

A STUDY OF THE CATION EXCHANGE CAPACITY AND  
TYPES OF CLAY MINERALS IN OKLAHOMA SOILS  
AND SOIL MATERIALS

By

R. T. SUTTON

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1950

Submitted to the Faculty of the Graduate School of  
the Oklahoma Agricultural and Mechanical College  
in Partial Fulfillment of the Requirements  
for the Degree of  
MASTER OF SCIENCE

1951

OKLAHOMA  
AGRICULTURAL & MECHANICAL COLLEGE  
LIBRARY

NOV 26 1951


A STUDY OF THE CATION EXCHANGE CAPACITY AND  
TYPES OF CLAY MINERALS IN OKLAHOMA SOILS  
AND SOIL MATERIALS

R. T. SUTTON  
MASTER OF SCIENCE  
1951

THESIS ABSTRACT APPROVED:

  
\_\_\_\_\_  
Thesis Adviser

  
\_\_\_\_\_  
Faculty Representative

  
\_\_\_\_\_  
Dean of the Graduate School )

283544

## ACKNOWLEDGMENT

The author is indebted to Dr. Horace J. Harper, Professor of Soils, Oklahoma A. & M. College, for his suggestions and guidance during the course of this study.

R. T. S.

## TABLE OF CONTENTS

	Page
INTRODUCTION . . . . .	1
REVIEW OF LITERATURE . . . . .	3
Origin of Clays and Clay Minerals . . . . .	3
Chemical Structure of Clay Minerals . . . . .	4
Specific Gravity of Clay Minerals . . . . .	6
Identification of Clay Minerals . . . . .	7
Base Exchange Capacity. . . . .	9
Measurement of Exchangeable Cations . . . . .	11
Purification of Clay Minerals . . . . .	14
Distribution of Clays and Shales in Oklahoma. . . . .	15
MATERIALS AND METHODS . . . . .	18
Sources of Materials . . . . .	18
Methods of Dispersing and Collecting Clay Fractions . . . . .	20
Method of Obtaining Clay Fractions. . . . .	22
Base Exchange Capacity Determinations . . . . .	23
Clay Fraction Determinations . . . . .	25
DISCUSSION OF RESULTS . . . . .	27
Mechanical Analyses . . . . .	27
Removal of cementing agents and Inert Material from Clay Fractions . . . . .	31
Cation exchange Determinations	
SUMMARY . . . . .	38
LITERATURE CITED. . . . .	40

## LIST OF TABLES AND FIGURES

	Page
TABLE I Description and location of soils and samples of soil material collected from twelve Oklahoma counties. . . . .	21
TABLE II Average quantity of clay two microns and less in diameter and pH values in duplicate samples of soil and soil materials . . . . .	28
Figure 1. Dispersion curves for particles with diameters of 2 microns or less in red shale from Perry, Oklahoma. . . . .	29
TABLE III A comparison of two methods of determining the cation exchange capacity of soils with neutral normal ammonium acetate. . . . .	34
TABLE IV Cation exchange capacities and calculated exchange capacities from mechanical analysis date of soils and soil materials and clay fraction from samples . . . . .	37

A STUDY OF THE CATION EXCHANGE CAPACITY AND  
TYPES OF CLAY MINERALS IN OKLAHOMA SOILS  
AND SOIL MATERIALS

INTRODUCTION

Clays are formed by chemical weathering processes acting upon complex silicate minerals. Type of climate and time are important factors which determine the kind of clay mineral produced. Climatic conditions in Oklahoma vary from fifty inches rainfall in the southeast to twenty inches in the Panhandle.

The major portion of Oklahoma is covered with different types of sedimentary rocks of varying geological age. The origin of these sediments and the climatic conditions which affected the formation of the clays in them is unknown.

Clay minerals have different physical and chemical properties. Consequently they have an important influence on the physical and chemical character of soil in which they are found. Very little information is available on the types of clays which occur in the sedimentary rocks in Oklahoma. Sheerar (68) made a study of clays in relation to their suitability for ceramic materials. Middleton, Slater and Byers (51) analyzed a soil colloid extracted from Vernon fine sandy loam near Guthrie, Oklahoma.

Most of the clays in Oklahoma are quite plastic, which could indicate that they have not been subjected to strongly

acid weathering. This study was conducted to obtain more information on the kind of clay minerals present in various climatic belts and in different geological formations.

## REVIEW OF LITERATURE

### Origin of Clays and Clay Minerals

Sheerar (69) defined clays as weathered products of silicate rocks, containing sufficient hydrous silicate or alumina to produce a plastic or semi-plastic mass when tempered with water. He stated that clays are found in nature as decomposition products resulting from alteration of silicate minerals which make up the rocks of the earth's surface. According to him, the accumulation of clays depends upon the magnitude of erosion and sedimentation. He listed two geologic types of clays, classified according to origin, as follows: a. Residual clay superimposed upon parent material. b. Transported clay appearing in marine, lake, alluvial, glacial and wind deposits. In addition to the above types, he also recognized alteration clay which has undergone modification as a result of the action of percolating waters and temperature changes.

Kaolinite Group. Ross and Kerr (65) named feldspars as the chief source of kaolinite with augite and biotite as minor sources. They postulated profound leaching, action of sulfate waters and hydrothermal action as the processes that are responsible for the formation of kaolin minerals. Acid solutions up to 350 degrees C, high aluminum, and low potassium were factors named by Folk (17) as favoring the formation of kaolin minerals. He stated that kaolin is formed near the surface by



acid waters and may replace sericite through leaching with carbonate and sulfate waters.

According to Ross and Hendricks (64), the formation of the kaolin group of minerals is favored by:

- a. Oxidizing conditions.
- b. Ferric iron in parent material.
- c. An acid environment.
- d. Wet, warm climate.

Montmorillonite Group. The following conditions were mentioned by Ross and Hendricks (64) as favoring the formation of montmorillonite:

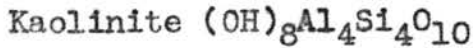
- a. Alkaline conditions.
- b. Salts of alkalies and alkaline earths, especially magnesium.
- c. Presence of ferrous or ferric iron.
- d. Presence of necessary silica and alumina.
- e. Moderately high temperatures (200 degrees C) and a dry climate.
- f. Absence of potassium.

Illite Group. Folk (17) stated that illite can form under a variety of conditions. Muscovite, which is similar, but not identical to illite, forms at a temperature as low as 200 degrees C in slightly basic and acid solutions if potassium and aluminum are high.

#### Chemical Structure of Clay Minerals

The important clay minerals and their chemical formulas have been summarized by Grimm (21) (22) as follows:

## Kaolinite group.

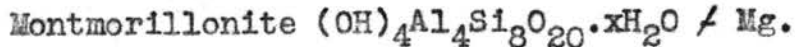


Dickite

Nacrite

Anauxite

## Montmorillonite group.

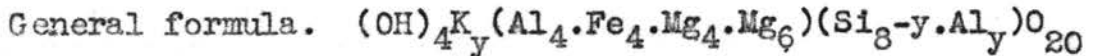


Beidellite. Lower Si and higher Al.

Nontronite. Al replaced by ferric iron.

Saponite. Al replaced completely by Mg.

## Illite group.



When y equals 2 and Mg and Fe are absent, the mineral is muscovite.

Silicates. Pauling (56) stated that in silicates each Si ion is surrounded by four oxygen ions (tetrahedron). According to Kelley and Jenny (40), each oxygen ion is part of an adjacent tetrahedron in quartz. The negative charges of the oxygen ions are balanced by the positive charges of the silicon ions and the compound is neutral except on the surface.

Amphiboles. Some of the oxygen ions lie between two silica ions and some are attached to silica on one side only. Enough metallic ions are present to balance the remaining oxygen ions (40).

Alumino-silicates. Aluminum ions are present in tetrahedra, being surrounded by four closely packed oxygen ions. The aluminum bears only three positive charges, therefore an

alumino-silicate mineral must contain additional cations (bases). In orthoclase, biotite and muscovite, potassium makes up the major portion of the additional base. Sodium performs this function in albite, analcite and natrolite. Calcium makes up the additional base in anorthite (40).

Pyrophyllite. Each aluminum ion is surrounded by four oxygen ions and two hydroxide ions (40).

Kaolinite. Each aluminum ion is surrounded by four oxygen ions and two hydroxide ions. The aluminum is said to occur in the octahedral position and the positive charges of silica and aluminum are balanced by the negative charges of the oxygen and hydroxide ions. As a result, these minerals contain no bases (40).

Chlorites. Pauling (55) stated that chlorites are made up of alternating layers of brucite and mica consisting of two tetrahedral layers and two octahedral layers.

#### Specific Gravity of Clay Minerals

Early work by Haines (23) indicated that the specific gravities of clay minerals in soils range from 2.2265 to 2.637. Makower, et al. (45) found the following specific gravities, montmorillonite, 2.53; bentonite, 2.74 and halloysite, 2.55.

Recent work by DeWit and Arens (13) indicates that the densities of clay minerals are drastically affected by hydration. They reported that montmorillonite varied from a density of 2.348 when oven-dry to 1.772 at 100% relative humidity. Kaolinite varied from a density of 2.667 when oven-dry to 2.427 at 100% relative humidity. Illite varied from a density of 2.642 when oven-dry to 1.48 at a relative humidity of 100%.

### Identification of Clay Minerals

Kelley (38) has presented a brief review of the most important methods used in the identification of clay minerals.

Data presented by Hendricks and Fry (30) which indicated that the fine-grained inorganic material of soils is crystalline, paved the way for further research into clay minerals by means of the X-ray.

Jackson and Hellman (32) found that distinct X-ray diffraction patterns were obtained by saturating montmorillonite with calcium ions.

In general, it may be said that identification of clay minerals by X-ray analysis is based upon the fact that the diffraction patterns of (001) spacings of each clay mineral are distinctive (38). This is one of the most widely used methods.

Dehydration methods for the identification of clay minerals have been used by Nagelschmidt (54) and Ross and Kerr (65). The loss in weight of a soil colloid upon heating to a higher temperature is recorded and plotted against temperature. The resulting curve is then compared with the curve obtained from standard minerals.

Jeffries (34), Alexander, et al. (1), Kelley and Page (41), Russell and Haddock (66), and Hendricks and Alexander (26) have presented much detailed data obtained from differential thermal analysis of clay minerals. This method of identification is based upon the fact that as clay minerals are heated to higher temperatures volatilization of water is accompanied by absorption of energy which is reflected by a reduction in temperature;

oxidation of carbonaceous material and certain molecular rearrangements set energy free and result in gains in temperature. Endothermic reactions at certain temperatures are specific for certain clay minerals.

Pennington and Jackson (57) made use of differential electrophoresis as a method of identifying clay minerals.

The fact that montmorillonite preferentially absorbs cerium ions was used as the basis for a method of identification by Hendricks and Alexander (27).

Ross and Hendricks (64) made use of the optical properties of clay minerals as a method for identification. The index of refraction of montmorillonite and kaolinite is fairly distinct. However, this method is not well suited for general use.

Clay mineral identification by the electron microscope was discussed by Kelley (38), who stated that the hexagonal plates of kaolinite can be easily distinguished from the needle-like crystals of halloysite. Montmorillonite and hydrous mica are difficult to identify because of their irregular shaped crystals.

Kelley (38) also stated that the chemical analysis of a clay cannot be used to identify the mineral present because samples are usually mixtures of different minerals and that the ratios of elements may vary in the purest samples.

Base exchange capacities have often been used as criteria for determining the clay minerals that are present in clays. According to Kelley (38), base exchange capacities are difficult

to interpret in terms of clay minerals because the exchange capacity varies according to particle size and samples are usually composed of mixtures of minerals.

Hendricks and Alexander (28) used benzidine hydrochloride as a qualitative color test for montmorillonite. This color test is supposed to identify montmorillonite in the presence of other clay minerals.

Dyal and Hendricks (15) (16) (29) have recently worked out a method of measuring the total surface of clays by the retention of ethylene glycol. Total surface has been proposed as a characteristic index of certain clay minerals.

#### Base Exchange Capacity

In 1922, Gedroiz (20) reached the conclusion that inorganic exchange material of soils is composed of fine-grained rock fragments or precipitated colloidal silicic acid. He concluded that both types are probably present in soils. Two possibilities of origin were as follows, (a) particles weather into colloidal particles with high specific surfaces, and (b) colloidal hydroxides of silicon, aluminum, and iron may mutually precipitate to give mixed gels.

Perkins (55) has interpreted base exchange capacity to be a function of surface area because grinding kaolin markedly increased its cation exchange capacity.

Kerr (42) stated that  $H_2O(Al_2O_3 \cdot 6SiO_2) \cdot 8H_2O$  is possibly the predominant, if not the only, mineral involved in inorganic base exchange.

Mattson (46) (47) believed that the exchange complex was colloidal in nature and postulated the isoelectric precipitation theory. According to him, these precipitates are composed of aluminum and iron hydroxides combined in various ways and proportions with silicic acids. The manner of combination depends upon the proportion of basoid and acidoid and on the pH of the medium. The precipitate formed will tend to have a composition which is most nearly isoelectric at the prevailing pH.

Ross and Hendricks (62) (64) and Hendricks and Fry (30) have done much fundamental work in regard to the crystal structure of clay in relation to cation exchange capacity. Hendricks (25) has stated that base exchange is determined by two competing factors, (a) internal compensation of charge, and (b) compensation of charge by cations external to a lattice layer.

The conditions essential to ion exchange were named by Kelley, et al. (40) as physical accessibility of the ion and strength of the force by which the ion is held to the lattice.

The crystal structure of base exchange materials has been summarized by Kelley (38) as follows:

Clay minerals are platy and characterized by a layer lattice structure. Layers are composed of planes of silicon ions in which each silicon ion is situated at the center of a tetrahedron formed by four oxygen ions, and planes of aluminum, iron, or magnesium ions surrounded by six oxygen or OH ions arranged in the form of an octahedron."

Pyrophyllite, according to Kelley, is electrically neutral and unable to attract ions except by weak forces. In the case

of muscovite, potassium ions hold the layers together and are prevented from entering into an exchangeable form. In montmorillonite the (001) spacings are a function of water content. It is probable that cation exchange properties in this mineral are due to negative charges occasioned by a deficiency of positive charges in the octahedral layer of the lattice. Beidellite is similar to montmorillonite. Not much is known about hydrous mica, but it is probably similar to montmorillonite. In kaolinite and halloysite, lattice charges are balanced internally. These minerals are unable to attract cations except by negative charges of terminal oxygen ions on the lattice edge.

Vanderford (76) studied loess samples from Iowa, Missouri, and Arkansas and found that (a) the base exchange capacity decreased with increasing rainfall, (b) was independent of particle size and (c) indicated a change in chemical composition of the clay corresponding to differences in climatic conditions under which the clay was formed.

#### Measurement of Exchangeable Cations

Various methods have been employed for the purpose of measuring the cation exchange capacity of soils and clay minerals. Usual methods consist of saturating the soil with an ion to replace the bases already present in the exchange complex and then measuring the quantity of ions absorbed from the solution. Neutral salt solutions are usually used since cation exchange capacity is a function of pH.

In 1918, Gedroiz (18) used normal ammonium chloride for replacing bases in soils. In a later paper, he stated that the



reaction between the ammonium ion and soil bases was very rapid. One minute was sufficient time to bring about equilibrium (19).

Schollenberger and Dreibelbis (67) recommended the use of normal ammonium acetate for determining base exchange capacity because of its ease in replacing cations and the simplicity of the technique involved. They found that leaching a soil gave slightly higher values than extraction methods. Schollenberger and Simon (68), in a recent paper, have recommended two normal ammonium acetate for base exchange capacity determinations.

Bray (8) recommended the ammonium acetate method, but suggested that the soil should be leached with 0.1 normal hydrochloric acid after saturation and subsequent removal of the excess ammonium acetate from the soil with alcohol. The ammonium ion is distilled from the acid extract and measured by absorption in a standard acid.

Golden, et al. (20) found that the potassium or barium acetate method was superior to ammonium acetate in measuring total base exchange capacity.

Borland and Reitemeier (4) made studies with radioactive calcium to determine speed and efficiency of equilibrium between calcium saturated soils and the ammonium ion. They found that the equilibrium of calcium between the solution and solid fraction of aqueous systems of kaolinite, halloysite, hydrous mica, beidellite and montmorillonite is complete or virtually

so after thirty minutes to one hour. Saturation methods were used.

Mehlich (49) (50) compared ammonium hydroxide, ammonium acetate, barium acetate and barium chloride-triethanolamine for determining exchange capacities on a variety of soils and clay minerals. He concluded that the true exchange status cannot be correctly determined in the presence of carbonates by the ammonium acetate method. According to him, 0.2 normal barium chloride buffered at pH 8.2 with triethanolamine should yield maximum values for base exchange capacities.

Kelley (38) stated that cation exchange capacities at pH 7.0 of inorganic soils are most accurately determined with an acetate solution such as ammonium acetate or barium acetate. He said that reasonably accurate exchange capacities can be determined with this method in the presence of carbonates.

Mukherjee, et al. (53) calculated base exchange capacities from curves of hydrogen saturated kaolinite titrated with metal hydroxides. They obtained values of 5.05 at pH 7.0, 13.0 at pH 8.0, and 23.0 at pH 9.0. The same type of experiment was performed by Mitra, et al. (52), who worked with hydrogen-saturated montmorillonites and bentonites and obtained values from 52.5 to 62.5 at inflection point.

A method for the rapid determination of base exchange was presented by Rendig (60). The soil was saturated with a potassium acetate solution, then exchangeable potassium was extracted and determined with a flame photometer. This method gave slightly higher capacities than the ammonium acetate method.

Electrodialysis has been used as a method of determining base exchange capacity, but it is tedious and time consuming. Humfeld and Alben (31) have presented a study of the method.

Caldwell and Marshall (9) found the following base exchange capacities: nontronite, 57.0 to 64.3; attapulgite, 18.0 to 22.2; and saponite 69.3 to 86.3.

Bower and Truog (5), using ammonium acetate, found the cation exchange of montmorillonite, 116.7; bentonite, 90.0; beidellite, 80.0; and illite, 24.2 m.e./ 100 grams.

Grimm (21) (22) listed the following cation exchange capacities:

Kaolinite	3.0 to 15.0
Halloysite	6.0 to 10.0
Illite	20.0 to 40.0
Attapulgite	25.0 to 30.0
Montmorillonite	60.0 to 100.0

The following cation exchange capacities were found by Kelley and Jenny (40):

Talc	trace
Albite	1.0
Anorthite	2.0
Biotite	3.0
Pyrophyllite	4.0
Orthoclase	5.0
Chlorites	6.0
Muscovite	10.0
Beidellite	50.0
Bentonite	126.0

#### Purification of Clay Minerals

A rapid method for removal of free iron oxides in soils prior to petrographic analysis has been described by Jeffries (35). The sample is treated with potassium oxalate and oxalic acid, and magnesium ribbon is used as a reducing agent.

Truog, et al. (74) have described a procedure for removal of colloidal binding and interfering agents present in soils prior to mechanical analysis. The addition of oxalic acid to a soil suspension containing sodium sulfide produces nascent hydrogen sulfide which speeds up the process of reduction of the iron oxides. The alkalinity of the sodium sulfide and the acidity of the oxalic acid help bring free alumina into solution. The alkalinity of the suspension also dissolves out colloidal silica. The sodium disperses inorganic base exchange material which may cause flocculation. Organic matter is removed by hydrogen peroxide.

They found that this treatment, if repeated, slightly lowered the exchange capacity of bentonite. It destroyed about 80% of the exchange capacity of nontronite, but had little effect upon the exchange capacity of true aluminum exchange material. The exchange capacity of true iron exchange material was largely destroyed. The more drastic treatment prescribed for lateritic soils lowered the exchange capacity of Lufkin clay.

#### Distribution of Clays and Shales in Oklahoma (69)

Igneous rocks of the Archean era are limited to the Wichita and Arbuckle Mountains. Near Tishomingo, small pockets of clays resembling kaolin have been reported.

Sedimentary rocks deposited during the Paleozoic, Mesozoic, and Cenozoic periods may be observed in the following formations.

Cambrian. The Reagan sandstone outcrops in the Arbuckle Mountains. The Collier shale outcrops in McCurtain County.

Ordovician. Considerable shale is found in the Simpson

formation which outcrops in the Arbuckle Mountains; The Sylvan shale outcrops in the Arbuckle Mountains region; other formations are the Stringtown shale and the Tyner formation which consists of shales, sandstones and limestone.

Mississippian. Mississippian rocks occur in three large areas of the State, the Ozark Mountain Region, the Ouachita Mountain Region, and the Arbuckle Mountain Region. In the Ozark Mountain region, the formation is composed of limestone and flint. In the Ouachita Mountains, the formation is composed of shales and sandstone. In the Arbuckle region, the formation is known as Caney shale.

Pennsylvanian. Pennsylvanian rocks occupy a broad area in eastern Oklahoma. In the southern and eastern parts of the area, the formation consists of sandstone and shale. Further north, limestone is interbedded with the shales and sandstones. The Labette shale lies within this area. The outcrops occur in a belt extending south from the Kansas line to Big Creek Valley, then to the junction of Big Creek and Verdigris River, then southwest to Broken Arrow. These shales have been used for brick.

Shales found in the Pennsylvanian System are quite variable. Some of them swell extensively when wet, while others have little to medium swelling characteristics.

Permian. With few exceptions, rocks of this formation outcrop over the entire western part of the State. The formations are generally known as Red Beds because of their color. In general, the Red Bed formations consist of red shales and

sandstones. The red color of the shales is due to ferric iron which forms a thin coating over the particles. The amount of iron varies from five to twenty per cent. These shales usually have high swelling properties. Considerable gypsum is found in the shales of the higher formations, running as high as fifty to sixty per cent. Dolomite is also found in the Woodward formation of this system.

Cretaceous. The principal area of Cretaceous rocks is in the southern part of the state, south and east of the Arbuckle Mountains. Formations in this area include the Trinity sand, which consists of conglomerate and sand with sandy clay and limestone. Shales in this formation are highly calcareous. Several shales occur in this system, one of which is the Bokchito formation of red and blue shale, with ferruginous sandstone and friable limestone.

Tertiary. Tertiary rocks occupy large areas in northwestern Oklahoma. The deposits are heterogeneous masses of clays, sand and gravel.

## MATERIALS AND METHODS

### Sources of Materials

Soils and soil materials were collected from thirteen counties in Oklahoma, ranging in location from the northeast to the southwest and from the northwest to the south-central parts of the state. The description and location of these samples is presented in Table I.

The Albion sample was collected from north of Pawnee. This series includes soils which have developed from beds of unconsolidated gravelly Tertiary and Quaternary formations. The material was probably originally transported from the Rocky Mountains, but also includes some material from local sedimentary rocks.

The Bethany sample was collected near Morrison. Soils of this series have developed on high stream terraces from reddish clays, silts or shales.

A calcareous shale was collected approximately seven miles north of Caddo in the Coastal Plains region and is of Cretaceous origin.

A sample classified as the B horizon of a Clarksville soil was collected east of Spavinaw in Mayes County.

The Craig soil sample was collected three miles northwest of Rose. Soils of this series have developed over residuum from cherty limestone in the Ozark Plateau.

The Denton soil was collected northwest of Durant. This soil has developed on interbedded limestone and marl under warm humid conditions.

The Foard soil was collected north of Lugert in Kiowa County. Soils of this series have developed on nearly level topography in the drier parts of Oklahoma from clayey Red Beds.

A sample of weathered granitic material was collected north of Tishomingo. This soil did not have a series name.

The Kirvin sample was collected south of Atoka. This soil has developed in the Red and Yellow Podzolic zone of the Gulf Coastal Plain.

Labette soil material was collected at Kaw junction on highway 77 in Kay County. This was a calcareous Pennsylvanian shale (69).

The loess-like sample was collected from weathered parent material in the eastern part of Kay County. It was mapped as Derby silt loam in the Kay county soil survey.

The Osage sample was collected west of Shidler in Osage County. This series includes soils that have developed on materials washed from areas of limestone and shale.

Two samples of Perry shale were collected from an exposure in the east edge of Perry. These shales are of Permian origin. The gray shale is an outcrop of the Wellington Formation (69).

The Portland sample was collected west of Clinton. Soils of this series have developed on alluvium from Red Beds.

The Prague sample was collected north of Stroud in Lincoln County. This is a claypan soil developed in reddish and yellowish



weakly calcareous to acid shales.

The Renfrow sample was collected from the Oklahoma A. & M. College campus. Soils of this series have developed from weakly calcareous Red Beds.

The Summit sample was collected from weathered parent material east of Nowata in Nowata County. Soils of this series have developed on limestone residuum and calcareous shale.

The Vanoss sample was collected east of Skedee in Pawnee county. These soils have developed from reddish aeolian or alluvial silty or loamy Pleistocene or Recent sediments that are relatively high in weatherable minerals.

A kaolinite sample from South Carolina and a kaolin sample from Georgia were obtained from the Oklahoma A. & M. College Soils Department. One sample of bentonite shale from Wyoming was obtained from the Oklahoma A. & M. College Geology Department. Another bentonite sample from Western Oklahoma was obtained from the Oklahoma A. & M. Soils Department.

#### Methods of Dispersing and Collecting Clay Fractions

Different soils and soil material may require different treatment to obtain a complete dispersion of the clay because of the presence of various cementing agents.

Robinson (62) found that the addition of hydrogen peroxide as an oxidation agent helped to prevent flocculation and gave increased clay contents in high organic matter soils. Similar methods have been used by Bodman (3), Thomas (72), Haskings (24) and Drosdoff and Miles (14).

TABLE I

Description and location of soils and samples of soil material  
collected from twelve Oklahoma counties.

Soil series or type of material	Color	Location collected	Description of Sample
Albion	reddish brown	North of Pawnee, Pawnee Co.	subsoil
Bethany	gray	Near Morrison, Payne Co.	subsoil
Calcareous shale	light gray	7 mi. N. of Caddo, Atoka Co.	surface soil
Clarksville	red	East of Spavinaw, Mayes Co.	B horizon
Craig	light gray	3 mi. NW of Rose, Mayes Co.	subsoil
Denton	very dark gray	NW of Durant, Marshall Co.	B horizon
Foard	gray	North of Lugert, Kiowa Co.	B horizon
Granitic material	brown	N. of Tishomingo, Johnston Co.	weathered parent material
Kirvin	yellow	South of Atoka, Atoka Co.	subsoil
Labette	lt. reddish br.	Kaw junction, highway 77, Kay Co.	weathered parent material
Loess-like material	lt. gray	Eastern part of Kay Co.	weathered parent material
Osage	dark gray	West of Shidler, Pawnee Co.	B horizon
Perry shale	light gray	Perry; Noble Co.	surface soil
Perry shale	lt. purplish rd.	Perry, Noble Co.	surface soil
Portland	red	West of Clinton, Custer Co.	weathered parent material
Prague	yellowish brown	North of Stroud, Lincoln Co.	B horizon
Renfrow	reddish brown	College campus, Stillwater, Payne Co.	weathered parent material
Summit	gray	East of Nowata, Nowata Co.	weathered parent material
Vanoss	light red	East of Skedee, Pawnee Co.	B horizon

The use of both hydrogen peroxide and dilute hydrochloric acid as dispersing agents has been recommended by Jeffries (34), Olmstead (55) and the Sub-committee of the Agricultural Education Association (70).

Beal (2), Puri (59) and Bouyoucos (6) have found that the addition of both sodium hydroxide and sodium oxalate helped prevent flocculation and gave increased clay contents in many soils.

Joseph and Snow (37) and Jackson, et al. (33) have used sodium carbonate as a dispersing agent. Sodium hypobromite has been recommended by Chakraborty(10) and Troell (73).

The use of sodium metaphosphate for the dispersion of podzolic, calcareous and southern red and yellow soils was recommended by Tyner (75).

#### Method of Obtaining Clay Fractions

From three hundred to six hundred grams of each sample were crushed, then dispersed 25 grams at a time in electric stirring cups. Five cc of normal sodium hydroxide and 5 cc of 0.4 normal sodium oxalate were added to each cup as dispersing agents. Distilled water was added and the sample was stirred for five minutes. This method of dispersion is similar to the one recommended by Bouyoucos (6).

After dispersion, the soil suspensions were poured into 18 liter glass bottles and distilled water added. The suspension was allowed to settle until all particles larger than 2 microns in diameter had moved downward 10 cm as calculated by Stoke's formula. Densities of clay particles were considered

\*cc = cubic centimeter

to be 2.33. This is the approximate density that DeWit and Arens (13) found for oven-dry montmorillonite. Corrections were made for changes in settling rates due to temperature changes. The top 10 cm of liquid was then siphoned into 1 liter beakers and calcium acetate in amounts sufficient to cause flocculation was added to each beaker. The supernatant liquid was then siphoned off and the excess water removed by evaporation on a steam plate.

Truog, et al. (74) has recommended that the colloidal binding and interfering agents be removed from clay fractions by the addition of oxalic acid to suspensions of clay containing sodium sulfide. All of the clays were subjected to this treatment.

#### Base Exchange Capacity Determinations

Soil and Soil Material. Five gram samples were placed in 400 cc beakers and ten cc of 30% hydrogen peroxide was added to each beaker. The beakers were then covered and contents digested on a steam place until reaction had subsided. Covers were then removed from the beakers and the excess liquid evaporated. This treatment was repeated, using 5 cc of hydrogen peroxide at a time, until oxidation of organic matter was apparently complete. Where reactions were too vigorous, 3 to 4 drops of 0.1 normal hydrochloric acid were added to each beaker.

After the excess liquid had been evaporated from the samples, 5 grams of silica flour, from which the finer particles had been removed by sedimentation and decantation, were

added to each beaker; 50 cc of neutral normal ammonium acetate was then added and the contents were stirred and allowed to set one-half hour.

The soil or soil material was then transferred to a Buchner funnel and leached under suction with 120 cc of neutral normal ammonium acetate solution. Each sample was then leached with 200 cc of neutral ethyl alcohol to remove the ammonium acetate without hydrolyzing the ammonia combined with the clay complex. This was followed by a leaching with 120 cc of 0.1 normal hydrochloric acid into a clean flask. The leachate was transferred to a Kjeldahl distilling flask and the volume made to approximately 300 cc with distilled water. Two and one-half grams of sodium hydroxide pellets and a piece of zinc metal were added to each flask and the contents were distilled into 0.1 normal hydrochloric acid to which had been added a few drops of a mixture of methylene blue and methyl red indicators. One hundred fifty cc of distillate was collected and titrated with standard sodium hydroxide. Blank determinations were run. This procedure has been presented by Bray (8).

Clay fraction. After treatment by the Truog process (74), 1 gram samples were mixed with 2 grams of silica flour, from which the finer particles had been removed, and placed in centrifuge tubes. Fifty cc of neutral normal ammonium acetate were added and each tube was shaken thoroughly at thirty minute intervals for two hours. The tubes were then centrifuged and the clear supernatant solution of ammonium was de-

canted. The above procedure was repeated twice at one hour intervals to obtain complete saturation of the clay complex. Each sample was washed four times in the centrifuge with 50 cc of neutral ethyl alcohol and transferred to a kjeldahl distilling flask. The volume was made to 300 cc by adding distilled water. One gram of magnesium oxide was added to each flask and distillations performed in the same manner as for soil samples.

#### Clay Fraction Determinations

Calcareous samples were treated with 100 cc of 0.1 normal hydrochloric acid to destroy carbonates and allowed to set overnight. They were filtered and washed with distilled water in a Buchner funnel and then treated as described in the following paragraph.

Ten gram samples were mixed with one tablespoon of coarse sand and placed in 400 cc beakers. Thirty percent hydrogen peroxide was added 10 cc at a time and the contents digested on a steam plate. Additional hydrogen peroxide was added 5 cc at a time until the organic matter was oxidized. Samples containing considerable amounts of manganese were treated with a few drops of glacial acetic acid during the digestion to prevent a rapid decomposition of the hydrogen peroxide. The samples were next washed with distilled water in Buchner funnels and the contents transferred to electric stirring cups. Five cc of normal sodium hydroxide and 5 cc of 0.4 normal sodium oxalate were added to each stirring cup; distilled water was added and the samples were stirred for 15 minutes. The

contents from the stirring cups were transferred to 1 liter cylinders. The cylinders were filled to 1 liter with distilled water and an additional volume of water equal to the volume of sand was added. The cylinders were shaken and allowed to set until only particles with a diameter of two microns or less and a density of 2.33 would be found at the 10 cm level as calculated by Stoke's Formula.

Twenty-five cc aliquots were removed from each cylinder at the proper time. Aliquots were taken accurately at 10 cm depths by a simple arrangement: a hole was bored through the center of a rubber stopper which was slightly larger than the diameter of the cylinder. The stopper was placed on top of the cylinder and a pipette pushed down through the hole until it barely touched the surface of the liquid. The pipette was withdrawn and a 10 cm distance was marked on it, measured from the top of the stopper. The pipette was then pushed through the hole to the mark. It was again placed into the cylinder and an aliquot withdrawn.

The aliquots were evaporated to dryness, weighed and a correction made for the weight of dispersing agent added.

## DISCUSSION OF RESULTS

### Mechanical Analyses

Results of the pipette analyses for clay content are recorded in Table II. Albion subsoil contained only 8.5% of particles 2 microns or less in diameter, which was the lowest fraction of any of the samples. On the other hand, the Clarksville subsoil contained 97.8% particles of this size. This sample was taken from the B horizon of the soil profile and a large percentage of hydrated iron oxide was present.

It was found that the addition of a tablespoon of coarse sand to a clay sample before dispersion would increase the percentage of clay obtained. The dispersion curves obtained from the red Perry shale with and without the addition of sand are shown in Figure 1. The addition of sand gave an average increase of slightly more than 3.0%. This gain in the clay fraction was probably caused by the mechanical action of the sand in breaking down clay aggregates.

The curve obtained from dispersion of red Perry shale with sand increased sharply up to approximately 20 minutes then leveled off, showing very little increase from 25 to 33 minutes. On the other hand, the curve obtained from dispersion without sand assumed a straight line characteristic and increased steadily from 5 to 33 minutes. These two curves show the difficulty in obtaining accurate information on the quantity of clay in a sample because of the incomplete dispersion



TABLE II

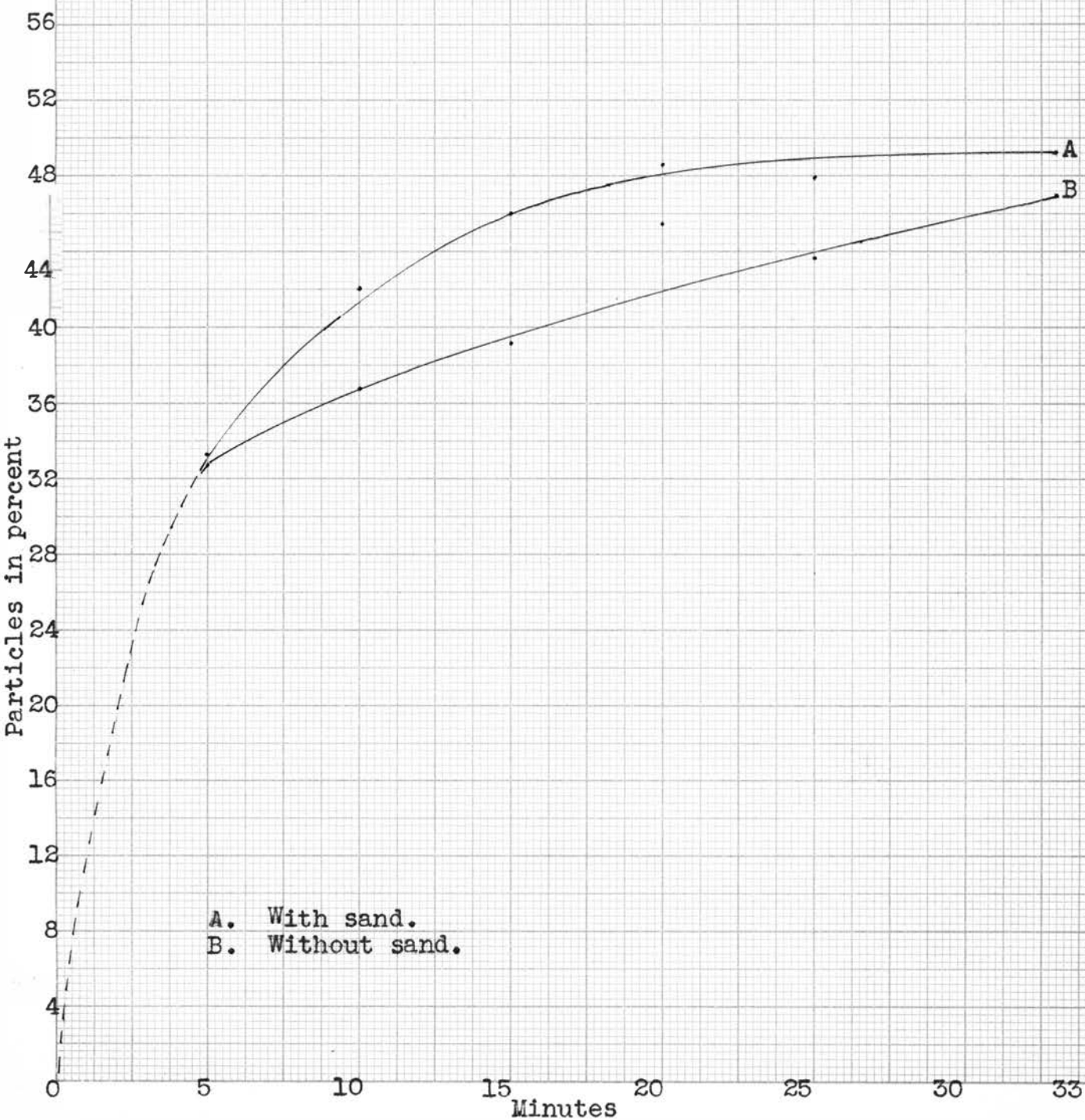
Average quantity of clay two microns and less in diameter and pH values in duplicate samples of soil and soil materials.

Sample	Percent of sample	pH values
Albion	8.5	5.8
Bethany	46.8	6.7
Calcareous shale*	62.9	7.3
Clarksville	97.8	4.0
Craig	22.5	4.5
Denton	46.6**	5.4
Foard*	41.1	7.7
Granitic material	28.9	6.3
Kirvin	22.5	5.0
Labette*	42.3	7.2
Loess-like material	24.2	7.2
Osage	32.9	5.9
Perry shale (gray)*	39.1	7.9
Perry shale (red)	45.9	7.8
Portland*	15.4	8.0
Prague	45.1	6.5
Renfrow*	31.0	7.4
Summit	36.4	5.7
Vanoss	31.4	5.1

\* Sample contained free calcium carbonate

\*\* Average of six determinations.

Figure 1. Dispersion curves for particles with diameters of 2 microns or less in red shale from Perry, Oklahoma



of the aggregated material. This can account for a considerable error in calculating the exchange capacity of a clay based on the exchange capacity of a soil in relation to the mechanical composition. Since the samples in this study were dispersed for 15 minutes and the blades on the dispersing machines had been reduced in size by abrasion, it is probable that the percentages of clay as recorded are too low in most cases.

An attempt was made to determine the clay fractions without washing the soluble salts from the samples following the hydrogen peroxide treatment, but considerable difficulty was experienced with partial or complete flocculation. This was probably caused by the presence of large amounts of soluble divalent ions in the calcareous soils. The flocculation of some of the acid soils was probably caused by salts produced by the small amount of glacial acetic acid added during the hydrogen peroxide treatment. The removal of soluble salts by washing the samples in a Buchner funnel eliminated this difficulty, and duplicate results agreed rather closely in most cases.

Wide differences were obtained in the amount of clay present in a sample of Denton subsoil. Six determinations were made and the results were averaged. This sample was high in calcium and organic matter content. Consequently the incomplete removal of soluble salts may have caused partial flocculation.

## Removal of cementing agents and Inert

### Material from Clay Fractions

An attempt was made to use the technique recommended by Jeffries (35) for removing iron oxides from the samples because of its simplicity. This method did not remove all of the iron from the Red Beds material, as evidenced by the red color that remained after treatment. This method would probably be satisfactory if it were applied to soils with smaller amounts or less resistant forms of iron oxide.

Little difficulty was experienced with the Truog method (74). However, it was necessary to use the drastic treatment which he recommended for lateritic soils on several of the samples. Iron compounds were more difficult to remove from Red Beds material than from samples obtained from other geological parent material. Although the Clarksville sample was collected from a zone of  $\text{Fe}_2\text{O}_3$  accumulation, the iron compounds in this soil were relatively easy to remove.

The colors of all but three of the clays were changed to white or very light gray after treatment. However, the Denton, Osage and Bethany samples ranged in colors from light gray to gray. Incomplete oxidation of resistant types of organic matter could account for these slightly darker colors. The clay fractions seemed to be well dispersed, crushed easily, and assumed a fluffy, powdery physical state after treatment.

### Cation exchange Determinations

Difficulty was experienced in obtaining closely agreeing results of cation exchange determination on the same sample.

The principal problem encountered was the inability to leach or extract all the excess ammonium acetate from samples before distilling. Mixing the sample with Celite filter-aid improved, but did not correct this condition. However, mixing silica flour with the sample improved filtering and washing to the extent that closely agreeing duplicates could be obtained. It was found that the addition of ethyl alcohol in small amounts at a time was the most efficient means of removing excess ammonium acetate from the sample.

As indicated under methods of procedure, the cation exchange capacities of the clay fractions were obtained by a slightly different method than used for the soils and soil material.

Table III. indicates that differences in the results obtained by these two methods were slight, the Bray (8) procedure giving slightly lower values than the method suggested by Schollenberger (67).

A comparison between cation exchange capacity of the samples studied as found by analysis and that obtained by calculation is given in Table IV. Calculated values were obtained in the following manner:

Calculated values for cation exchange capacities of the clays are probably too high in most cases because of incomplete dispersion of the original sample. Figure 1. indicates that the dispersion values are approximately  $6\frac{1}{2}\%$  too low. However, in some cases this figure may be exceeded because

some of the samples were dispersed with an electric stirring machine on which the stirring blades were well worn.

The presence of silt and other unweathered exchange material could have slightly increased the exchange capacities in the soils and soil materials which would be reflected in the calculated values. Kelley and Jenny (40) found that finely ground feldspar had a cation exchange capacity of 91.5 m.e./100 grams and that finely ground mica had cation exchange capacities from 72.5 to 76.0 m.e./100 grams.

During the course of the evaporation of water from the clay fractions, it was impossible to prevent some of the clay fractions from drying around the edge of the beakers. This dehydration made subsequent dispersion difficult and may have caused a lower cation exchange capacity for some of the clay fractions.

The presence of iron-exchange material in the Clarksville clay and its destruction by the Truog process could account for the fact that its cation exchange capacity was higher than the calculated value.

An analysis of the data recorded in Table IV. shows that two of the samples had cation exchange capacities greater than 60 m.e./100 grams. This definitely indicates that the predominant clay mineral present was of the expanding 1:2 lattice type which is a characteristic of montmorillonite. The presence of these clay minerals agrees with the theory that Bethany soils have developed on high terrace positions under alkaline

TABLE III.

A comparison of two methods of determining the cation exchange capacity of soils with neutral normal ammonium acetate.

Name of soil*	Cation Exchange capacity in m.e./100 grams of soil	
	Ammonia distilled from soil with MgO	Soil washed with N/10 HCl and ammonia distilled from the acid
Kirvin	11.4	10.6
Bethany	37.8	38.1
Craig	13.3	12.7
Portland**	13.0	11.8

\* Treated with hydrogen peroxide to remove organic matter.

\*\* Contained free calcium carbonate.

conditions, and the clays of the granitic material have developed from the alkaline weathering of feldspars. Ross and Hendricks (64) have stated that these conditions favor the development of montmorillonitic types of clay minerals.

Cation exchange capacities indicate that illite was probably the predominant clay mineral present in five of the soils. However, exchange capacities of Kirvin subsoil and the calcareous shale sample indicate the presence of a mixture of montmorillonitic and other types of clay minerals. Clarksville subsoil and the two Perry shales showed the lowest cation exchange capacities. Field observations and pH values indicate that the Clarksville soil developed under an environment favorable for the formation of illite and kaolinite. Since the red and gray shales from the Perry area are unweathered sedimentary rocks, no accurate information concerning the climatic conditions under which they were formed would be available. These shales, however, would have an important influence on the type of clay mineral present in the soils which would develop on them. Ross and Hendricks (64) reported that illite developed under either an alkaline or an acid environment.

Illite would make up less than 50% of the clay minerals in twelve of the samples. These samples showed cation exchange capacities ranging from 50 to 57 m.e./ 100 grams. This relatively high exchange capacity would indicate the presence of some 1:2 lattice clays.



Data in this study indicate that present geological parent material and recent climatic environment have had no marked effect upon the type of minerals that are present in clays. This may be explained by the fact that little or no definite climatological data is available for the periods during the time of the development of these clay minerals.

The Albion, Renfrow and Ford soils have developed on Permian shales; Pennsylvania shales are the parent material of Prague and Labette soils; Osage, Summit and Denton soils have developed on limestone or calcareous deposits; alluvium from recently formed glacial flour may have been the parent material of the loess-like sample.\*

Ross and Hendricks (64) and Ross and Kerr (65) stated that both weathering processes and hydrothermal reactions have influenced the formation of particular types of clay minerals. They have also stated that the availability of iron, aluminum, silica, magnesium and potassium are important factors in the formation of many types of clay minerals. Previous climatic environment and the availability of elements during that period have undoubtedly influenced the development of clay minerals in Oklahoma.

\*Data from Division of Soil Survey, Agr. Res. Adm., U.S.D.A.

TABLE IV.

Cation exchange capacities and calculated exchange capacities from mechanical analysis data of soils and soil materials and clay fraction from samples.

Kind of sample	Exchange capacity in m.e./ 100 grams		
	Soil and soil material*	2 micron or less clay fraction**	Calculated values
Albion	5.9***	52.8***	69
Bethany	38.1	61.9	98
Calcareous shale	36.2	45.8	58
Clarksville	24.4	32.5	25
Craig	12.7	40.9	56
Denton	34.1	57.0	72
Foard	30.2	51.6	72
Granitic material	23.4	64.8	82
Kirvin	10.6	42.7	47
Labette	20.5	55.9	48
Loess-like material	18.5	52.8	76
Osage	21.4	53.8	60
Perry shale (gray)	19.0	29.0	48
Perry shale (red)	21.7	35.0	47
Portland	11.8	46.5	77
Prague	26.1	50.0	57
Renfrow	20.8	51.5	67
Summit	21.9	55.5	59
Vanoss	46.8	51.2	145
Bentonite shale (Wyo.)	69.1		
Bentonite shale (Okla.)	63.2		
Kaolinite (So. Carol.)	1.5		
Kaolin (Georgia)	5.6		

\* All samples treated with hydrogen peroxide to remove organic matter except the kaolin, kaolinite, and bentonite.

\*\* Subjected to the Truog treatment to remove free iron and aluminum oxides and colloidal silica.

\*\*\* All analyses in this column are averages of duplicate samples.

## SUMMARY

A study was made of nineteen samples of soil and soil material collected from different geological formations and climatic areas of Oklahoma. Cation exchange capacities were determined and clay fractions with diameters of two microns and less were isolated from the original samples. The clay fractions were treated to remove free iron and aluminum and colloidal silica from the inorganic base exchange material. Cation exchange capacities were then determined for the clays in an effort to identify the clay mineral that was present. An attempt was made to correlate climatic and geological environment with the particular type of clay mineral that was present in the different samples.

Cation exchange capacities indicated that two of the samples were composed largely of a montmorillonitic type of clay. Illite was indicated as the dominant clay mineral in five of the samples, while mixtures of illite in percentages up to 50 were indicated for the remaining samples.

There was no definite correlation between the type of clay mineral believed to be present and the geographical area from which the sample was collected. The reason for the lack of correlation was explained on the basis that climatic environments during previous geological periods have greatly influenced the development of the clay minerals found in many Oklahoma clays.

Data indicate that more complete dispersion of the aggregated material that was present in the samples studied would have resulted in more closely agreeing values between calculated cation exchange capacity and that found by analysis.

## LITERATURE CITED

1. Alexander, L. T., Hendricks, S. B. and Nelson, R. A.  
Minerals present in soil colloids: II. Estimations  
in some representative soils. *Soil Sci.*, 48: 273-  
279. 1939.
- ✓ 2. Beale, O. W.  
Dispersion of lateritic soils and the effect of or-  
ganic matter on mechanical analysis. *Soil Sci.*, 48:  
475-482. 1939.
- ✓ 3. Bodman, G. B.  
The hydrogen peroxide-hydrochloric acid treatment  
of soils as a method of dispersion in mechanical  
analysis. *Soil Sci.*, 26: 459-470. 1928.
4. Borland, J. W. and Reitemeier, P. F.  
Kinetic exchange studies on clay with radioactive  
calcium. *Soil Sci.*, 69: 251-260. 1950.
5. Bower, C. A. and Truog, E.  
Base exchange capacity determination as influenced  
by nature of cation employed and formation of basic  
exchange salts. *Soil Sci. Soc. Amer. Proc.* 5:  
86-89. 1940.
- ✓ 6. Bouyoucos, G. J.  
The hydrometer method for making a very detailed  
mechanical analysis of the soil. *Soil Sci.*, 26:  
233-238. 1928.
- ✓ 7. Bouyoucos, George J.  
A comparison of the hydrometer method and the pipette  
method for making mechanical analysis of soils, with  
new directions. *Jour. Amer. Soc. Agron.* 22: 747-  
751. 1930.
8. Bray, R. H.  
Base exchange procedures. Dept. of Agron., Agr.  
Exp. Sta., Univ. of Illinois, Urbana, Illinois.  
1942. (mimeographed).
9. Caldwell, O. G. and Marshall, C. E.  
A study of some chemical and physical properties of  
the clay minerals, nontronite, attapulgite and  
saponite. Univ. of Mo., Col. of Agr., Agr. Exp.  
Sta., Res. Bul. 354. 1942.
- ✓ 10. Chakraborty, Jugendra Nath  
The applicability of alkaline permanganate for oxi-  
dation of organic matter in soils for mechanical  
analysis. *Soil Sci.*, 42: 261-266. 1936.

11. Day, Paul R.  
Physical basis of particle size analysis by the hydrometer method. Soil Sci. 70: 363-374. 1950.
12. Deb, B. C. and Chowdhury, A. A.  
Failure of the international soda method in estimating clay in a subsoil, as revealed by the base-exchange capacity. Soil Sci. 68: 251-257. 1949.
13. DeWit, C. T. and Arens, P. L.  
Moisture content and density of some clay minerals and some remarks on the hydration pattern of clay. Fourth International Congr. of Soil Science, Trans., II: 59-62. 1950.
14. Drosdoff, M. and Miles, E. F.  
Action of hydrogen peroxide on weathered mica. Soil Sci., 46: 391-396. 1938.
15. Dyal, R. S.  
Total surface of clays in polar systems and a method for estimation of interlayer swelling. U.S.D.A., Agr. Research Adm., Bureau of Plant Ind., Soils and Agr. Eng., Research report No. 140. 1948.
16. Dyal, R. S. and Hendricks, S. B.  
Total surface of clays in polar liquids as a characteristic index. Soil Sci., 69: 421-432. 1950.
17. Folk, Robert L.  
The alteration of feldspar and its products as studied in the laboratory. Amer. Jour. Sci., 245: 388-394. 1947.
18. Gedroiz, K. K.  
Contribution to the method of determining zeolitic bases in the soil. Mimeographed and distributed by U.S.D.A. Published originally in Zhur. Opyt. Agron., 19: 269-244. 1918.
19. Gedroiz, K. K.  
On the absorptive power of the soil. Mimeographed and distributed by U.S.D.A. Published originally by Peoples Commissariat of Agr. 1922.
20. Golden, L. B., Gammon, N. and Thomas, R. P.  
A comparison of methods of determining the exchangeable cations and the exchange capacity of Maryland soils. Soil Sci. Soc. Amer. Proc., 7: 154-161. 1942.
21. Grimm, Ralph E.  
Relation of the composition to the properties of clays. Jour. of the Amer. Ceramic Soc., 22: 141-151. 1939.

22. Grimm, R. E.  
Modern concepts of clay material. Jour. Geol.,  
50: 225-275. 1942.
23. Haines, W. B.  
The volume-change associated with variations of  
water content in soil. Jour. Agr. Sci., 13: 296-  
300. 1923.
- ✓ 24. Hosking, J. S.  
The influence of hydrogen ion concentration on the  
decomposition of soil organic matter by hydrogen  
peroxide. Jour. Agr. Sci., 22: 92-100. 1932.
25. Hendricks, Sterling B.  
Lattice structure of clay minerals and some proper-  
ties of clays. Jour. Geol., 50: 276-290. 1942.
- ✓ 26. Hendricks, S. B. and Alexander, L. T.  
Minerals present in soil colloids: I. Descriptions  
and methods for identification. Soil Sci., 48: 257-  
271. 1939.
27. Hendricks, S. B. and Alexander, L. T.  
Semiquantitative estimation of montmorillonite in  
clays. Soil Sci. Soc. Amer. Proc., 5: 95-99. 1940.
28. Hendricks, S. B. and Alexander, L. T.  
Qualitative color test for the montmorillonite type  
of clay minerals. Jour. Amer. Soc. Agron., 32:  
455-458. 1940.
29. Hendricks, S. B. and Dyal, R. S.  
Surface measurement for ethylene glycol retention  
of clays and its application to potassium fixation.  
Fourth International Congr. of Soil Sci., Trans.,  
2: 71-72. 1950.
30. Hendricks, S. B. and Fry, W. H.  
The result of X-ray and microscopical examinations  
of soil colloids. Soil Sci., 29: 457-476. 1930.
31. Humfeld, H. and Alben, A. O.  
Electrodialysis of the soil I. A study of the  
method. Jour. Amer. Soc. Agron., 19: 984-993. 1939.
32. Jackson, M. L. and Hellman, N. N.  
X-ray diffraction procedure for positive differen-  
tiation of montmorillonite from hydrous mica. Soil  
Sci. Soc. Amer. Proc., 6: 133-145. 1941.
- ✓ 33. Jackson, M. L., Whittig, L. D. and Pennington, R. P.  
Segregation procedure for the mineralogical analysis  
of soils. Soil Sci. Soc. Amer. Proc., 14: 77-81.  
1949.

34. Jeffries, Charles D.  
A quantitative approach to the study of the thermal characteristics of clays. Soil Sci. Soc. Amer. Proc., 9: 86-91. 1945.
- ✓ 35. Jeffries, Charles D.  
A rapid method for removal of free iron oxides in soil prior to petrographic analysis. Personal Communication to Dr. Horace J. Harper, Okla. A. & M. College.
- ✓ 36. Jennings, D. S., Thomas, M. D. and Gardner, William  
A new method of mechanical analysis of soils. Soil Sci., 14: 485-499. 1922.
- ✓ 37. Joseph, A. F. and Snow, O. W.  
The dispersion and mechanical analysis of heavy alkaline soils. Jour. Agr. Sci., 19: 106-120. 1929.
38. Kelley, Walter P.  
Cation Exchange in Soils. New York: Reinhold Publishing Company. 1948.
39. Kelley, W. P. and Brown, S. M.  
Ion exchange in relation to soil acidity. Soil Sci. 21: 289-302. 1926.
40. Kelley, W. P. and Jenny, Hans  
The relation of crystal structure to base exchange and its bearing on base exchange in soils. Soil Sci., 41: 367-382. 1936.
- ✓ 41. Kelley, W. P. and Page, J. B.  
Criteria for identification of the constituents of soil colloids. Soil Sci. Soc. Amer. Proc., 7: 175-181. 1943.
42. Kerr, H. W.  
The identification and composition of the soil alumino-silicate active in base exchange and soil acidity. Soil Sci., 26: 385-398. 1928.
43. Kerr, Paul F.  
A decade of research on the nature of clay. Jour. of the Amer. Ceramic Soc., 21: 267-286. 1938.
44. Kerr, Paul F., Main, M. S. and Hamilton, P. K.  
Occurrence and Microscopic Examination of Reference Clay Mineral Specimens. Amer. Petroleum Institute, Research Project 49, New York, Columbia University Press. 1949.



45. Makower, Benjamin, Shaw, Thomas M. and Alexander, Lyle T.  
The specific surface and density of some soils and their colloids. Soil Sci. Soc. Amer. Proc., 2: 101-108. 1937.
46. Mattson, Sante  
The laws of soil colloidal behavior: VI. Amphoteric behavior. Soil Sci., 32: 343-365. 1931.
47. Mattson, Sante  
The laws of soil colloidal behavior: V. Ion adsorption and exchange. Soil Sci., 31: 311-331. 1931.
48. Mattson, Sante and Hester, J. B.  
The laws of soil colloidal behavior: X. Exchange neutrality and combining capacity. Soil Sci., 34: 459-483. 1932.
49. Mehlich, Adolph  
Adsorption of barium and hydroxyl ions by soils and minerals in relation to pH. Soil Sci., 53: 115-123. 1942.
- ✓ 50. Mehlich, Adolph  
Effect of type of soil colloid on cation-adsorption capacity and on exchangeable hydrogen and calcium as measured by different methods. Soil Sci., 60: 289-304. 1945.
51. Middleton, H. E., Slater, C. S. and Byers, Horace G.  
Physical and chemical characteristics of the soils from the erosion experiment stations. U.S.D.A. Tech. Bul. No. 316. 1932.
52. Mitra, R. P., Bagchi, S. N. and Ray, S. P.  
The electrochemical properties of clay minerals and the differentiation of hydrogen clays and hydrogen bentonites by electrochemical methods. II. Montmorillonitic clays and bentonites. Jour. Ph. Chem., 47: 549-553. 1943.
53. Mukherjee, J. N., Mitra, R. P. and Mitra, D. K.  
The electrochemical properties of clay minerals and the differentiation of hydrogen clays and bentonites by electrochemical methods. I. Kaolinite and kaolinitic clays. Jour. Phy. Chem., 47: 543-549. 1943.
- ✓ 54. Nagelschmidt, G.  
The identification of minerals in soil colloids. Jour. Agri. Sci., 29: 478-501. 1939.

- ✓ 55. Olmstead, L. B., Alexander, Lyle T. and Middleton, H. E.  
A pipette method of mechanical analysis of soils  
based on improved dispersion procedure. U.S.D.A.  
Tech. Bul. No. 170. 1930.
56. Pauling, Linus  
The structure of the chlorites. Natl. Acad. Sci.  
Proc., 16: 578-582. 1930.
57. Pennington, R. P. and Jackson, M. L.  
Segregation of the clay minerals of polycomponent  
soil clays. Soil Sci. Soc. Amer. Proc., 12: 452-  
457. 1947.
58. Perkins, Alfred T.  
Kaolin and treated kaolin. Soil Sci., 65: 185-  
191. 1948.
- ✓ 59. Puri, Amar Nath  
Dispersion of soil for mechanical analysis by sodium  
carbonate or sodium oxalate treatment. Soil Sci.,  
42: 267-272. 1936.
- ✓ 60. Rendig, V. V.  
Rapid determination of the base exchange capacity  
of soils with the flame photometer. Soil Sci. Soc.  
Amer. Proc., 12: 449-451. 1947.
- ✓ 61. Robinson, Gilbert W.  
A new method for the mechanical analysis of soils and  
other dispersions. Jour. Agr. Sci., 12: 306-321.  
1922.
62. Robinson, Gilbert W.  
Note on the mechanical analysis of humus soils.  
Jour. Agri. Sci., 12: 287-291. 1922.
63. Ross, Clarence E. and Hendricks, Sterling B.  
Clay minerals of the montmorillonite group: their  
mineral and chemical relationships and the factors  
controlling base exchange. Soil Sci. Soc. Amer.  
Proc., 6: 58-62. 1941.
64. Ross, C. S. and Hendricks, S. B.  
Minerals of the montmorillonite group. Professional  
paper 205-B. Geol. Surv., U. S. Dept. Interior, pp.  
23-79. 1945.
65. Ross, C. S. and Kerr, P. F.  
The kaolin minerals. U. S. Geol. Surv. Professional  
paper 165-E. 1931.

66. Russell, M. B. and Haddock, J. L.  
The identification of clay minerals in fine Iowa soils by the thermal method. Soil Sci. Soc. Amer. Proc., 5: 90-94. 1940.
67. Schollenberger, C. J. and Dreibelbis, F. R.  
Analytical methods in base exchange investigations on soils. Soil Sci., 30: 161-173. 1930.
68. Schollenberger, C. J. and Simon, R. H.  
Determination of exchange capacity and exchangeable bases in soil - ammonium acetate method. Soil Sci., 59: 13-24. 1945.
69. Sheerar, Leonard Francis  
The clays and shales of Oklahoma. Division of Engineering Publication. Oklahoma A. & M. College, Vol. 3, No. 5. 1932.
- ✓ 70. Sub-Committee of the Agriculture Education Association  
The mechanical analysis of soils: A report on the present position, and recommendations for a new method. Jour. Agri. Sci., 16: 123-144. 1926.
- ✓ 71. Tanner, C. B. and Jackson, M. L.  
Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. Soil Sci. Soc. Amer. Proc., 12: 60-65. 1947.
- ✓ 72. Thomas, Moyer D.  
Replacable bases and the dispersion of soil in mechanical analysis. Soil Sci., 25: 419-427. 1928.
- ✓ 73. Troell, Erik  
The use of sodium hypobromite for the oxidation of organic matter in the mechanical analysis of soils. Jour. Agri. Sci., 21: 476-484. 1931.
- ✓ 74. Truog, E., Taylor, J. R., Jr., Pearson, R. W., Weeks, M. E. and Simonson, R. W.  
Procedure for special type of mechanical and mineralogical soil analysis. Soil Sci. Soc. Amer. Proc., 1: 101-112. 1936.
- ✓ 75. Tyner, Edward H.  
The use of sodium metaphosphate for dispersion of soils for mechanical analysis. Soil Sci. Soc. Amer. Proc., 4: 106-113. 1939.
- ✓ 76. Vanderford, H. B.  
Variations in the silt and clay fractions of loessial soils caused by climatic differences. Soil Sci. Soc. Amer. Proc., 6: 83-90. 1941.

- ✓ 77. Winters, Erick and Harland, M. B.  
Preparation of soil samples for pipette analysis.  
Jour. Amer. Soc. Agron., 22: 771-779. 1930.

TYPIST PAGE

THESIS TITLE: A Study of the Cation Exchange  
Capacity and Types of Clay Minerals  
in Oklahoma Soils and Soil Materials.

NAME OF AUTHOR: R. T. Sutton.

THESIS ADVISER: Dr. Horace J. Harper

The content and form have been checked and approved by the author and thesis adviser. "Instructions for Typing and Arranging the Thesis" are available in the Graduate School office. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

NAME OF TYPIST: Carolyn Leonard

\* \* \* \* \*