crystals.

Heating experiments were conducted by Kelley, Dore, and Brown using a muffle furnace controlled by a

pyrometer. The samples were held in the furnace at each temperature until constancy of weight was attained. At 350 degrees centigrade no effect was produced on the replaceable bases of the soil colloids and bentonites. Above this temperature there was a gradual falling off in the content of replaceable bases, until at a temperature of 750 degrees centigrade the base exchange power was practically destroyed.

Drosdoff (11) in 1935 subjected two different samples of bentonites, variously saturated, and a sample of finely powdered sericite, $(H,K)AlSiO_4$, to successively higher temperatures in a muffle furnace. The loss in water at the different temperatures was calculated in percentages of the weight of the sample after being heated at 100 degrees centigrade for 24 hours. In the case of the bentonites, there was a distinct maximum loss of water between 550 and 650 degrees centigrade. This temperature interval corresponded to that at which the base exchange material lost its base exchange properties, as shown by Kelley, Dore, and Brown.

Kelley, Jenny, and Brown (31) in 1936 made dehydration studies of several clay minerals and soil colloids. They concluded that soil colloids contain water of crystallization, or OH ions, as part of a crystal lattice structure. This was considered as an independent

proof of the crystalline nature of the colloidal particle. They found that unlike the minerals of known structure, the soil colloids lose their lattice water at lower temperatures. From their studies they concluded that at least two major classes of soil colloids appear to exist. The classes were those which resemble in some measure kaolinite and halloysite and those which appear to be related to (but not identical with) beidellite.

In 1939 Hendricks and Alexander (19) described a method of differential thermal analysis wherein both the differential and furnace temperatures were recorded photographically. The heating rate used was from 10 to 20 degrees centigrade per minute, and it was necessary to raise the sample to about 1000 degrees centigrade. Differential heating curves for kaolinite, montmorillonite, and hydrous mica were reproduced. They showed that below 200 degrees centigrade kaolinite lost adsorbed water endothermically, and there was some incidental change caused by differences in heat capacity, compaction etc., relative to the inert material.

According to Hendricks and Alexander the most characteristic feature of the kaolinite curve was the endothermic loss of water of composition between 550 and 600 degrees centigrade, and they stated that this can be used as a criterion for a kaolin material and as a basis for its semi-quantitative estimation.

In a like manner they assigned the most characteristic features of the montmorillonites and hydrous micas to their endothermic loss of water below 200 degrees centigrade and near 700 degrees centigrade. They indicated considerable variations for different samples at the lower temperature and danger of confusion with adsorbed water. They showed that the endothermic reaction of montmorillonite near 700 degrees centigrade was small compared with that of kaolin near 580 degrees centigrade and was not sufficiently different from that of hydrous mica to allow an unambiguous distinction between the two.

They indicated that thermal analysis for identification of clay minerals can be applied to the untreated soil, but it was desirable to remove the organic matter, since this burned exothermically over a wide region, sometimes obscuring kaolinite. They believed it was not absolutely necessary to separate the colloid, especially in heavy soils where it was a considerable fraction of the soil.

In a second publication in 1939 Alexander, Hendricks, and Nelson (1) reported the application of the method described above. Minerals present in the colloidal fraction of 15 soils from continental United States were identified and their amounts estimated by use of the chemical, thermal, and x-ray diffraction methods discussed in

detail in the preceding paper. They concluded that thermal analysis supplements the chemical information, in that it gives the best basis for determining the amount of kaolinite. They believed that the two methods gave a fairly satisfactory basis for estimating the component minerals of a soil colloid.

Kelley, Dore, Woodford, and Brown (29) in 1939 reported an extensive study of the colloidal constituents of several California soils. The dehydration curves appeared to be somewhat characteristic of each type of colloid, and they concluded the shape of the curve depended very largely on the kinds and relative proportions of the different clay minerals present. From the dehydration curves of the Yolo and Maxwell clays, they concluded a resemblance to those of the bentonitic clays, and the curves for the Sierra, Keefers, and certain Redding samples were shown to be similar to the curves for kaolinite and halloysite. A relatively good correlation was found between water loss at 100 degrees centigrade and 150 degrees centigrade, respectively, and base exchange capacity.

The optical properties showed that these colloids were preponderantly crystalline and the types of clay minerals determined by x-ray analysis confirmed the dehydration studies.

The San Joaquin and Hanford colloids were shown to be composed largely of the "x" clay mineral, similar to illite.

The types of clay minerals present in soil colloids were determined by comparing the x-ray diffraction patterns with those of known minerals. The determination was facilitated by x-raying the samples at widely varying moisture contents. From the dehydration curves of the different clay minerals it was shown that OH lattice constituents passed off as water vapor at temperatures which were characteristic for each class. The consequence was their x-ray diffraction pattern was destroyed at these temperatures.

In 1941 Kelley, Dore, and Page (28) reported a study of the colloidal constituents of American alkali soils. The soils used in this investigation were drawn from several different localities in western United States. The base exchange capacities for the soil colloids ranged from 25.7 to 58.4 milliequivalents per 100 grams. The white-alkali soil colloids gave smooth wave-like dehydration curves which resemble those of Yolo soil colloids, whereas the curves for several of the black-alkali soil colloids showed pronounced breaks between 400 and 500 degrees centigrade. The latter phenomenon was traced to the loss of carbon dioxide from calcium carbonate.

X-ray investigations showed that the white-alkali soils contained a mixture of montmorillonitic, kaolinitic, and mica-like clays, whereas mica-like clays greatly predominated in the black-alkali soils.

Because of considerable variation in the characteristics of the mica-like clays it was suggested that this was due, in part at least, to variations in the type of mica in the parent rocks from which the soil materials were derived.

The x-ray results, according to the interpretation of Kelley, Dore, and Page failed to support the idea that the base exchange capacity of soil colloids was necessarily due to montmorillonitic clay. The sample with the highest base exchange capacity gave virtually no x-ray evidence for the presence of montmorillonite.

It was concluded that the apparent effects produced on American alkali soils by the accumulation of soluble sodium salts consisted primarily in the exchange of cations together with the dispersion of the clay particles, but these processes probably produced very little alteration in the essential structure of the clay minerals originally present. No convincing evidence was obtained that crystalline minerals peculiar to alkali soils were synthesized in either the soda-containing type or white alkali, or the type which shows the black-alkali morphology.

Implication

Although the implication is present it could hardly be concluded from the literature review that it is generally recognized that the colloidal portion of soils is made up of one or a mixture of the three general groups of clay minerals, kaolinite, montmorillonite, and illite. A much more general background is desirable, but hardly possible at this point. Three excellent reviews of the clay minerals which give adequate background can be found in a study of the kaolin minerals by Ross and Kerr (40) in 1931, a general review of modern concepts of clay minerals by Grim (17) and published in 1942, and a study of the minerals of the montmorillonite group compiled by Ross and Hendricks (39) and published in 1945.

Because of the multitude of more concise implications which appear in the literature it appears advisable not to discuss these now, but to consider these more in detail under the discussion in chapter V.

Chapter III

METHODS AND MATERIALS

In all of the investigations and analyses the different samples were subjected to, as nearly as possible, the same treatment so that results would be readily comparable. Because of the wide variance in the nature and properties of the samples this was not always possible. Where deviations were necessary they are indicated in the procedure.

The samples consisted of two soils and two clays subjected to all of the tests and a third clay, available only in a limited amount, was used where it was felt the comparison would be most helpful.

One soil sample was taken from the agronomy farm at Fort Collins. This is a productive soil of the Fort Collins sandy loam series. The sample was taken by usual procedures (38) for obtaining laboratory samples from a 0 to 6 inches depth. Other samples from the same location were available at 0 to 12, 12 to 36, 36 to 60, and 60 to 72 inches. These samples were used only in obtaining thermal curves as explained later.

The second soil sample was collected in the

Grand Junction, Colorado, area in 1946 as a part of the soil survey of that area. It was classified as a saline-alkali soil. The immediate area was bare ground, no cultivation being attempted. The texture was described as silty clay loam to heavy silt loam surface with a lighter texture below 20 inches. Samples were available from 0 to 8, 8 to 20, 20 to 32, and 32 to 44 inches. Only the 0 to 8 inches sample was used except for thermal curves. The area number for this sample was 57-A.

The clay samples consisted of bentonite from Wyoming, kaolinite from the J. T. Baker Chemical Co., and a limited supply of illite.

Unless otherwise stated the following procedures were carried out on the Fort Collins, and Grand Junction soils and on the bentonite and kaolinite. The Grand Junction area soil will be referred to as soil 57-A in agreement with the original survey number and so will not be confused with productive soils from that area.

The experimental procedure logically falls into several sections and each procedure will be presented separately.

Determination of particle size fractions in soils and clays

The particle size fractions were determined essentially by the standard pipette method of Olmstead et al. (35), with some modification.

Triplicate samples of each of the soils and clays were taken so that after removal of the sand fraction, the remaining portion would weigh from 10 to 11 grams. The samples were transferred to 100 milliliter plastic centrifuge tubes and 50 to 60 milliliters of distilled water were added. Carbon dioxide was passed through the mixture for 15 minutes. The supernatant liquid was decanted and the washing and centrifugation repeated until the clay remained slightly dispersed after centrifugation. This was obtained with the second washing of the Fort Collins soil, but several washings were needed with soil 57-A. The washed samples were then oven-dried and weighed. This weight was taken as the basis for calculations rather than the original oven-dry weight.

The samples were then quantitatively transferred to 250 milliliter wide mouth bottles and diluted to 125 milliliters with distilled water; 2 milliliters of 0.5 normal sodium hydroxide and 2 milliliters of 0.25 normal sodium oxalate were then added to each sample. The samples were dispersed for 10 minutes with a motor stirrer and then washed with distilled water through a 300-mesh wire screen into a 1000 milliliter sedimentation cylinder. The particles remaining on the seive (sand fraction) were thoroughly washed to remove smaller particles and the washings added to the cylinder. The sand fraction was trans-

ferred to a tared dish, dried, and weighed. The suspensions in the cylinders were made-up to exactly 1000 milliliters with distilled water, and placed in a constant temperature bath at 20 degrees centigrade.

After each suspension was brought to constant temperature, it was thoroughly dispersed by shaking, end over end, and samples were drawn off with a 50 milliliter Lowy automatic pipette (cathetometer arrangement) at the time and depth calculated for the desired fractions by Stokes' equation. The sample and washings were transferred to tared 50 milliliter conical centrifuge tubes, dried at 110 degrees centigrade for 24 hours, and weighed. Accounting for the dispersing reagents the mechanical fractions were calculated.

It appeared possible that organic matter, slightly soluble and acid soluble salts, some acting as binding agents, might interfere with the mechanical analyses and subsequent ionic exchange capacities. Since the mineral constituents were considered to be of primary importance in this investigation the organic matter and acid soluble salts were removed. This was accomplished by following the suggestions of Olmstead et al. (35), and Truog et al. (45). The samples were treated with a 6 per cent hydrogen peroxide solution and alternately brought to dryness until no further reaction resulted when hydrogen peroxide was

added. The samples were then treated with 100 to 200 milliliters of 0.1 normal hydrochloric acid for one hour. Washings to remove excess acid were accomplished by use of a Mandler filter, since it was found that dispersion of the sample prevented the use of centrifugal washings as was done with the first set of samples. The samples were washed 6 to 8 times with the filtering thimble, then dried and weighed. This weight was used for future calculations. From this point the samples were treated in exactly the same manner as the first set of samples.

From observations on the first set it appeared that the kaolinite was dispersing to a lesser degree than the other samples. Consequently separate portions of kaolinite were arbitrarily dispersed with sodium hydroxide, sodium oxalate, sodium silicate, sodium meta phosphate, and sodium stearate. From a visual examination it was apparent that the sodium silicate and sodium stearate were superior to the other dispersing agents when used with this particular sample of kaolinite. It was not known what effect sodium stearate might exercise on the sample so sodium silicate was used for dispersion with the kaolinite samples. The dispersion was found to be more complete than when dispersed with sodium oxalate and sodium hydroxide, but in drying the samples the kaolinite was rendered useless for ionic exchange determinations.

When the kaolinite samples were dried to obtain their weights, it appeared that some reaction was affected with the sodium silicate. This was evidenced by the fact that the kaolinite was incapable of exchanging or retaining any ammonium ions when treated with ammonium acetate solution for the subsequent determination of ionic exchange capacity. It was impossible to repeat the entire procedure because of insufficient amount of this particular kaolinite sample.

In chapter IV the data will be presented so that the two sets of samples may be easily distinguished according to the treatments above. The samples where organic matter and binding agents were not removed will be referred to as the untreated samples, and the samples subjected to hydrogen peroxide and hydrochloric acid treatment will be referred to as the treated samples.

Determination of total ionic exchange capacity and distribution of exchange capacity in fractions of soils and clays.

The fractions obtained from the mechanical analysis were employed directly in the determination of ionic exchange capacity. The method developed for this determination was essentially a semi-micro adaptation of the ammonium acetate method as developed by Schollenberger and Simon (42) and used by Gardner, Whitney, and Kezer (16).

The method used for both the treated and untreated samples from the mechanical analysis is as follows: To the dry samples contained in the 50 milliliter conical centrifuge tubes, 25 milliliters of 1 normal ammonium acetate adjusted to pH 7 were added and the tube stoppered and shaken on a mechanical shaker for one hour. It was necessary to loosen some of the colloidal material adhering to the sides of the tubes with a rubber policeman and wash down with more ammonium acetate solution. The samples were allowed to stand over night in the ammonium acetate solution, shaken for 15 minutes, and then centrifuged at 2000 revolutions per minute for 5 minutes. The supernatant liquid was then decanted. 10 to 15 milliliters of ammonium acetate solution were added to each tube. The tubes were placed on the mechanical shaker for 15 minutes then centrifuged. The procedure was repeated 4 times.

The excess ammonium acetate was removed by washing 4 to 6 times, or until free of ammonium ions, with 15 to 20 milliliter portions of 95 per cent ethyl alcohol then centrifuging as long as necessary to throw down the dispersed portion. It was found with the last washings that 2 to 3 hours at higher speeds was necessary to produce a clear supernatant liquid in the tubes.

Alcohol with a higher percentage of water caused dispersion usually on the second washing which prohibited

separation even with prolonged centrifugation at high speeds. A small amount of ammonium chloride added to the first alcohol wash gave a convenient way to test for the complete removal of the ammonium ion indirectly by testing for chlorides (37). If the tubes were inverted on paper towelling after each decantation and allowed to drain free of alcohol the number of washings required for the removal of excess ammonium ions was reduced.

When the sample was free from excess ammonium ions it was transferred quantitatively with 300 milliliters of distilled water to a Kjeldahl flask. About one gram of heavy magnesium oxide was added and the flask immediately connected to the distillation apparatus. About 200 milliliters of distillate were collected in 25 milliliters of saturated boric acid solution. It was not found necessary to add glass beads or oil to prevent bumping or frothing during distillation. The distillate was titrated with 0.010 normal sulfuric acid using methyl red-brom cresol green indicator. From the milliliters of acid required for each titration the milliequivalents corresponding to each sample weight were calculated. Any other desired relationship pertaining to exchange capacity can then be calculated from these data.

The ionic exchange capacity of the natural unfractionated soils and clays was obtained using one gram

samples, weighed after washing, or treatment, and the same procedure followed as given above for each individual fraction.

Determination of relative specific surface of the colloidal fraction of soils and clays

The procedure used in determining the relative specific surface of the colloidal fraction of soils and clays was taken directly from a research report from the laboratories of the U. S. Department of Agriculture, Beltsville, Maryland. The procedure was developed by Dyal (12). Since the report appears only in mimeograph form the entire procedure is reproduced here.

The following procedure can be used in applying the ethylene glycol retention method.

Apparatus: Two Pyrex vacuum desiccators
(12") with porcelain plates
Vacuum pump (Welch, Hy-Vac)
Analytical balance
Shallow weighing bottles with covers

Chemicals: CaCl_2 , anhydrous
 P_2O_5
Eastman ethylene glycol, purest grade

Redistill the ethylene glycol in vacuum discarding the first and last 10 per cent of distillate. Dry the CaCl_2 at 100 degrees centigrade overnight.

Separate the less than 2 micron fraction of the soil or clay and saturate with hydrogen by leaching with dilute HCl. Dry about 1.1 grams at 100 degrees centigrade partially in order to destroy endellite and then over P_2O_5 in vacuum to constant weight. The preliminary

drying should be omitted if information is desired about endellite in some unusual instance. Heat about 1.2 grams of separated clay to 600 degrees centigrade for at least two hours.

After the sample has reached constant weight add about 1 milliliter of ethylene glycol to the weighing bottle and place in vacuum desiccator above about one-half pound of dry CaCl_2 . Evacuate. Weigh after about 16 hours, replace in desiccator, evacuate to less than 0.1 mm. of mercury, and finally weigh after 24 hours. Discard CaCl_2 after use with about 10 samples.

If the loss in weight between 16 and 24 hours is less than 0.020 gram the 16-hour value should be used as that for ethylene glycol retention. The 24-hour value should be used as that for ethylene glycol retention if the weight loss is greater than 0.020 gram provided the retention at 16 hours is less than 0.35 gram indicating adequate vacuum and anhydrous character of desiccant. A preliminary test of vacuum conditions is desirable. One milliliter of ethylene glycol should evaporate in less than twelve hours. (12:11)

With the exception of the redistillation of the ethylene glycol the procedure was followed as given. Two samples were placed in a desiccator for all evacuations. A larger number of samples in the desiccator caused an increase in the amount of ethylene glycol retained so the same conditions were used for all samples. The method was also applied to whole soil and silt plus clay fractions rather than just to the colloidal fraction (less than 2 microns in diameter). All of the samples other than whole soil were obtained by sieving separations and sedimentation of suspensions using Stokes' equation.

Identification of clay minerals in the soils by dehydration

A procedure for the identification of clays by their hydration properties as given by Kelley, Jenny, and Brown was adapted. The procedure as given follows:

Samples were brought to equilibrium above 50 per cent sulfuric acid at a constant temperature of 25 degrees centigrade. Approximately one gram samples were used in duplicate and were kept at each temperature until loss in weight ceased. (31:261)

Hendricks and Alexander (19) reported that in differential thermal studies the silt and sand fractions would not interfere with the curves unless present in much larger proportions than the clay. Organic matter was reported to interfere with the kaolin type curves, but not with clays where the linear portion was at higher temperatures.

With these previous investigations as the basis a procedure was developed as follows: 10 gram samples were treated with 25 milliliters of 10 per cent hydrogen peroxide. Cold digestion was allowed for 2 to 3 hours then at higher temperatures until dryness, but not to boiling. After three such treatments the inactivity upon addition of the peroxide indicated that most of the organic matter was removed from the Fort Collins soil, the bentonite, and the kaolinite. Several additional treatments plus an acetic acid treatment, because of the

apparent presence of manganese dioxide, were necessary with soil 57-A before the inactivity indicated complete removal of the organic matter. One gram samples of bentonite and kaolinite were placed in platinum crucibles, dried at 110 degrees centigrade, and weighed. These were then subjected to temperatures of 50 degree centigrade intervals until 800 degrees centigrade was reached. The samples were left in the furnace at each temperature for one hour, removed to a calcium chloride desiccator, cooled for 45 minutes, weighed, and replaced in the furnace at the next temperature.

Additional samples of the clays and soils were brought to dryness at 110 degrees centigrade after treatment with hydrogen peroxide, broken up, but not finely ground, with a mortar and rubber pestle, and placed in an atmosphere chamber containing 50 per cent sulfuric acid for 8 days. One gram samples were then placed in tared platinum crucibles and subjected to temperatures at 100 degree Fahrenheit intervals and held at each temperature for $1\frac{1}{2}$ hours, then cooled and weighed to four places.

From comparison of samples held in the furnace for one hour with those held for $1\frac{1}{2}$ hours it was found that one hour was sufficient time to allow for the loss in weight. In a like manner it was found that 8 days in the atmosphere chamber over 50 per cent sulfuric acid were

sufficient for the sample to come to a reasonable balance with the atmosphere.

In order to obtain more information concerning the colloidal fractions, samples of the clays, plus a sample of illite, and samples from the profile of soil 57-A corresponding to the depths 0 to 8, 8 to 20, 20 to 32, and 32 to 44 inches, and samples from the Fort Collins soil profile corresponding to the depths of 0 to 12, 12 to 36, 36 to 60, and 60 to 72 inches were dispersed in 1000 milliliters of water, as described in the procedure for the mechanical analysis. The time of sedimentation was calculated for particles greater than 2 microns in diameter and the suspension above this was siphoned off. The suspension was flocculated with calcium chloride solution, filtered with Whatman 40 filter paper, leached with dilute hydrochloric acid for removal of lime, and subjected to 3 to 4 leachings of calcium chloride solution (approximately 2 normal). Excess calcium chloride was removed with distilled water washings. The colloids were treated with 10 per cent hydrogen peroxide for removal of organic matter as described above. The colloidal material was then brought to dryness at 110 degrees centigrade and placed over 50 per cent sulfuric acid for 8 days. Intervals of one hour at each successive temperature (100 degree Fahrenheit) change were used in the muffle furnace.

Two other soils from the Grand Junction area were treated as described above and the colloids used for this determination. The survey numbers for these soils are 15-C and 8-A. Only the 0 to 8 inch samples were used.

Chapter IV

PRESENTATION OF DATA

It was proposed in the introduction to this thesis that the relation of the ionic exchange capacity to various other properties of the soils and clays under consideration could be studied by a breakdown of the problem into four sub-investigations. The results of these investigations are presented here.

Mechanical analyses and ionic exchange relations

For ease of comparison the particle size distribution and the ionic exchange capacities of each sample and its fractions are placed in Tables 3, 4, 5, and 6.

In soil 57-A the water soluble material was 2.6 per cent, and for the Fort Collins soil was 0.5 per cent. An additional 4.6 per cent of soil 57-A was removed by treatment with hydrogen peroxide and hydrochloric acid, making a total of 7.2 per cent of the original soil removed by treatments as described in the procedure. For the Fort Collins soil an additional 2.2 per cent was removed by acid and peroxide treatments, making a total of 2.7 per cent of the original soil removed. These figures were based on dry weight samples of the soils before and

Table 3.--MECHANICAL ANALYSES AND IONIC EXCHANGE RELATIONS OF FORT COLLINS SOIL

Description	Particle Size Values			Ionic Exchange Values			
	Diameters in mm.	Summation percent	Actual percent	Summation percent	Actual percent	Summation* m.e./100g.	Actual m.e./100g.
<u>Untreated Fort Collins Soil</u>							
Sand	2.00-.050	100	52.6	100	8.0	16.6	2.5
Coarse silt	.050-.034	47.4	7.7	92.0	4.0	32.2	8.6
Medium silt	.034-.018	39.7	6.9	88.0	0.6	36.8	14.4
Fine silt	.018-.002	32.8	14.2	87.4	26.5	44.3	30.9
Coarse clay	.002-.001	18.6	5.9	60.9	17.7	54.3	49.7
Medium clay	.001-.0002	12.7	9.7	43.2	30.6	56.5	52.3
Fine clay	<.0002	3.0	3.0	12.6	12.6	69.8	69.8
<u>Treated Fort Collins Soil</u>							
Sand	2.00-.050	100	53.6	100	3.0	15.5	0.9
Coarse silt	.050-.034	46.4	6.2	97.0	2.2	32.4	5.5
Medium silt	.034-.018	40.2	7.3	94.8	2.5	36.6	5.3
Fine silt	.018-.002	32.9	11.9	92.3	17.7	43.5	23.1
Coarse clay	.002-.001	21.0	4.1	74.6	10.2	55.1	38.6
Medium clay	.001-.0002	16.9	10.1	64.4	34.5	59.2	53.6
Fine clay	<.0002	6.8	6.8	29.9	29.9	68.2	68.2

The values presented are taken as the best value of triplicate samples run simultaneously.

*Values represent fraction indicated plus all smaller fractions.

Table 4.--MECHANICAL ANALYSES AND IONIC EXCHANGE RELATIONS OF 57-A SOIL

Description	Particle Size Values			Ionic Exchange Values			
	Diameters in mm.	Summation percent	Actual percent	Summation percent	Actual percent	Summation* m.e./100g.	Actual m.e./100g.
<u>Untreated 57-A Soil</u>							
Sand	2.00-.050	100	2.5	100	0.5	13.9	2.8
Coarse silt	.050-.034	97.5	3.0	99.5	1.7	14.2	7.8
Medium silt	.034-.018	94.5	15.0	97.8	3.2	14.4	3.0
Fine silt	.018-.002	79.5	43.5	94.6	28.7	16.5	9.2
Coarse clay	.002-.001	36.0	9.9	65.9	10.3	25.4	14.5
Medium clay	.001-.0002	26.1	17.4	55.6	31.5	29.7	25.1
Fine clay	<.0002	8.7	8.7	24.1	24.1	38.6	38.6
<u>Treated 57-A Soil</u>							
Sand	2.00-.050	100	2.0	100	0.2	15.1	1.5
Coarse silt	.050-.034	98.0	3.7	99.8	1.9	15.4	7.7
Medium silt	.034-.018	94.3	9.9	97.9	4.1	15.7	6.2
Fine silt	.018-.002	84.4	45.2	93.8	21.0	16.8	7.5
Coarse clay	.002-.001	39.2	8.9	72.8	7.2	28.0	12.2
Medium clay	.001-.0002	30.3	17.9	65.6	30.1	32.7	25.4
Fine clay	<.0002	12.4	12.4	35.5	35.5	43.2	43.2

The values presented are taken as the best value of triplicate samples run simultaneously.

*Values represent fraction indicated plus all smaller fractions.

Table 5.--MECHANICAL ANALYSES AND IONIC EXCHANGE RELATIONS OF BENTONITE

Description	Particle Size Values			Ionic Exchange Values			
	Diameters in mm.	Summation percent	Actual percent	Summation percent	Actual percent	Summation* m.e./100g.	Actual m.e./100g.
<u>Untreated Bentonite</u>							
Sand	2.00-.050						
Coarse silt	.050-.034	100	2.9	100	0.8	81.3	22.4
Medium silt	.034-.018	97.1	1.7	99.2	1.0	83.0	47.8
Fine silt	.018-.002	95.4	6.5	98.2	2.1	83.8	26.2
Coarse clay	.002-.001	88.9	6.2	96.1	5.5	87.9	72.2
Medium clay	.001-.0002	82.7	28.8	90.6	30.7	89.2	86.6
Fine clay	<.0002	53.9	53.9	59.9	59.9	90.4	90.4
<u>Treated Bentonite</u>							
Sand	2.00-.050						
Coarse silt	.050-.034	100	3.4	100	3.0	82.1	72.2
Medium silt	.034-.018	96.6	2.5	97.0	0.7	82.5	23.0
Fine silt	.018-.002	94.1	16.7	96.3	10.7	84.0	52.6
Coarse clay	.002-.001	77.4	9.2	85.6	9.0	90.9	80.3
Medium clay	.001-.0002	68.2	31.9	76.6	34.0	92.3	87.5
Fine clay	<.0002	36.3	36.3	42.6	42.6	95.4	95.4

The values presented are taken as the best value of triplicate samples run simultaneously.

*Values represent fraction indicated plus all smaller fractions.

Table 6.--MECHANICAL ANALYSES AND IONIC EXCHANGE RELATIONS OF KAOLINITE

Description	Particle Size Values			Ionic Exchange Values			
	Diameters in mm.	Summation percent	Actual percent	Summation percent	Actual percent	Summation* m.e./100g.	Actual m.e./100g.
<u>Untreated Kaolinite</u>							
Sand	2.00-.050						
Coarse silt	.050-.034	100	9.6	100		2.2	
Medium silt	.034-.018	90.4	40.7		29.8	2.9	1.6
Fine silt	.018-.002	49.7	36.2	70.2	52.0	3.6	2.5
Coarse clay	.002-.001	13.5	10.1	18.2	11.3	3.7	3.1
Medium clay	.001-.0002	3.4	2.8	6.9	6.9	5.5	5.5
Fine clay	<.0002	0.6	0.6	--	--	--	--
<u>Treated Kaolinite</u>							
Sand	2.00-.050						
Coarse silt	.050-.034	100	1.5	--	--	2.6	--
Medium silt	.034-.018	98.5	5.4	--	--	--	--
Fine silt	.018-.002	93.1	41.1	--	--	--	--
Coarse clay	.002-.001	52.0	20.6	--	--	3.0	--
Medium clay	.001-.0002	31.4	30.0	--	--	--	--
Fine clay	<.0002	1.4	1.4	--	--	--	--

The values presented are taken as the best value of duplicate samples run simultaneously.

*Values represent fraction indicated plus all smaller fractions.

after leaching. The weight before treatment was used for calculating percentages.

In the bentonite sample organic matter was found to be negligible and the acid and water soluble salts only about 1.1 per cent. Water soluble material was about 0.5 per cent.

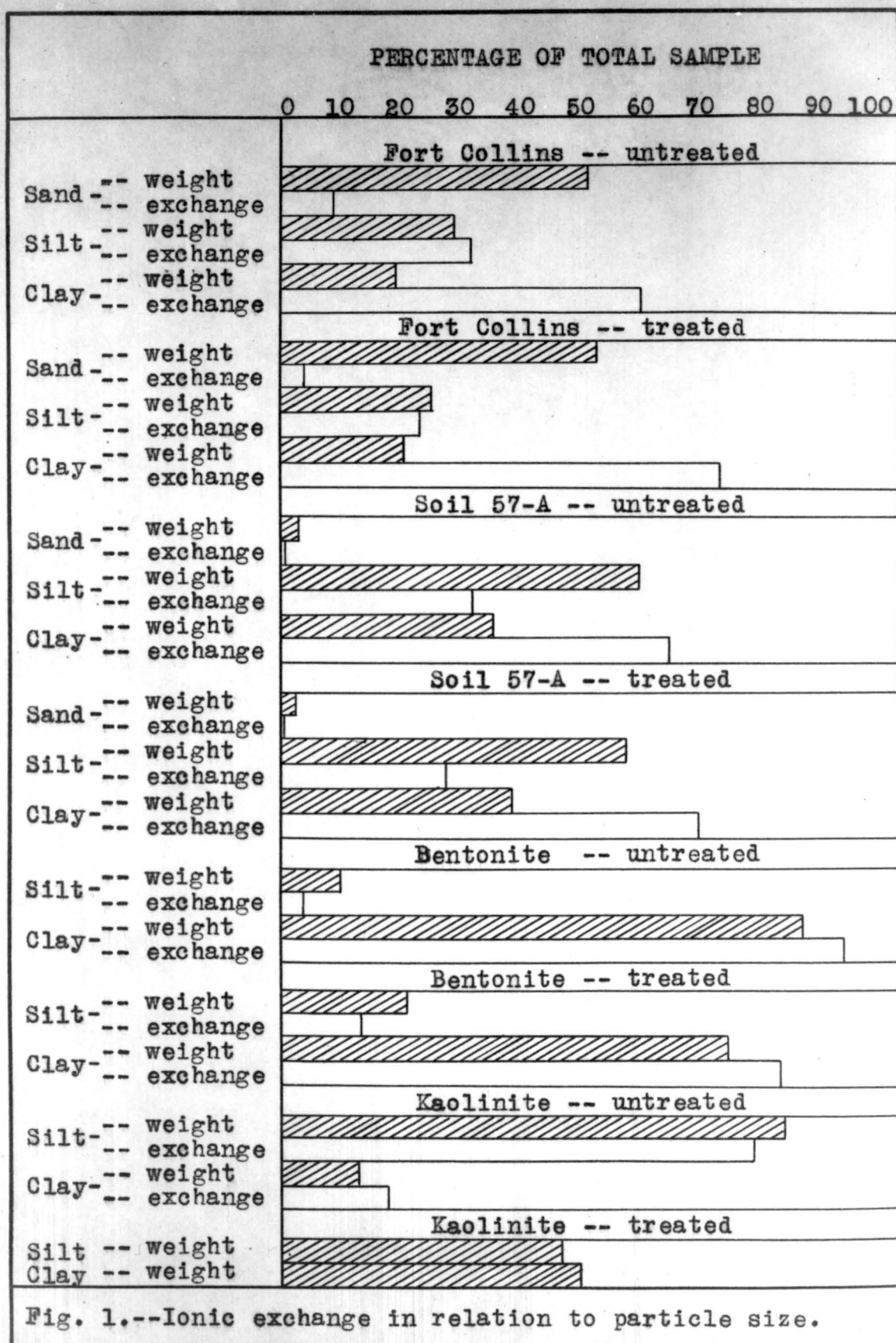
Because of the differences in the methods of dispersion used with the treated and untreated samples of kaolinite, summarized in Table 6, it is difficult, if not impossible, to determine what contribution was made by the acid treatment. It is apparent that the degree of dispersion of the treated sample was greater than that of the untreated.

In the kaolinite sample the amount of organic matter was negligible as was the acid soluble material. As was explained in the procedure the sodium silicate used for the dispersing agent of the treated kaolinite samples rendered the samples useless for determination of ionic exchange relations.

In Tables 3, 4, 5, and 6 the values for the sand (2.00-0.50 mm.) and coarse silt (0.050-0.034 mm.) fractions for all of the ionic exchange relations must be obtained by interpolation from curves drawn from the rest of the data. These curves are included in the appendix. It is apparent that this procedure leaves considerable

source of error in these two fractions, and especially so in the coarse silt, since that value, even in the mechanical analysis, must be obtained by difference. The accumulative error might be of considerable magnitude since it is not only additive in the mechanical analysis, but the final value obtained for actual milliequivalents per 100 grams may represent the product of two accumulative errors, one from the mechanical and one from the ionic exchange values. The values expressed in the column for actual milliequivalents per 100 grams for the coarse silt although apparently not consistent in some cases might be expected to be even further in variance considering the possible sources of error.

So that all of the data may be considered by comparisons of the total sand, silt, and clay fractions, that is, considering the samples as they naturally occur, a bar diagram has been constructed giving actual percentages of each fraction and the percentage ionic exchange contributed by each fraction. These data appear in Figure 1.



Retention of ethylene glycol

The retention of ethylene glycol by the clay fraction, as given in Table 7, probably presents the best means of comparison since varying amounts of silt and sand were present in the other samples. It is not known that the retention of ethylene glycol by particles larger than 2 microns in diameter is comparable to the retention by colloidal particles. The difference between the retention of the unheated sample and the heated sample has been attributed by Dyal (12) to internal swelling. Dyal believes that a difference of less than 0.005 gram of glycol per gram of clay is insignificant. Values obtained after 24 hours of evacuation were used throughout for these differences.

An approximate comparison of the base exchange capacities and the retention of ethylene glycol of the clay fractions (2 microns and less in diameter) indicates that the two methods do not give values of the same magnitude, but there is a parallelism in the order. (See Figure 2.

Table 7.--ETHYLENE GLYCOL RETENTION UNDER VACUUM BY SOILS
AND CLAYS PREVIOUSLY DRIED OVER P_2O_5

ETHYLENE GLYCOL RETAINED IN GRAMS PER GRAM					
	<u>Unheated</u>		<u>Heated to 600°C.</u>		<u>For</u>
	16 hrs.	24 hrs.	16 hrs.	24 hrs.	<u>Internal</u>
					<u>Swelling</u>
<u>Bentonite</u>					
untreated	0.258	0.246	0.006	0.006	0.240
H-treated	0.267	0.255	0.021	0.019	0.236
H-clay	0.265	0.255		0.020	0.235
<u>Kaolinite</u>					
untreated	0.004	0.004	0.002	0.002	0.002
H-treated	0.003	0.003	0.003	0.002	0.001
H-clay	0.005	0.004		0.003	0.001
<u>Illite</u>					
H-clay	0.038	0.036		0.022	0.014
<u>Fort Collins</u>					
untreated	0.023	0.022	0.012	0.012	0.010
H-treated	0.020	0.018		0.008	0.010
H-clay - silt	0.044	0.039	0.022	0.018	0.021
H-clay	0.094	0.081	0.030	0.027	0.054
<u>Soil 57-A</u>					
untreated	0.025	0.024	0.011	0.011	0.013
H-treated	0.024	0.022	0.013	0.012	0.010
H-clay - silt	0.028	0.025	0.015	0.013	0.012
H-clay	0.079	0.069	0.035	0.030	0.039

The following particle size groups are represented:

Untreated & H-treated --- 2 mm. and less
H-clay - silt --- 0.050 mm. and less
H-clay --- 0.002 mm. and less

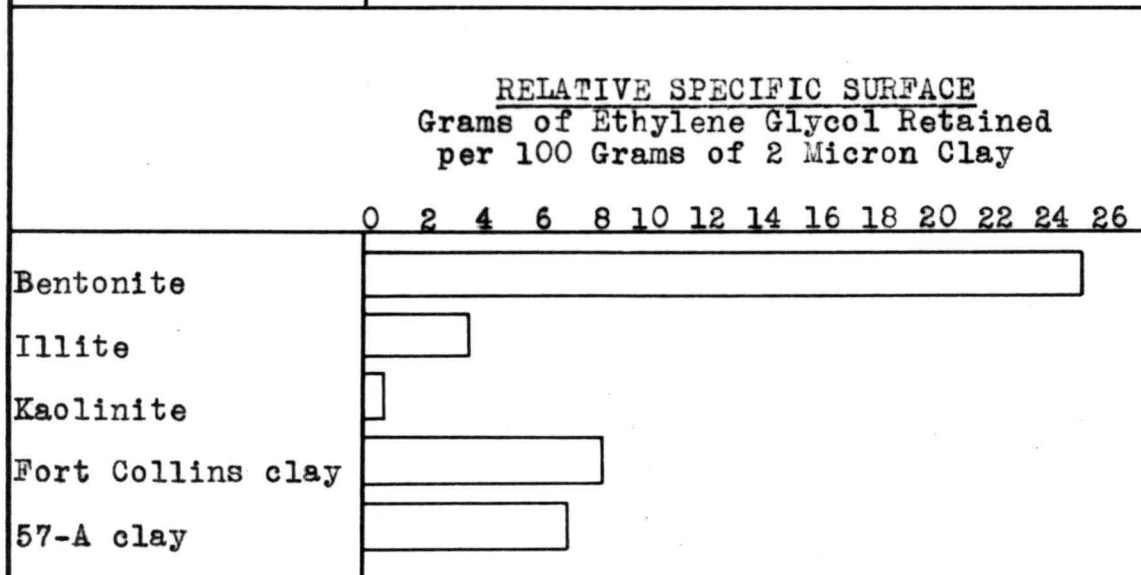
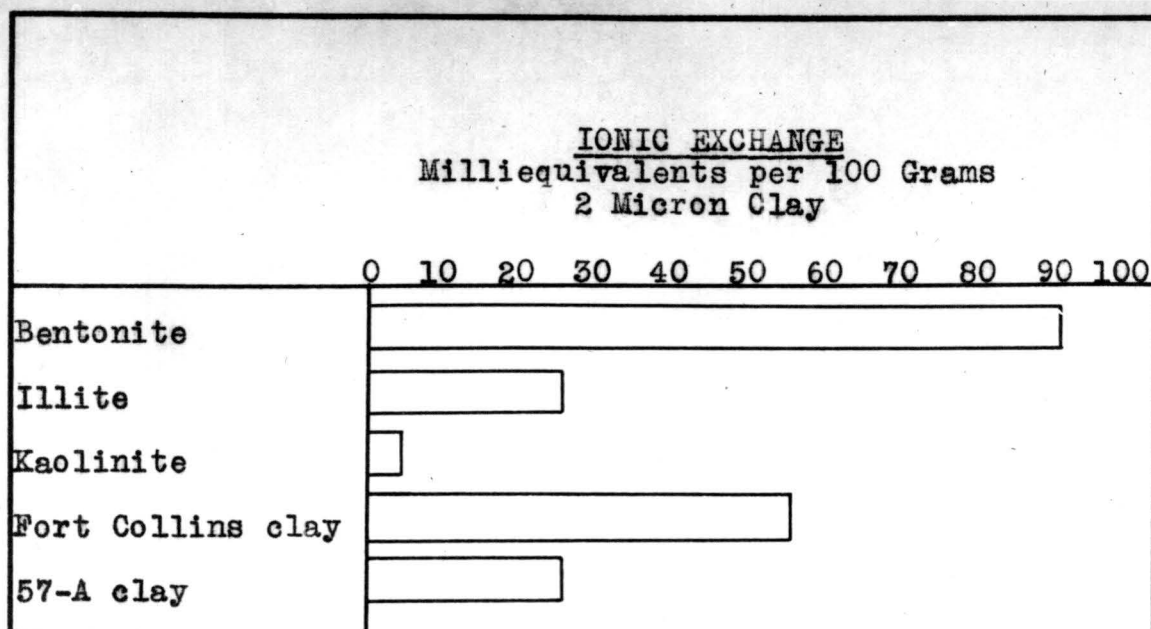


Fig. 2.--Ionic exchange in relation to relative specific surface.

Values for relative specific surface after 24 hours under vacuum are used.

Dehydration studies

The data obtained from the dehydration of the soil, soil colloid, and clay samples are most readily presented in the form of graphs, as the values in table form are not readily comparable.

It was found that the bentonite and kaolinite curves obtained from samples heated at 110 degrees centigrade were distorted in that the first linear portion was entirely lacking. When placed over 50 per cent sulfuric acid at 20 degrees centigrade for 8 days before subjecting to dehydration analysis, the characteristic rapid loss in weight of the bentonite up to 110 degrees centigrade was apparent. The initial curve of the kaolinite was little affected whether it was heated at 110 degrees centigrade or allowed to adsorb moisture at 20 degrees centigrade before heating to obtain the dehydration curve. There was no apparent effect on the remainder of the curves, either for bentonite or kaolinite, in relation to the initial treatment.

The curves of the natural soils, Fort Collins and 57-A, placed at 20 degrees centigrade over 50 per cent sulfuric acid, do not to any great extent differ from those of the soil colloids although the total loss in weight was less where the sand and silt were present.

The curves obtained from the colloidal fraction

of the kaolinite, bentonite, and illite are shown in Figure 3. The soil colloids, of the surface soils, Fort Collins and 57-A, together with two other soil colloids of the Grand Junction area, Figure 4, present curves with some characteristics in common.

The profile studies of the Fort Collins, Figure 5, and 57-A, Figure 6, colloids indicate that the surface soil colloid does not vary greatly from that of the lower horizons. Only the surface and lowest sample of the 57-A profile are shown. The other two curves fall between the two plotted and give little additional information.

The curves in Figures 7 and 8 are a redistribution of values so that the values interpolated from Figures 3 and 4 are presented. The loss in weight calculated in per cent weight loss per each 100 degrees centigrade rise in temperature relative to the total loss is plotted against the temperature. It is apparent that each value must be plotted at the mid-point of each temperature range. This allows an error of plus or minus 25 degrees in plotting each point, so the peaks, which are most easily compared, might be in error to about that extent. However, a general means of comparison is presented which might not be possible from the original figures.

A more precise comparison is possible by calculating the percentage loss over a defined range in com-

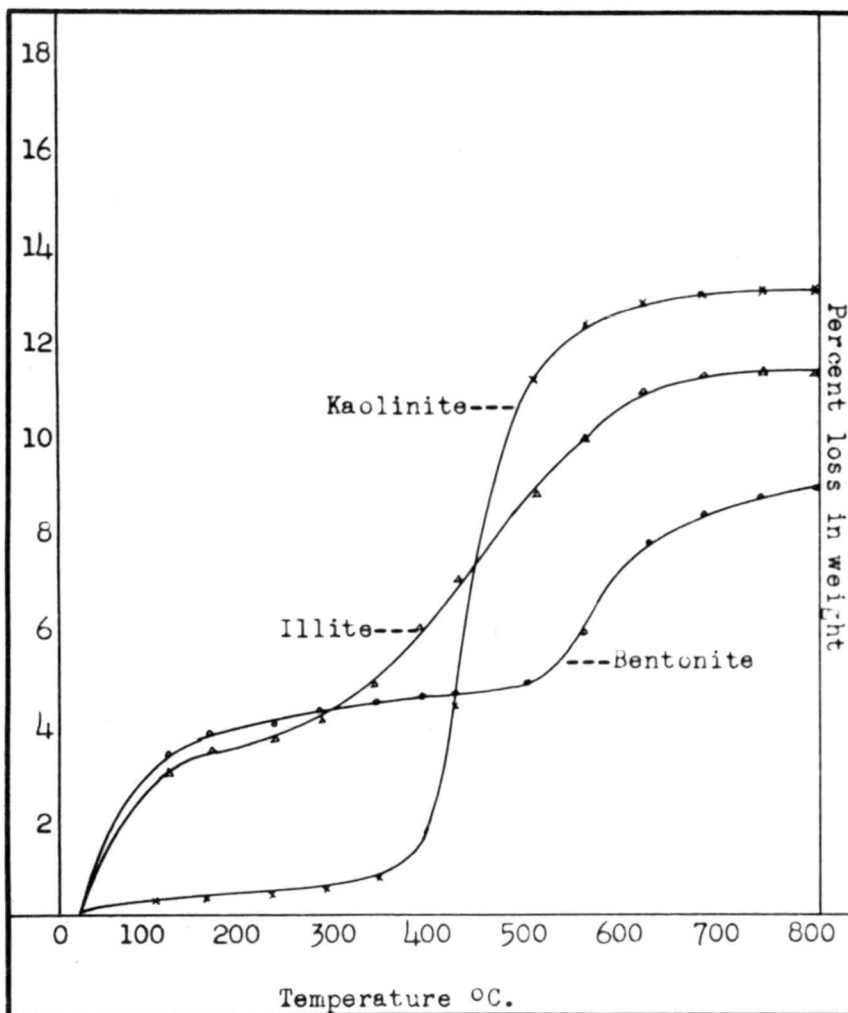


Fig. 3.--Dehydration of clay colloids; Bentonite, Illite, and Kaolinite.

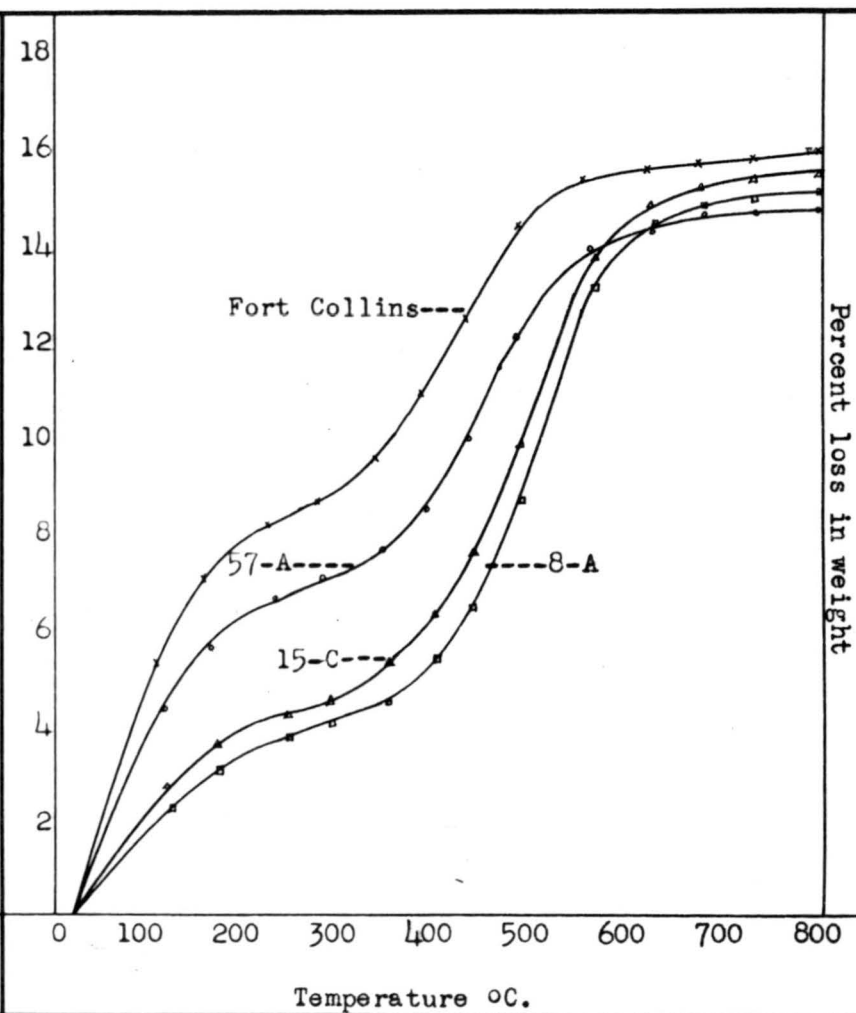


Fig. 4.--Dehydration of soil colloids; Fort Collins, 57-A, 15-C, and 8-A.

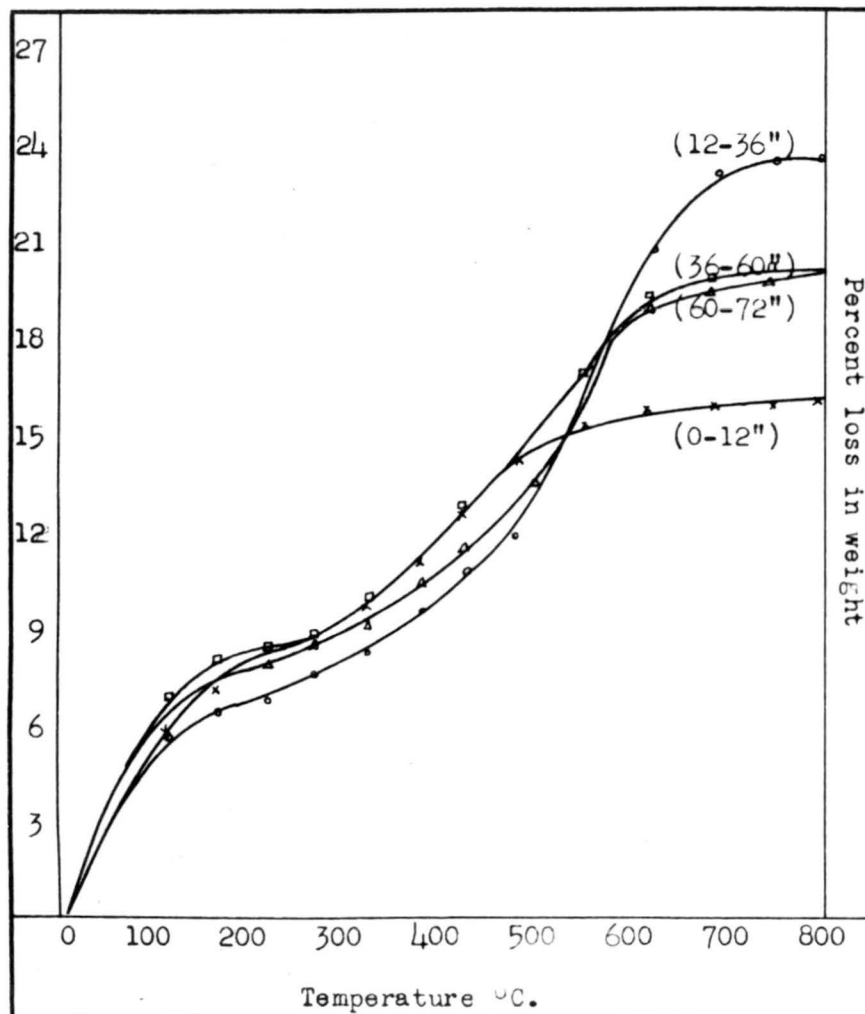


Fig. 5.--Dehydration of the colloids of the Fort Collins profile.

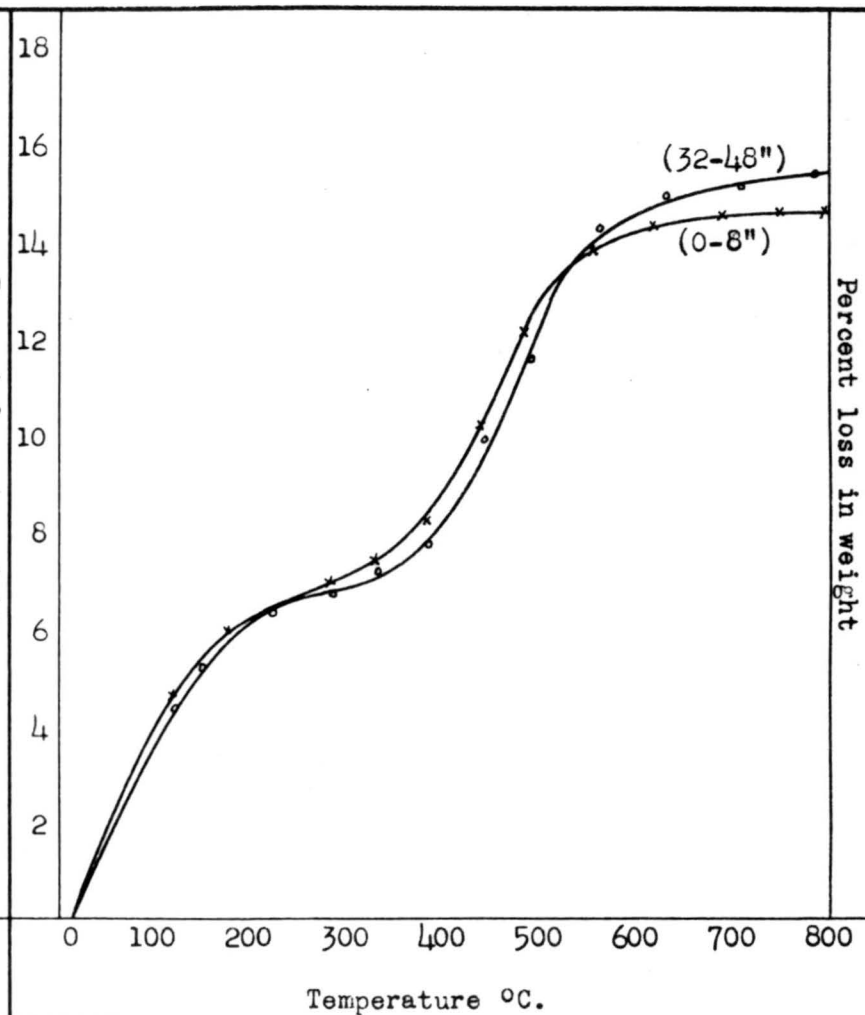


Fig. 6.--Dehydration of the colloids of the 57-A profile.

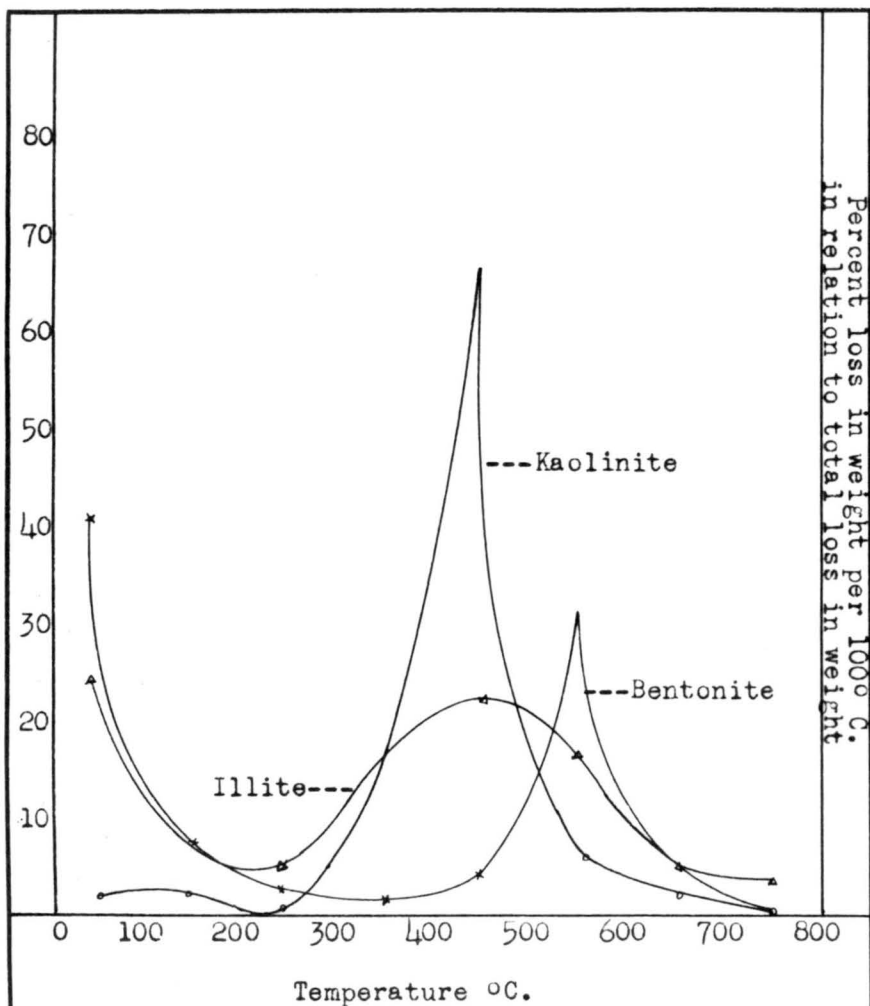


Fig. 7.--Rate of water loss from dehydration of Bentonite, Illite, and Kaolinite.

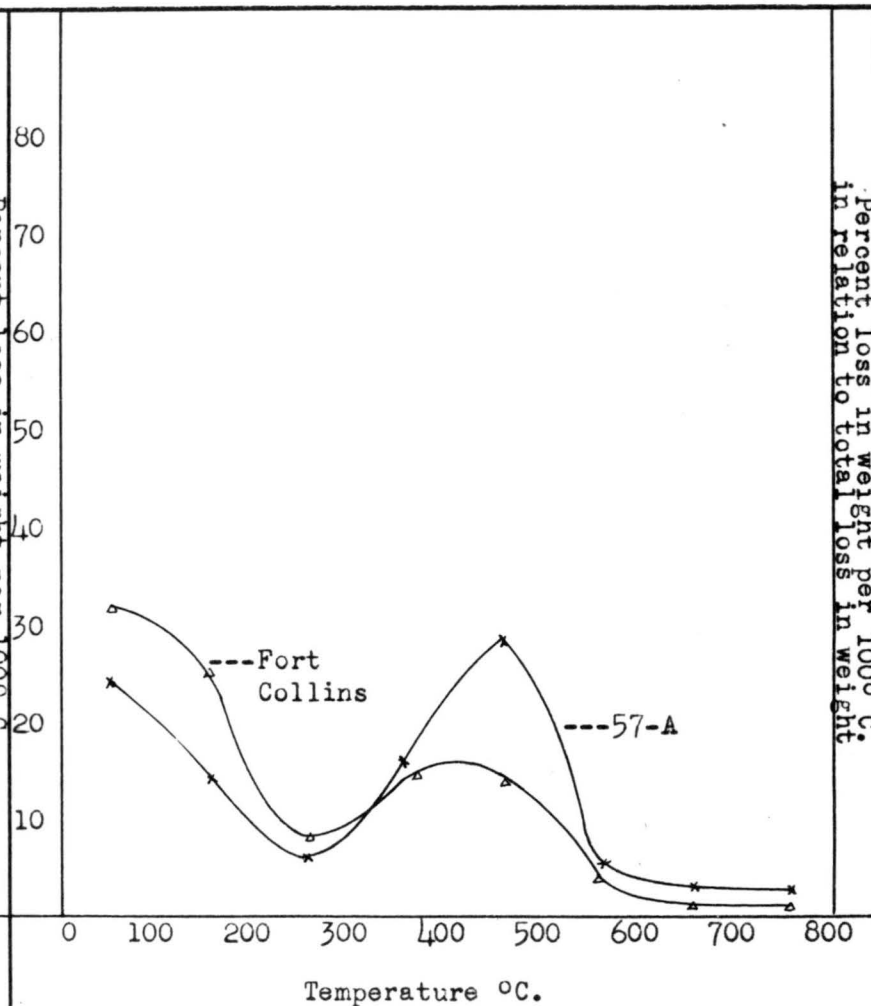


Fig. 8.--Rate of water loss from dehydration of Fort Collins and 57-A colloids.

parison with the total loss over the entire range. These values are presented in Table 8.

Table 8.--PERCENTAGE LOSSES IN WEIGHT OVER SPECIFIED RANGES OF COLLOIDAL FRACTIONS

Colloidal material less than 2 microns	Percent loss 20°-150° C.	Percent loss 150°-600° C.
Bentonite	41.2	44.4
Kaolinite	0.3	94.0
Illite	29.9	65.0
Fort Collins clay	43.8	52.4
57-A clay	37.8	59.5

All values are interpolated from curves in Figures 3 and 4.

A colloidal material containing a mixture of two clays might be expected to be present in a soil colloidal fraction. So that a comparison might be made of a mixture of 50 per cent illite and 50 per cent montmorillonite with the soil colloids, the values for these two clays were averaged and plotted. The similarity of the curve obtained to that of the Fort Collins clay at a depth of 36 to 60 inches may be seen in Figure 9. The two curves are plotted on different percentage loss scales, but they are still directly comparable.

A comparison of the dehydration curve of the

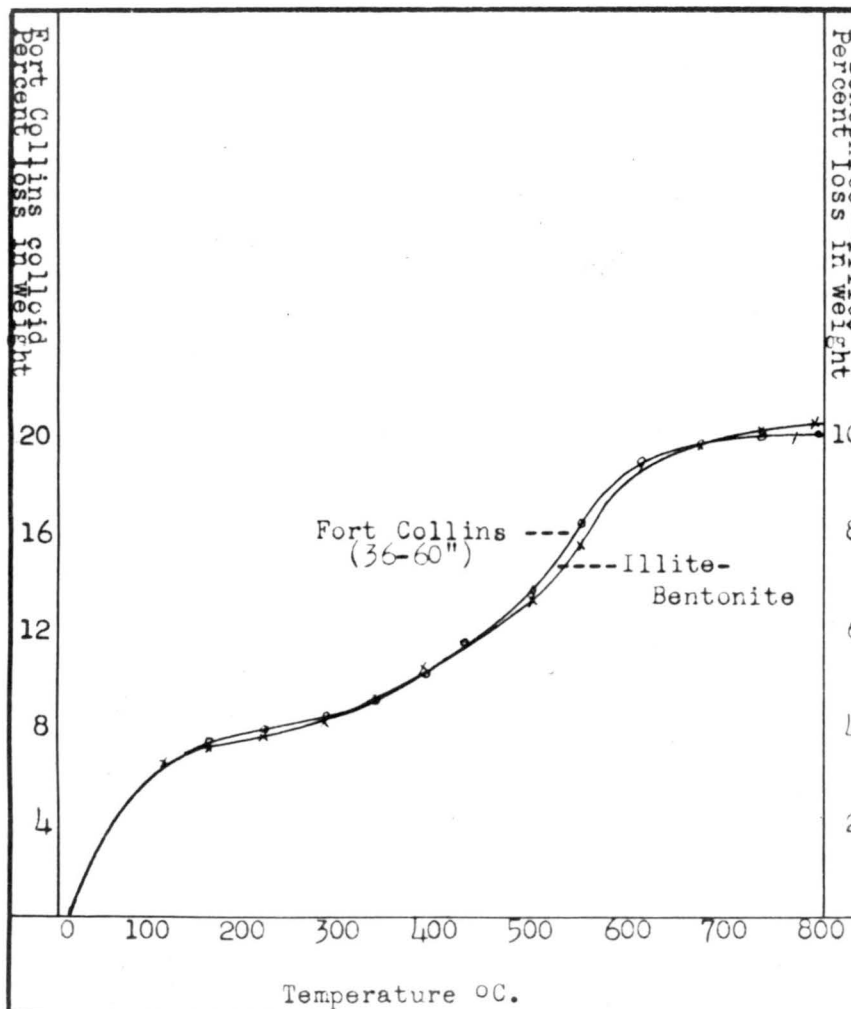


Fig. 9.--Dehydration of Fort Collins colloid and a calculated 50 per cent Bentonite 50 per cent Illite mixture.

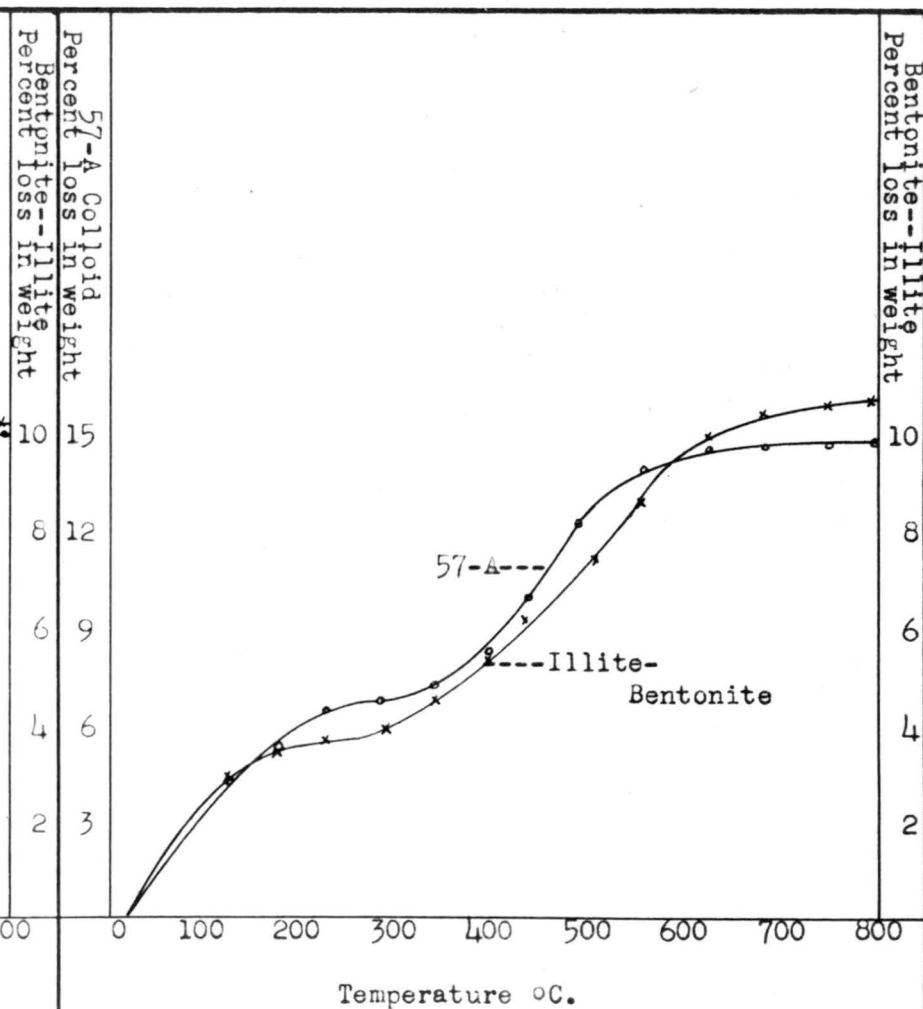


Fig. 10.--Dehydration of 57-A colloid (0-8") and a calculated 75 per cent Illite 25 per cent Bentonite mixture.

57-A colloid with a mixture of 75 per cent illite and 25 per cent montmorillonite (calculated) is shown in Figure 10.

Although the purpose of this section on dehydration studies was to identify the clay minerals in the soil colloids it does not appear that this can be done conclusively merely from the data at hand. A complete comparison and relation of these data with that obtained from the other procedures and with data from the literature offers support which can better be handled in the discussion of Chapter V.

Chapter V

DISCUSSION

In this study where ionic exchange capacity is being related to relative specific surface, particle size, and types of minerals present in certain soils and clays, it becomes more and more obvious that the identification of the clay minerals present in the soils may be of primary importance. This importance is especially understandable after a careful survey has been made of the literature. Not in every instance, but in most cases where significant contributions in advances of knowledge along this line have been made, it has been shown that the activity of the soil may be related to the type of clay minerals present. This concept may be erroneous to a degree and a few authors have attempted to show the significance of the larger particles of the soil.

Although it may appear that the chief object, then, is the identification of the clay minerals by relegating all the investigations to this end, the converse is also true. If the clay minerals are identified then the results of all the separate investigations are far more significant. There are also certain implications

which should be more thoroughly investigated.

If the best use is to be made of the studies every available association should be made with existing knowledge pertaining to the particular study. Since the soil samples are of primary importance a brief review of their geologic formation may be helpful.

Grim (17) in a review of the occurrence of clay minerals in soils presents observations from many sources, some of which were available to him in unpublished manuscripts and other sources which under present conditions are unavailable for first-hand observation. In this review he states that it is likely that illite is formed infrequently in soils, whereas kaolinite and montmorillonite are commonly formed by soil-forming processes. A portion of Grim's review is pertinent to the extent that direct reference seems justified.

Illite is present in many soils, but usually as a remnant of the composition of the parent-rock under different environmental conditions. Hosking (22) has shown that in Australia, under conditions of abundant rainfall and active leaching, kaolinite soils form on basic igneous rocks, whereas under conditions of low rainfall and poor leaching montmorillonite soils form from the same igneous rocks.

Some soils contain mixtures of clay minerals, but in many soils there is a single clay mineral that is the dominant component. These are primarily mature soils in which there has been time for the clay mineral to develop, that is, in equilibrium with the environmental factors under which the soil has formed.

Montmorillonitic and kaolinitic soils may form from illitic material, and kaolinitic soils may form from montmorillonite parent-material. As far as the writer is aware, there is no unquestioned example of a montmorillonite soil that has developed from a kaolinite parent-material.

Work to date suggests that illite is the most widely distributed clay mineral in present-day marine argillaceous sediments, that kaolinite is also widely distributed but generally less abundant than illite, and that montmorillonite is usually either absent or of very minor abundance. Dietz (10) suggests that illite is forming in the marine environment of accumulation, perhaps chiefly from montmorillonite. Correns (9) has, however, concluded that there is little transformation of clay minerals on the sea floor.

In most of the shales that have been studied illite is the dominant clay mineral, and there is some reason to believe that the shaly structure is related to the presence of illite.

The argillaceous material of till and loess, so far as is known, is composed of a mixture of illite, kaolinite, and montmorillonite, with illite the more abundant. (17:259-261)

If the Fort Collins and Grand Junction soils follow the trends as given above it might be expected that the Grand Junction soil, formed almost exclusively from the Mancos shale, a recognized ocean deposit, would be dominantly related to illitic material. The Fort Collins soil largely of alluvial origin and formed under conditions of low rainfall might be suspected of having a mixture of montmorillonitic and illitic materials as its base. However, to conclusively make any such deductions would be unwise as there are numerous unknown factors

which may have dominated the formation of either or both soils.

It has been demonstrated by Grim (17) that when clay mineral particles are agitated in water they tend to break up into smaller-sized units. He further shows that because of lattice characteristics, montmorillonite breaks down more readily than kaolinite. In a study of a large number of clays Grim has shown that montmorillonite and some illite minerals readily breakdown in a suspension into particles less than 0.1 micron in diameter while kaolinite and most illite minerals are broken down with difficulty, or not at all, to particles of 1 to 0.1 micron in diameter.

If Grim's statement that kaolinite and most illite minerals are broken down, with difficulty, or not at all, to particles of 1 to 0.1 micron in diameter is taken to mean that these clay minerals also do not appear in nature with diameters that small, some significant indications may be drawn from the experimental data.

The relatively large amounts of clay in the soil samples falling in the finer fractions might be an indication of the presence of montmorillonitic material. The small amount in the fine clay fractions of the kaolinite and large amount in the bentonite is substantiated by Grim's observations.

Comparison of particles, as to size and distribution, can give only an indication of the type of clay mineral present in a soil, but does lend support when used to confirm findings from other procedures. Processes in the development of soils may vary greatly, so the particle size distribution of different samples is not always directly comparable. The Fort Collins and Grand Junction soils as well as the bentonite were naturally occurring samples. The kaolinite was obtained from a commercial source and possibly may have been subjected to treatment other than might naturally occur.

The base or ionic exchange properties in relation to particle size should present evidence of a more conclusive nature. The relative increase in ionic exchange capacity of the bentonite with relation to particle size is not great when compared with the increase of the kaolinite fractions. The bentonite of 34 microns and less had an exchange capacity of 82.6 milliequivalents per 100 grams as compared with 88.0 for the 2 microns and less and 90.6 for the 0.2 micron and less fraction. This would indicate a difference of about 2.8 per cent between the exchange capacity of the 2 micron and 0.2 micron fractions. The values for the kaolinite indicated a 32 per cent difference in exchange capacity between the 2 micron and 1 micron fractions. The difference would probably be

even greater between the 2 micron and 0.2 micron fractions. The Fort Collins colloidal fraction indicated a difference of about 22 per cent in exchange capacity between the 2 micron and the 0.2 micron fractions, and for the same fractions soil 57-A showed a difference of 34 per cent in exchange capacity. The corresponding acid treated samples are not at variance to any extent with the differences in capacities as shown above.

Joffe and Kunin (24) reported no significant change in base exchange capacity in montmorillonite in relation to particle size. The procedure used by Joffe and Kunin allowed the colloidal material to stand for several days in suspension before the separations were made. This procedure would assuredly eliminate all particles except those smaller than 0.5 micron in diameter and possibly the sizes would be more limited depending on the shape of the sedimentation container.

Grim (17) gives the following values for base exchange capacity in milliequivalents per 100 grams of clay: montmorillonite 60-100, kaolinite 2-15, and illite 20-40. The spread in values is explained from the facts that all the members in a single group do not have exactly the same capacity and that for certain clay minerals the capacity varies with particle size. The experimental values using the 2-micron-and-less as representative

indicate that the methods used are comparable to current procedure and accepted standards. The value for the bentonite representing the montmorillonite group, in milliequivalents per 100 grams was 88.0, the kaolinite, 3.7, and for the illite, 25.6. The Fort Collins soil sample gave a value for the 2-micron-and-less fraction 54.3 milliequivalents per 100 grams, which does not fall within the limits of any of the accepted groups. The less than 0.2 micron fraction, however, gives a value of nearly 70 milliequivalents per 100 grams. Kelley (26) states that the exchange capacity of highly montmorillonitic soil colloids has rarely been found to exceed 75 milliequivalents per 100 grams, but does not define the limits of the colloid. Soil 57-A for the comparable 2-micron and less fraction had a value of 25.7. This value falls within the illite grouping, but the fact is not excluded that a mixture of kaolinite and montmorillonite might also give such a value.

From the previous discussion of particle size it was indicated that the kaolinite was rarely present in the less than 0.2-micron clay group. If then, the exchange capacity of soil 57-A in the less than 0.2-micron group is approximately 40 milliequivalents per 100 grams it would require an almost equal mixture of montmorillonite and kaolinite to obtain such a value. This would indicate

a weight of kaolinite present in soil 57-A in much larger quantities in the fine clay fraction than was found in the pure kaolinite sample. The presence of illite then seems more probable than a mixture of kaolinite and montmorillonite.

It is of far more than passing interest to note that the percentage base exchange contributed by the sand and silt fractions of both the Fort Collins and 57-A soils is a very significant amount. The values from Table 3 indicate that the sand and silt of the Fort Collins soil (untreated) contribute 29.1 per cent of the total exchange capacity. The treated sample sand and silt fractions indicate a value of 25.4 per cent of the total exchange capacity. For soil 57-A the comparable values for the untreated sand and silt indicate 34.1 per cent exchange capacity, and for the treated, 27.2 per cent. If it were assumed that the sand and silt were contaminated with enough clay particles to account for the exchange values, it would be found that the total clay percentage would be so high as to classify the soils as being far heavier than they possibly could be by any existing method.

For example in the untreated Fort Collins soil, if the entire base exchange capacity were attributed to the less than 0.2 micron fraction, 23.7 per cent of the

soil would necessarily fall in the less than 0.2 micron group as compared with 3.0 per cent by the mechanical analysis. If the entire base exchange capacity were attributed to the less than 2 micron fraction the total clay would amount to 30.5 per cent rather than 18.6 per cent as indicated by the mechanical analysis. Either of the calculated figures would place the soil in a heavy clay classification rather than a sandy loam as it is.

Joffe and Kunin (24) emphasized the importance of the silt fraction in its contribution to the exchange capacity of a soil. They calculated the probably clay fractions for a series of profiles upon the basis that only the clay contributes to the exchange. Their evidence is conclusive in showing that the clay fraction cannot be responsible for the total exchange of a soil. For a sample of Colt's Neck loam they assign 40 to 50 per cent of the exchange to the silt fraction.

From results of investigations conducted by Seay and Weeks(43) it was possible to calculate the percentage of exchange due to the sand and silt fraction of a Maury silt loam. A value of 35 to 45 per cent of the total exchange capacity was indicated.

Of the three investigations cited the present investigations give results for the exchange capacity of the sand and silt which are lower than the results of the

other investigations, but still assigning a significant portion of the exchange to the silt and sand. A wide variety of textural grades of soils are considered here. The Fort Collins is a sandy loam, the 57-A, a silty clay loam, the Colt's Neck, a loam, and the Maury, a silt loam. The second soil investigated by Joffe and Kunin was a Montaldo silt loam. This would indicate that the silt activity is of more than a localized origin, and possibly of far more importance than has been accredited to it up to this time.

In summarizing the implications drawn from the data of the mechanical analysis and the ionic exchange relations it appears that possibly montmorillonite is dominant in the Fort Collins soil and illite is strongly favored in the Grand Junction soil. From the ionic exchange relations it is implied that a considerable portion of the exchange capacity of both soils may be attributed to the fractions of the soil coarser than 2 microns in diameter.

Aside from this study, but lending support to it, Whitney (48) made a chemical analysis of the soil clay from the Western Colorado area, which would have the same parent material as soil 57-A. The analysis showed a percentage of 2.03 potassium oxide, while a bentonite sample from west of Fort Collins contained 1.13 per cent

potassium oxide.

Ross and Hendricks (39) indicate that hydrous micas (illite) may have a potassium oxide content of from 1 to 11.8 per cent. In numerous analyses, which they present from several sources, the montmorillonite clays rarely reach 1 per cent potassium oxide and usually are much less.

This evidence would give additional support to the establishment of the presence of illite in soil 57-A.

Dyal (12) in a recent research report on the ethylene glycol retention method of estimating relative specific surface indicates that an approximate parallelism might be expected between the surface for retention of polar solvents and base exchange. He further indicates that the parallelism can only be approximate, however, for montmorillonite can vary in exchange capacity, as shown for instance when ferric ions are reduced in the lattice, and part of the surface of kaolinite minerals is probably neutral. He suggests that the degree of parallelism should be studied in detail.

The present study gives an opportunity for comparison of base exchange with relative specific surface as well as giving aid in identification of the clay minerals of the soils.

The reproducibility of the method is evident

from the use of the Wyoming bentonite in both investigations. Dyal uses this bentonite as a comparison for all of his work and indicates a value of 0.24 grams of ethylene glycol retained per gram of unheated clay. For the same sample the results of the present experiment indicate a value of 0.25 grams of ethylene glycol retained per gram of clay. Both values were obtained after the unheated samples were subjected to a vacuum of less than 0.1 millimeters of mercury for 24 hours. Dyal indicates that a difference of greater proportions could result depending on the method of treating the sample during the original drying period.

The values of unheated samples for 24 hours of evacuation in grams of glycol per gram of clay (less than 2 microns in diameter) as presented by Dyal indicate a variance of 0.223 to 0.273 in six clays of montmorillonitic origin. As shown in Table 7, the bentonite in the present investigation was found to have a value of 0.255. Dyal gives values for six illite samples which vary from 0.014 to 0.074 as compared with 0.036 for the illite sample herein examined. Two kaolinite samples examined by Dyal gave values of 0.014 as compared with 0.004 for the kaolinite sample herein examined.

Clay fractions of soils examined by Dyal gave retentions ranging from 0.043 to 0.175. These values are

compared with a value of 0.081 for the Fort Collins clay fraction, and 0.069 for the clay fraction of the soil 57-A.

It is well known that the high adsorptive powers of the montmorillonitic clays are due largely to internal surfaces and subsequent swelling of the parallel plate-like structure which makes up the crystal structure. This condition does not exist in the crystal structure of either the kaolinite or illite clays. Consequently when the various clays are subjected to high temperatures there is a resulting break down of the expanding lattice structure of the montmorillonite clays and the internal surfaces are no longer available for adsorption. This results in a loss of the retentive powers expressed in percentage ranging from 85 to 95 per cent of the original retention and in some instances cited by Dyal as even higher. Neither the kaolinite or illite clays experience such a loss upon heating because of their non-expanding type of crystal structure. Dyal indicates that samples of illite clay subjected to this treatment showed from no loss in retention of ethylene glycol to as much as 40 per cent. The kaolinite varied from 0 to 50 per cent loss in retention of ethylene glycol. However, in the method Dyal disregards differences where the loss was less than 0.005 gram of glycol per gram of clay. None of the

losses by kaolin then would be considered significant.

The values, as shown in Table 7, for the bentonite sample used in the present investigation experienced a loss of 92.2 per cent in retention of ethylene glycol, which corresponds to the value obtained by Dyal for the Wyoming bentonite. The illite sample showed a loss of 38.9 per cent in retention, and the kaolinite a loss of about 25 per cent. The Fort Collins clay experienced a loss of 66.6 per cent while that of the soil 57-A was 56.5 per cent. These values may to a degree correspond to the per cent internal surface.

The parallelism of the ethylene glycol retention of a clay with the ionic exchange capacity of the same clay is demonstrated effectively in Figure 2. Here the ionic exchange in milliequivalents per 100 grams of 2 micron and less particles is compared with the ethylene glycol retention in grams per 100 grams of the same size material. It is apparent that there is a certain degree of parallelism.

Hendricks and Alexander (19) use the differential thermal analyses for a basis of a semi-quantitative estimation of kaolinite in soil colloids, but do not believe that the thermal curves are sufficiently different for illite and montmorillonite to allow an unambiguous distinction between the two. Other investigations are in

general agreement with this, although Kelley et al. (29), assign a definite resemblance of several California soils to that of the bentonitic clays upon the basis of thermal curves, and do distinguish the bentonitic curves from those of the "x" clay mineral, now accepted to be illite or hydrous mica.

The curves of the Fort Collins and 57-A colloids of Figure 4 are best compared with the curves of the known clays by Figure 3. The curves of both of these figures are more easily interpreted by a breakdown into percentages of water loss over certain temperature ranges. These values are tabulated in Table 8.

It can be seen from this table that the kaolinite sample is distinctively characterized by this breakdown. From these values it would appear by means of comparison that kaolinite is not present in either of the soil colloids. In general the Fort Collins colloid more closely resembles that of bentonite, and the 57-A clay more nearly resembles the illite. However, a mixture of bentonite and illite could hardly be excluded in either of the soil colloids and perhaps is definitely supported.

In making comparisons it must be remembered that bentonite is only a representative of the montmorillonite group of clay minerals, and illite or hydrous mica is another group represented here by only one sample. It

appears that the bentonite and illite samples are fairly representative, or, to an extent, good "average" samples for the groups they represent.

On the other hand the clay minerals making up the Fort Collins and 57-A colloids might be "average" for the clay group they represent or their properties may cause them to be near the limits of a particular group. For these reasons probably no further comparison can be made.

The curves of Figure 9 are interesting conjectures, wherein a calculated curve of 50 per cent illite and 50 per cent bentonite is plotted and the curve of the Fort Collins colloid at a depth of 36 to 60 inches is practically super-imposed on it by merely reducing the percentage loss in weight scale by one-half. Figure 10 compares the 57-A colloid with a calculated 75 per cent illite and 25 per cent bentonite mixture. The resemblance is obvious, but the significance may be questionable.

A significant contribution, applicable to this study, was made by Kelley, Dore, and Page (28) in their studies of American alkali soils, when they demonstrated that the accumulation of saline and alkali deposits does not significantly alter the clay minerals of a soil. This would indicate then that the present study is not only applicable to soils affected by saline or alkali

deposits of the Grand Junction area, but to fertile soils as well.

It seems appropriate at this point to attempt a correlation which might lead to an identification of the clay minerals present in the soils under observation. The geologic origin of the Grand Junction soil, 57-A, gives definite support to the clay mineral as being illite, but neither of the other two groups are ruled out. For the Fort Collins soil, the indication from geologic studies might indicate a mixture of montmorillonitic and illitic materials.

The presence of the fine colloidal fraction is suggestive of montmorillonite in both soils, but does not exclude illite. The presence of kaolinite is not favored. The tendency can hardly be considered as more than suggestive of the presence of montmorillonite.

The actual ionic exchange capacities of the soil colloids give strong support of illite being present in the 57-A soil. The exchange capacity for the 2 micron and less material is nearly identical with that of the illite sample. However, a mixture of kaolinite and montmorillonite could give such a value, but is not probable because of the necessity of considerable amounts of kaolinite being present in the less than 0.2 micron fraction. The exchange value for the Fort Collins 2 micron

and less material falls half way between the values for illite and bentonite.

The studies of retention of ethylene glycol indicate that the Fort Collins clay falls above the limits for known illitic material, but not high enough to come into the range of montmorillonitic material. The 57-A clay falls just within the upper limit of the illitic material as cited by Dyal. Kaolinite retention is far below any of the other values. The percentage internal surface or retention caused by swelling calculated by the ethylene glycol retention, places the Fort Collins and 57-A samples between the montmorillonite and illite groups. The Fort Collins clay is about half way between the two groups, while the 57-A is somewhat lower and nearer to the values for illite.

Finally, evidence from the thermal curves appears to exclude kaolinite and probably favors a mixture of montmorillonite and illite for the Fort Collins soil colloid. The calculated curve of 50 per cent illite and 50 per cent bentonite strongly resembles the curve of the lower horizon of the Fort Collins clay, if such a calculated curve is permissible. The resemblance of the 57-A curve to that of a 75 per cent illite and 25 per cent bentonite is substantiated by the breakdown of the curve into percentages over specific ranges of temperature.

The evidence appears to exclude kaolinite from the Fort Collins soil colloid and favors a mixture of illitic and montmorillonitic material for this soil with possibly a mixture of near equal amounts. Although illitic material seems to be a logical make-up for the 57-A colloid, it could hardly be said that the evidence is conclusive in eliminating montmorillonite, but the presence of kaolinite seems extremely doubtful.

Perhaps the most profound implication of the entire study is a realization of the possibilities of the method offered for continued and allied studies, and the need for such studies. At the same time the limitations of the methods must be recognized.

X-ray diffraction patterns of the soil colloids would greatly facilitate, and it is hoped, confirm the findings of these investigations. It has been shown that throughout the literature the emphasis is placed on the x-ray analysis and differential temperature analyses because of the greater degree of certainty these methods offer.

The procedures as used in this investigation could be applied to good advantage to known samples of illite, and other materials of the kaolinite and montmorillonite groups. Data for definite mixtures of known clays and for soil colloids of identified clays would be

significant. It seems very probable that a classification of soils could thus be established and relationships set up so that a soil colloid might be quite readily classified.

Especially is this method promising in obtaining ionic exchange relationships relative to specific surface by the ethylene glycol method. The relationships should be investigated for clay fractions and sub-fractions as well as larger particles. The pipette method of obtaining samples offers a means of studying the relationships within a soil far better than obtaining fractions by centrifugation and drawing generalities which may be extremely biased and not present a true picture of the actual properties of a particular soil.

It does not seem premature in the light of these studies and the support offered by a very limited number of investigators, Joffe and Kunin being prominent among these, to point out the great importance of the silt fraction in the total soil. In nearly all of the literature the activity of the soil is placed directly upon the clay or colloidal portion. It is readily acknowledged that the activity of the clay is high in comparison with the activity of the silt or sand. It has been demonstrated, however, that even in soils with relatively high clay fractions the exchange capacity contributed by the silt and

sand is seldom less than one-fourth of the total, and has been demonstrated in other soils to be at least one-half.

It seems logical to propose then, that the silt fraction should be the object of as much investigation as has been placed upon the clay fraction. To a certain extent the silt fraction should be more easily investigated owing to the visibility of the particles by ordinary means. The avenues of research from the initial classification would be innumerable. Although complete separation of silt fractions is tedious, a modification of the sedimentation and pipette method might afford a means of obtaining fractions of soil large enough to actually test by plant growth the significance of the various fractions in supplying nutrient elements. A correlation of this with ionic exchange capacities and relative specific surface would provide a fascinating possibility for research.

Numerous other possibilities are evident for continued research with more than reasonable expectations of obtaining significant results.

Chapter VI

SUMMARY

In this study there has been an attempt to show, by various procedures, the relation of the ionic exchange phenomenon in certain soils and clays to the particle size, relative specific surface, and type of clay minerals present.

These studies were limited to a sample of fertile Fort Collins sandy loam, a non-productive silty clay loam from the Grand Junction area, and to identified samples of bentonite and kaolinite. A sample of illite was used in a few of the comparisons.

The procedure to obtain the particle size fractions was a modification of the Olmstead pipette method of mechanical analysis for soils. The soils and clays were fractionated into one sand, three silt groups, and three clay groups. Both acid and peroxide treated, and water washed samples were subjected to the mechanical analysis. Using the fractions from the mechanical analysis, the ionic exchange capacities were determined by a semi-micro adaptation of the ammonium acetate method.

Estimations of the relative specific surface

were established for the samples and fractions by the use of a recently developed method based on the retention of ethylene glycol under vacuum.

Dehydration curves of the samples and fractions were accomplished over a range of 20 to 800 degrees centigrade.

Data obtained as a result of these studies and comparison with the literature show that the silt and sand fractions of the soil may contribute from one-fourth to one-half of the total ionic exchange capacity, depending to a degree on the textural grade of the soil.

The exchange capacity of a soil can be approximated by the ethylene glycol retention under vacuum. A parallelism is observed between the exchange capacity and the relative specific surface as estimated by the ethylene glycol retention.

The Fort Collins soil colloid appears to be a mixture of montmorillonite and illite as a result of comparison of all the data. The colloid of soil 57-A may be illitic in nature, but it is impossible to rule out a mixture of possibly all three of the clay groups being present.

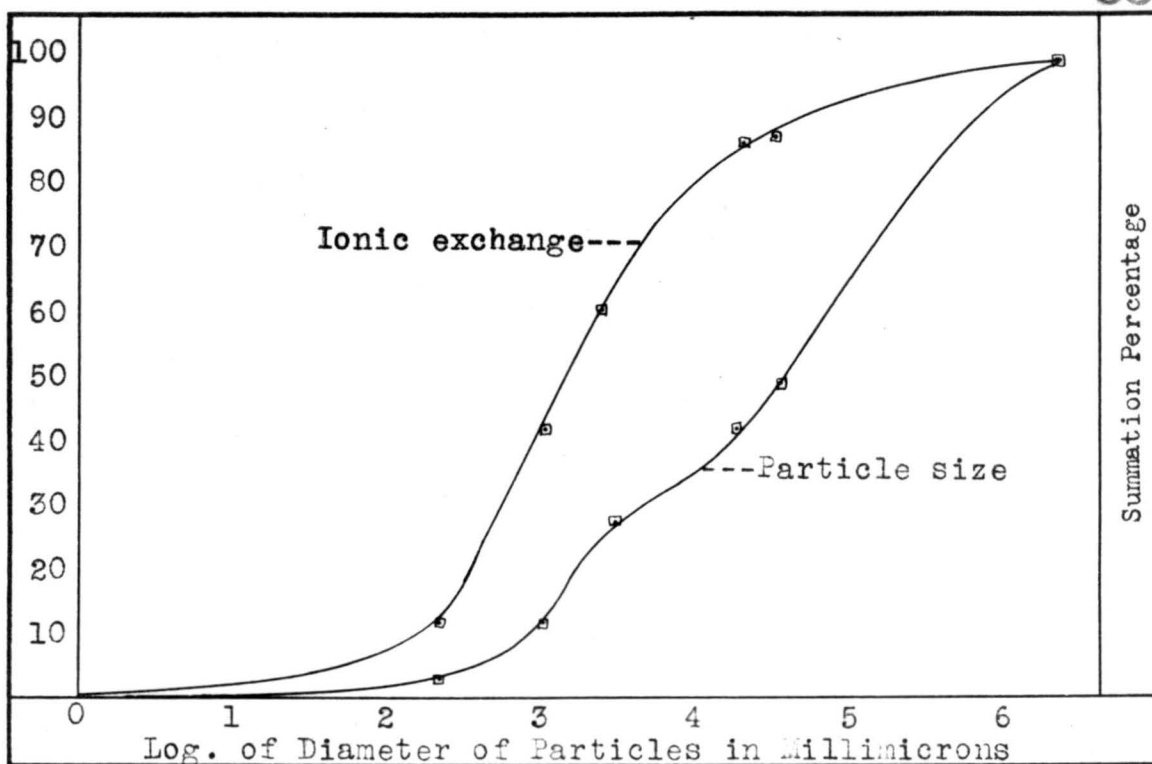
Important implications for continued study lie in the investigation of the activity of the silt fraction as indicated by its exchange capacity.

Classification of soil colloids by a combination of methods is suggested. The pipette method lends itself to a study of the soil with a minimum of bias. The retention of ethylene glycol by colloidal material is deserving of additional consideration.

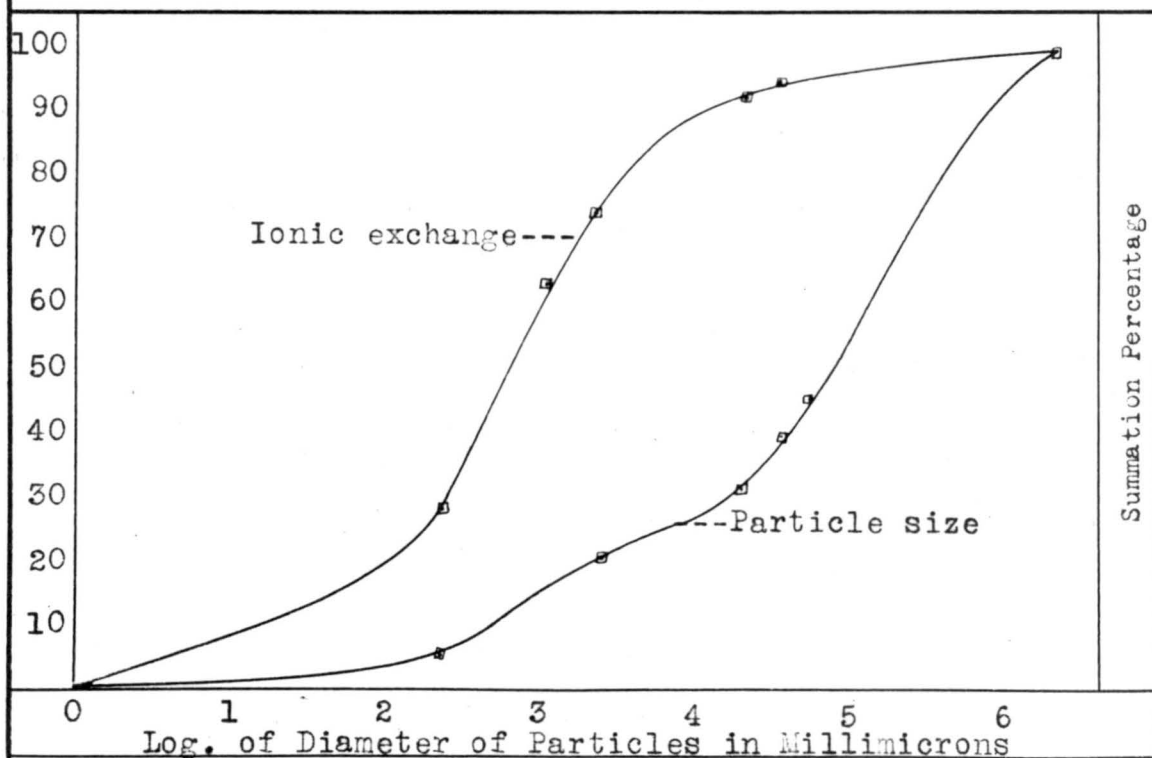
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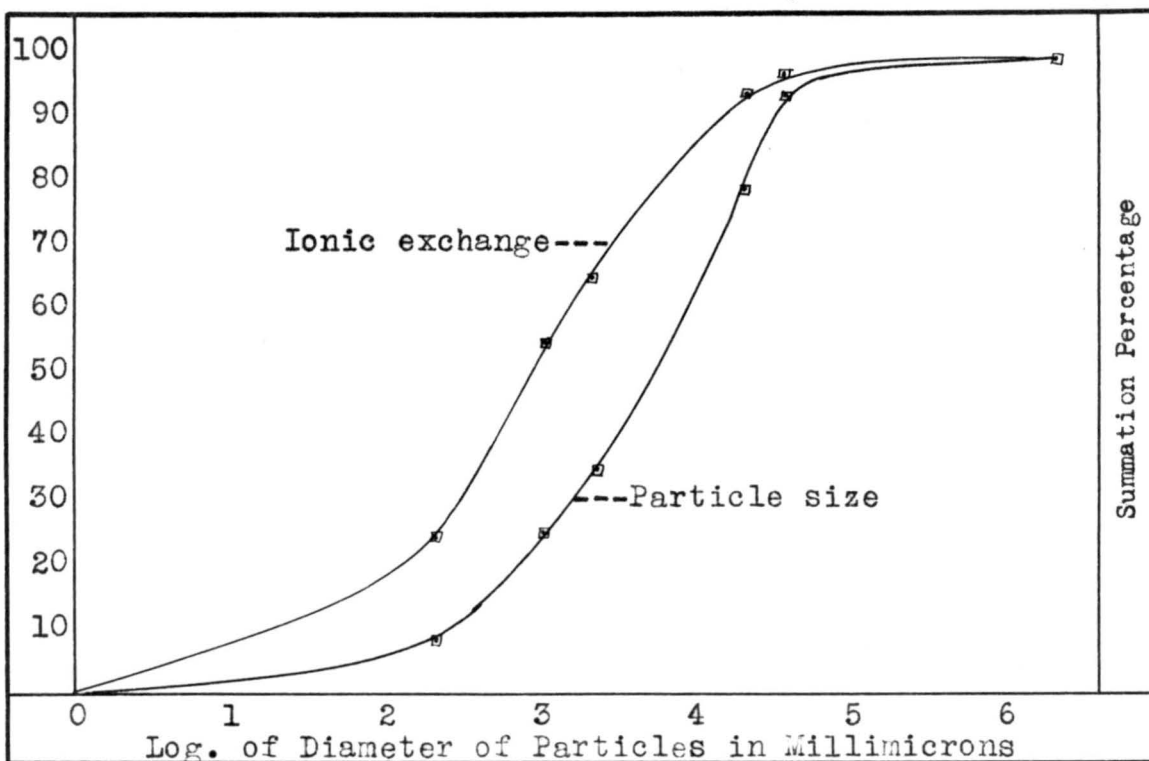
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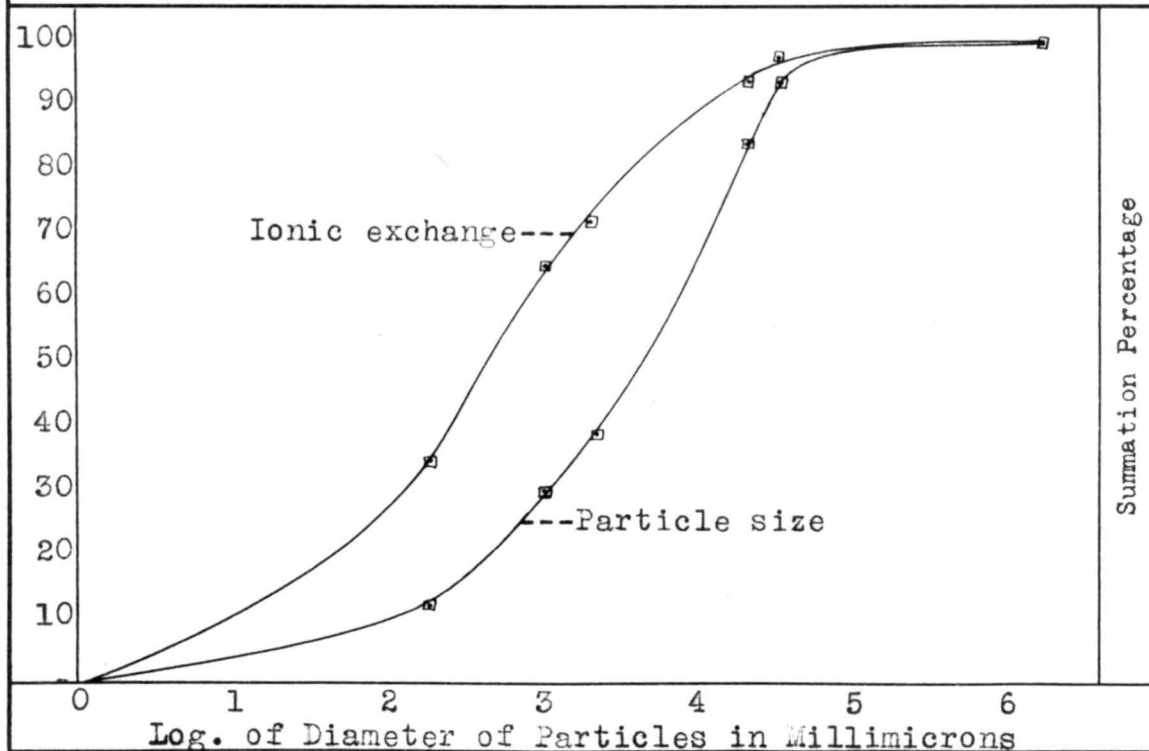
Distribution of particles and ionic exchange in untreated Fort Collins soil.



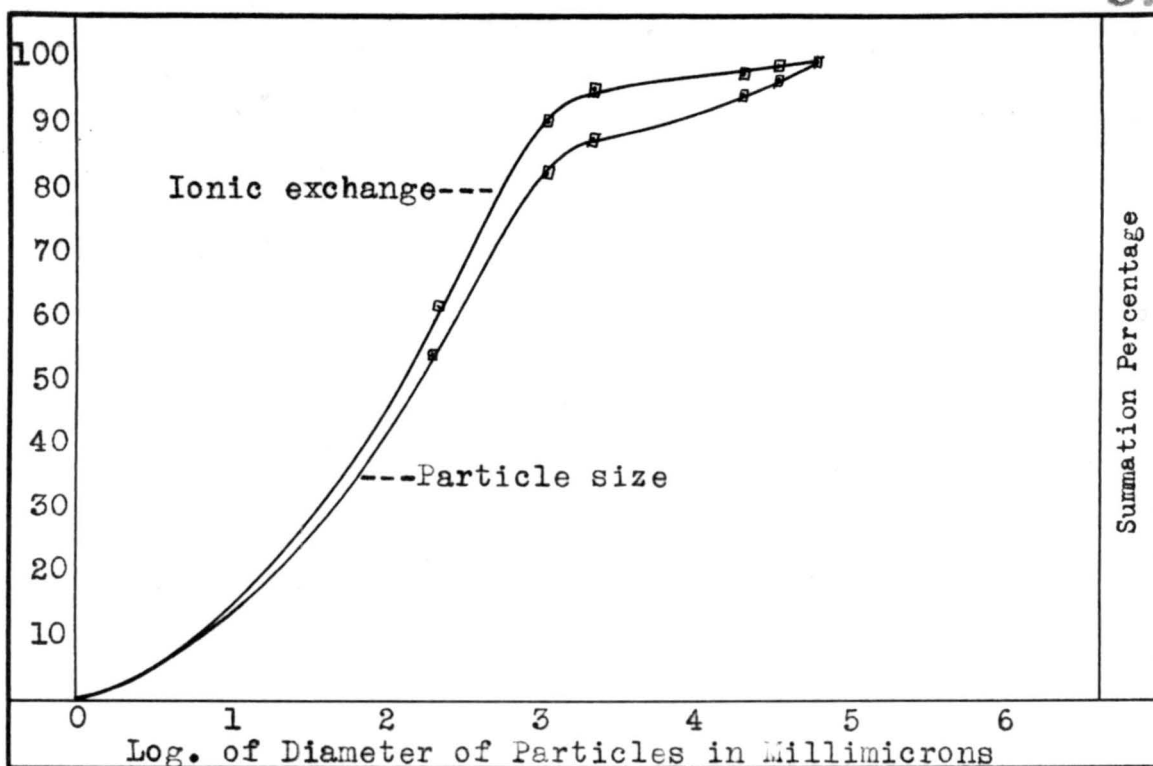
Distribution of particles and ionic exchange in treated Fort Collins soil.



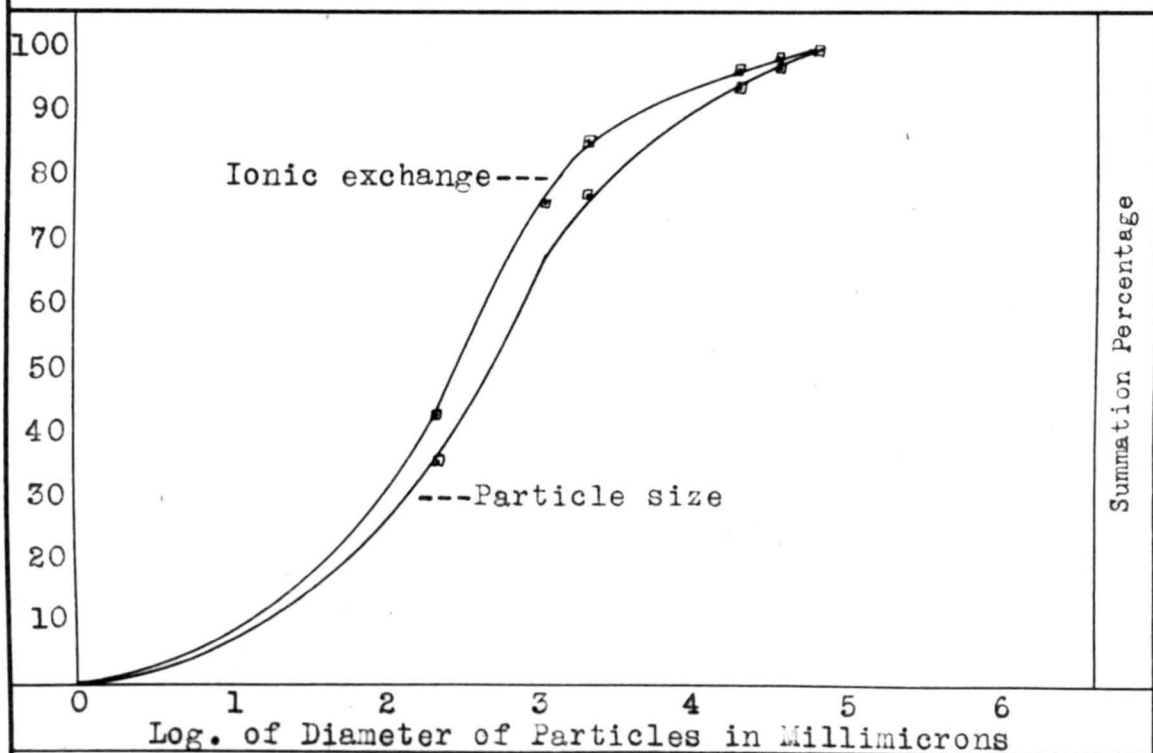
Distribution of particles and ionic exchange in untreated 57-A soil.



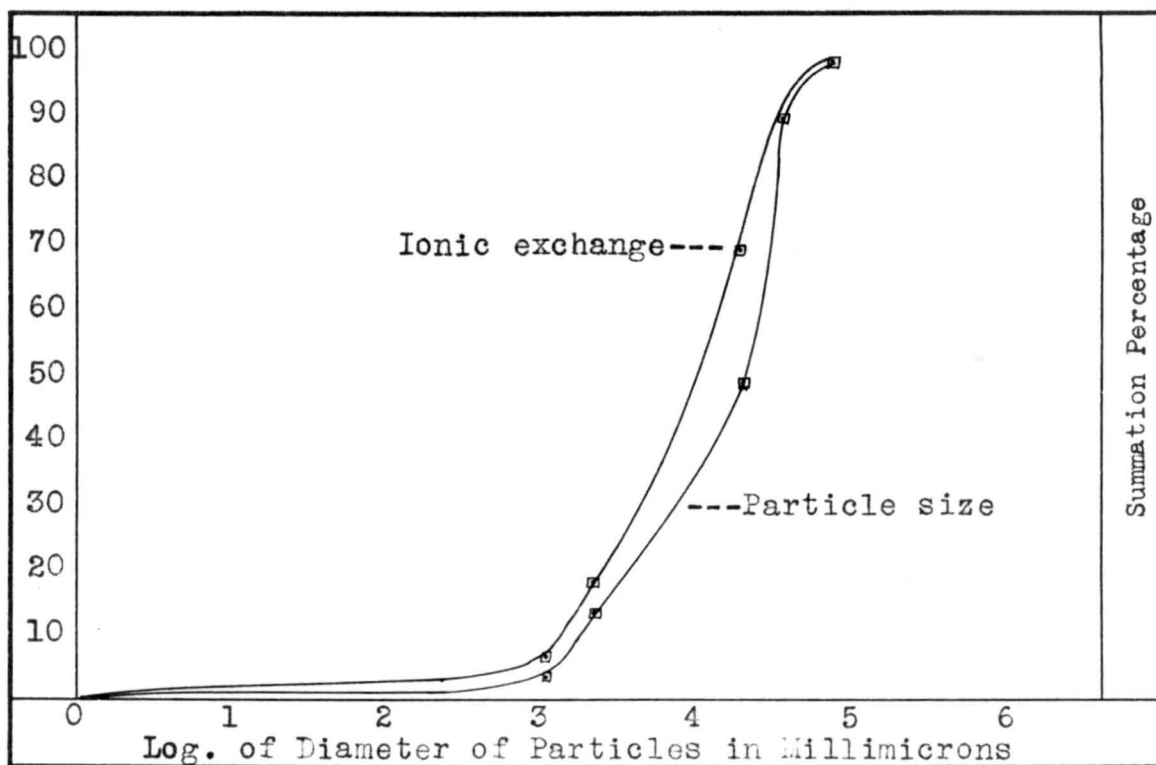
Distribution of particles and ionic exchange in treated 57-A soil.



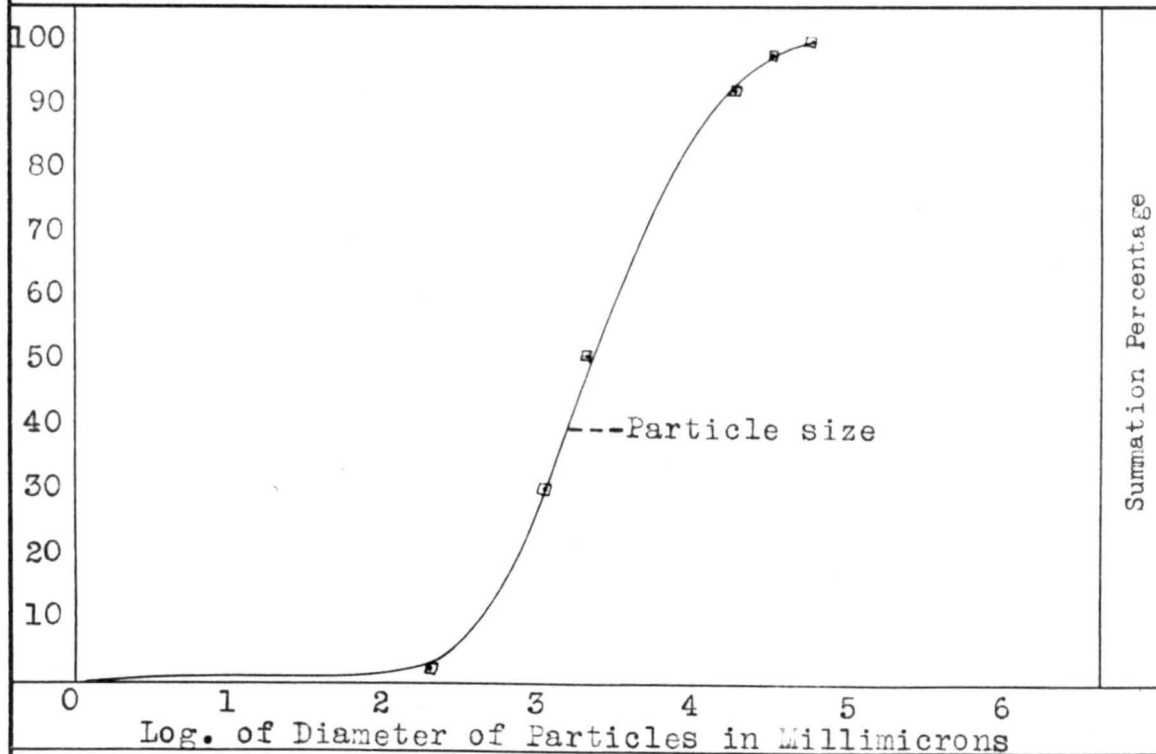
Distribution of particles and ionic exchange in untreated Bentonite.



Distribution of particles and ionic exchange in treated Bentonite.



Distribution of particles and ionic exchange in untreated Kaolinite.



Distribution of particles in treated Kaolinite.

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