COMPOSITION AND ENGINEERING PROPERTIES

OF SOME VERMICULITIC PRODUCTS OF WEATHERING

by

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ABSTRACT

Title of Thesis: COMPOSITION AND ENGINEERING PROPERTIES OF SOME
                   VERMICULITIC PRODUCTS OF WEATHERING

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degree of Doctor of Philosophy.

        The clay mineral weathering products, taken from a Podzolic
soil profile developed in a New England glacial till, consist of
variable amounts of illite, vermiculite, swelling clay, randomly
interlayered minerals, and chlorite. Clay soils of this type are
usually deficient in potassium and may fix potassium and change in
mineralogy if they enter a marine environment. Potassium fixation,
which was expected to produce pronounced changes in the mineralogy
and engineering properties of this soil, occurred to a minor degree
or not at all. Aluminum and iron, which are relatively mobile in
low pH ground water, replaced the stripped-out potassium resulting
in the chloritization of the previously existing 2:1 layer clays.
X-ray analyses, differential thermal analyses, glycol retentions,
cation exchange capacity determinations, total potassium analyses,
and extractable aluminum and iron determinations were performed on
the clay.

        Engineering tests were run on the clays to study the relative
effects of ordinary cation exchange and potassium fixation. The
effects of potassium fixation were minor and usually were swamped
by the effects of cation exchange. All clays were sedimented in
NaCl and leached with either NaCl or KCl. Differences in the
consolidation, permeability, and strength characteristics of the Na
and K clays were measured.

        In general, the K clays existed at a higher void ratio at
any given consolidation pressure within the range studied. The K
clays were as permeable or more permeable than the Na clays at any
consolidation pressure or void ratio within the range studied. At
a given water content, the K clays were stronger than the Na clays
in both drained and undrained shear. The drained friction angles
were greater for the K clays than the Na clays. For example, in one
of the test batches, the Na and K clays had drained friction angles
of 20 and 26 degrees respectively. In most of the tests, the K:Na
ratio in the pore water was found to play an important role. The changes
are consistent with either Rosenqvist's concepts of cation polariz-
ability or concepts of ionic potential and the size of the hydrated
radii of the adsorbed cations.

A preliminary fabric study, using x-ray diffraction methods, was performed on several test specimens. It is believed that this is the first organized attempt to use these methods to determine the fabric of clay soils. The shear zones in drained direct shear and undrained triaxial specimens were identified by measuring changes in clay particle orientation. These and additional test results were used to interpret some of the engineering test data.

Thesis Supervisor: Professor T. William Lambe

Title: Professor and Head of the Soil
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        Department of Civil and Sanitary
        Engineering.

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS AND SYMBOLS

$\overset{\circ}{A}$ angström unit $= 10^{-8}$ cm.

C.E.C.   cation exchange capacity (m.eq./100g.)

D.T.A.   differential thermal analysis

G.P.O.   glycerol saturated, pressure oriented samples for x-ray film studies, and glycol saturated, centrifuge oriented samples for x-ray diffraction studies.

e_f final void ratio

w_f final water content

S_t sensitivity

$K\alpha$ $K\alpha$ energy level x-ray emission quantitatively measured for Ba, K, Al and Fe determinations using x-ray spectrometer.

α cation polarizability as discussed by Rosenqvist

$\%_o$ parts per thousand (solution concentration)

μ micron $= 10^{-3}$ mm.

ϕ_{cu} undrained friction angle obtained from vane shear tests

ϕ_d drained friction angle obtained by direct shear tests

$\overline{\sigma}_c$ vertical consolidation pressure

$\overline{\sigma}_{ff}$ effective stress on the failure plane at failure in direct shear tests

$\overline{\overline{\sigma}}$ particle to particle contact stress

τ_{max} maximum shear stress

PREFACE

It has been known for some time that potassium deficient or degraded clays tend to fix potassium when they enter the marine environment. This fixation results in a layer lattice contraction and an expulsion of the interlayer water. These reactions have been called clay mineral "diagenesis" (change in mineralogy after deposition) by some writers and cation exchange with fixation by other writers.

The object of the research in this thesis was to determine the effects of potassium fixation and cation exchange on the engineering properties of degraded illite or vermiculite in saline environments. Existing data on the effects of cation exchange are fairly abundant but frequently difficult to assess. The effects of rapid mineralogical change resulting from potassium fixation were largely a matter of speculation.

Most of the research was done on a potassium deficient soil developed in a New England glacial till under conditions of Podzolic weathering. Initial engineering tests were run on clay batches containing about 15 per cent of collapsible vermiculite. The results were very encouraging; so a pilot run was made to see if the vermiculitic component could be increased by fractionation. The results of this run suggested that this could be done; so two more batches of fine clay were prepared. When these two batches did not fix potassium as expected, extensive mineralogical analyses were performed to find out why. These studies led to an analysis of the soil profile and some of the weathering conditions existing therein.

The thesis is divided into three parts to facilitate reading. Although somewhat related, each part is more or less a distinct unit. Part One, which is the geological part of the thesis, briefly describes the mineralogical analyses performed on the batches of clay. The relationship of the clay mineralogy to the soil profile and weathering conditions is discussed. Part Two describes the engineering analyses performed on the clays and Part Three contains the preliminary results of an x-ray diffraction study of soil fabric.

A summary of the results of all three parts may be found at the beginning of the thesis. The relationship between the three parts is brought out in this summary.

SUMMARY

The purpose of the research described in this thesis was to determine the relative effects of potassium fixation and ordinary cation exchange on the engineering properties of clays in controlled salt environments consisting of NaCl and KCl. It has been known for some time that degraded illites and vermiculites tend to fix potassium and alter to illite when they enter the marine environment. This change has been called "diagenesis" by some writers and cation exchange with fixation by other writers. It is hoped that the work in Parts One and Two of this thesis will help clarify the role that potassium fixation plays in the engineering properties of marine clays.

Part One of the thesis discusses the geological and mineralogical characteristics of the clays subjected to engineering testing. The clays were obtained from the upper part of a Podzolic soil profile developed in a New England glacial till. Acid weathering had been fairly extensive, reducing the potassium content of the clays to a low level. Unfortunately, the potassium fixation properties of the clays were not very pronounced despite the potassium deficiency. The reason for this is the presence of interlayer aluminum and iron which replaced the potassium. In the upper portion of the soil profile, this resulted in the chloritization of the 2:1 layer clays. This chloritized or partially chloritized clay will not fix much potassium, as the charge deficiency has already been balanced by the aluminum and iron.

The clay products of weathering developed in this type of soil profile are very complex, consisting in this case of illite, vermiculite, swelling clay, randomly interlayered minerals, and a variable amount of chlorite. Most of the minerals were probably developed from a primary mica which had much of its potassium striped out during weathering and replaced by variable amounts of aluminum and iron. Clay mineral assemblages very similar to this have been described recently by a number of agronomists and clay mineralogists. Some noteworthy contributions are by: Rich and Obenshain (1955), Rich (1960), Tamura (1956 and 1958), Sawhney (1958), and Brydon et al. (1961).

Long-term KCl treatments performed in an attempt to diffuse in potassium appear to have increased the cation exchange capacity by replacing some of the fixed aluminum. Only in Batches 1 and 2, which were the coarsest clays, was any permanent fixation of potassium observed.

Part Two describes the engineering tests performed on the clays analyzed in Part One.

The effects of potassium fixation and clay mineral collapse were picked up only in M21, Batches 1 and 2, and to some extent in an interlayered illite-montmorillonite from the Santa Monica region of California. Generally speaking, cation exchange (Na replaced by K during leaching) had the greatest effect on the clay. When deposited in an expanded form, the KCl and NaCl leached clays from M21, Batches 1 and 2, had similar shaped consolidation curves, but the

former existed at a higher void ratio at any given consolidation
pressure. When deposited in a semi-collapsed state, the curves of
the K and Na clays came much closer together. Although it is
believed that potassium fixation is responsible for the differences
in the two sets of results, the effect may be an indirect one.
Differences in the soil structure caused by differences in the
flocculated fabric may be the primary control.

In the clays of M21, Batches 3 and 4, which did not fix
potassium, the KCl leached clays invariably existed at a higher void
ratio at a given pressure than the NaCl leached clays. The greater
the K:Na ratio, the greater was the spread between curves.

The permeability differences were not large, but at either a
given void ratio or consolidation pressure, the potassium clays were
never less permeable than the sodium clays, and often more permeable.
The differences in permeability were largest for clays with the
highest K:Na ratios.

Although the undrained strengths of the sodium and potassium
clays were nearly the same, small interesting differences were
noticed. At a given water content, the potassium clays were always
stronger in undrained shear. This strength difference appeared to be
larger when the clay was collapsed before sedimentation. At a given
consolidation pressure, the strength relationship depended on the form
of the clay when deposited. When deposited in an expended form and
then KCl leached, the Na clays were stronger than the K clays.

When deposited in a collapsed state, the K clays were the stronger. It is thought that differences in the flocculated structure accompanied by different degrees of particle reorientation during consolidation are the explanation. The effects of layer lattice collapse are believed to be minor for this clay.

The effect of simple ion exchange was to increase the strength of the K clay at any consolidation pressure or water content. The effect of potassium fixation was to reverse this trend. For the clays studied here, fixation effects were minor because 1) only a small amount of the clay fixed potassium and 2) the clays were consolidated after KCl leaching.

The drained shear strengths showed that the potassium clays had much higher friction angles than the sodium clays. For instance, in one batch of clay, friction angles of 20° and 26° were obtained for the sodium and potassium leached clays respectively. Plots of drained shear strength versus water content at failure showed that the potassium clays were much stronger than the sodium clays at any given water content within the range studied. These plots also showed that the strengths were greatly dependent on the K:Na ratios.

Indeed, the K:Na ratio, which is a measure of the completeness of KCl leaching, had a large effect on the separation of consolidation curves, permeability plots, and the strength results.

The effects of KCl leaching on the engineering properties of the clays are consistent with either Rosenqvist's concepts of cation polarizability or concepts of ionic potential and the size of the hydrated radii of the adsorbed cations. Either theory indicates that the potassium clays should be stronger than the sodium clays, provided no interlayer water is forced out by the fixation of potassium. The role of the interlayer water was obscured by the effects of cation exchange in most of the tests. However, the un-drained strengths of M21, Batches 1 and 2 showed some indirect effects of this collapse as did the liquid limit results on the California clay.

It is observed in Part One that KCl leaching actually tended to increase the exchange capacity of some of the clays, probably by removing some adsorbed aluminum. For this reason the clay was used only once, if possible, for engineering testing. Consolidation 34, which was run on clay already used in Consol. 33 appears to have the only misplaced consolidation curve.

Some of the effects of cation exchange were also picked up in the fabric study and applied to the engineering test results. For example, the sodium clays of M21, Batch 3 existed at a lower void ratio than the potassium clay at any given consolidation pressure. The fabric study showed that the platelets of clay were more nearly parallel (horizontally) than the potassium clays, hence their lower void ratio (i.e., the Na clays were more easily reoriented from their original fabric during consolidation).

The fabric study in Part Three showed that x-ray diffraction methods could be used to determine average particle-to-particle arrangements. For instance, failure planes in triaxial and direct shear specimens were picked up by measuring changes in particle orientation brought about by shear.

Appendices containing the details of the mineralogical analyses and the details of some of the testing procedures may be found at the rear of the thesis.

PART ONE

MINERALOGICAL ANALYSES

I. INTRODUCTION

During acid weathering, previously existing soil micas and illities have some of their interlayer potassium removed. These "degraded" minerals generally expand to around 14Å and have x-ray characteristics somewhat similar to vermiculite. When treated with KCl solutions, they collapse back to 10Å illite or mica by fixing potassium and expelling the interlayer water.

When degraded illites enter the marine environment, potassium is selectively adsorbed from the sea water and fixes in the interlayer position. This reaction has been called "diagenesis" (mineral alteration after deposition) by some writers, and cation exchange with fixation by other writers.

The purpose of Parts One and Two of this thesis is to study the effects of potassium fixation and ordinary cation exchange on the engineering properties of degraded illites or vermiculites. The mineralogical analyses in Part One were originally intended to supplement the engineering test data presented in Part Two. When the degraded soils did not fix potassium as expected, extensive mineralogical tests were run to find out why. This led to a study of the soil profile and the weathering conditions existing in it. These studies proved to be very interesting and informative, and are presented in this part of the thesis, separately from the engineering analyses.

The mineralogical data from the clay batches are summarized and brought together with the soil profile data. The details of the mineral work on the four batches of engineering test clay are presented in Appendices B, C, and D.

The clay mineral assemblage is related to the weathering conditions and position within the soil profile. Extensive potassium treatments are described. The reason little or no fixation occurred has been determined and explained.

II. PREVIOUS WORK

A. General Discussion

The release and fixation of potassium in micaceous soils has been a subject of much study by agronomists for many years. Many laboratory and field studies have been performed and reported in the literature. The geological significance of potassium fixation, however, was not fully realized until recently when a great controversy arose over the causes and extent of clay "diagenesis" in the marine environment.

B. Potassium Release and Fixation in Micaceous Soils

According to Kunze and Jefferies (1953), potassium fixation in degraded soils was first recognized by Dyer in 1893. In 1934, Volk recognized more mica in potassium fertilized plots of ground and attributed the increase to potassium fixation. The work of Barshad (1948 and 1950) did much to explain the interrelationship between soil micas and vermiculites and the release and fixation of interlayer

cations. By leaching a biotite with 1 Normal $MgCl_2$ for about three months, Barshad (1948) was able to displace much of the interlayer potassium and induce a layer lattice swelling from 10.3 to 14.5 $\overset{o}{A}$. When potassium was added to this biotite and to vermiculites, they collapsed down to around 10$\overset{o}{A}$. He also found that the type of cation present greatly affected the differential thermal curves. This is discussed later.

Dyal and Hendricks (1952) produced a mixed layer assemblage by adding potassium to a montmorillonitic soil. They noticed a drop in glycol retention resulting from potassium fixation and layer lattice contraction.

Kunze and Jefferies (1953) measured basal spacing shifts in potassium treated soils and attributed the changes to fixation.

Williams and Jenny (1952) report carbonic acid leaching studies in which they removed fixed potassium at pH values less than 3 and exchangeable potassium only at higher pH values.

Recently (since 1957), a great deal of work has been reported on potassium release and fixation in micaceous soils. The kinetics of potassium release from mica has been reported in a number of articles by Mortland and Ellis. Ellis and Mortland (1959) report that potassium is released more rapidly from weathered than un-weathered biotite. They suggest that there is a loss of charge during weathering which enables easier release of potassium. This loss of charge is probably related to oxidation of ferrous iron in the octahedral position. Mortland (1958) showed that small biotite

particles lost their potassium before larger particles. Similar results are reported by Reed and Scott (1960). Other articles on the release and fixation of potassium are: Mortland and Ellis (1959), Mortland (1961), DeMumbrum (1958 and 1959), Sawhney, Jackson, and Corey (1959).

Jonas and Thomas (1960) conducted a series of experiments on a less than 2 micron clay having a cation exchange capacity of 70 m.eq./100 g. They found that the clay collapsed completely at high KCl concentrations (1 Normal). At very low concentrations the clay was fully expandable and at intermediate concentrations the clay would expand in glycol but not in water. At a threshold concentration of about 4×10^{-3}N KCl, a sudden marked collapse was observed. This effect of pore fluid concentration on the amount of layer lattice collapse would markedly affect any studies on the role of interlayer water on the engineering properties of a clay. This effect was noticed on the California illite-montmorillonite discussed in Part Two of this thesis.

Jonas and Roberson (1960) studied the effects of particle size on clay mineral expansion. They found that particles of very high charge deficiency would expand if the particles were fine enough. They hypothesized that size has little effect on the expansion properties of particles of low charge density. A large particle with a high charge, however, would be very difficult to expand. The previous two studies indicate that both the grain size of the clay fractions and the concentration of the KCl solutions will affect the degree of fixation and collapse.

C. Marine Clay Mineral Diagenesis

Clay mineral diagenesis means a change in mineralogy during and after deposition but before any lithification takes place. The significance of the term diagenesis depends in large measure on how the clay minerals are identified. The effects or ordinary cation exchange are excluded from diagenesis. The effect of cation fixation on the (00l) spacing of clay minerals forms the basis of current controversy on diagenesis. Some authors consider potassium fixation an exchange reaction only, despite its effect on degraded illites and vermiculites. They say that the 2:1 layer crystal units and the charge deficiency within these units have not changed, and we do not have diagenesis. Others consider the change in (00l) spacing from 14 $\overset{o}{A}$ to 10 $\overset{o}{A}$ to be a mineralogical change and hence diagenesis.

The widespread concept of diagenetic alteration of most clay minerals to illite under marine conditions (e.g., Taylor, 1952) has been strongly criticized recently and today much less importance is attached to it. Recent field and laboratory work has shown that diagenesis of clay minerals is a very slow and incomplete process and that only certain types of expandable clays are really susceptible to change. In general, the clay minerals found in a basin of deposition are the same as those formed in the source region.

Laboratory studies by Whitehouse and McCarter (1958) showed that their montmorillonite changed slowly with time to illite and chlorite. At the end of five years they observed a 25 per cent

modification to illite and chlorite. The changes they observed were
more dependent on the Mg:K ratio than the total salinity of their
artificial sea water. The most effective Mg:K ratio was about 9.4
for a chlorinity range from 7.2 to 19.4 g./kilogram and potassium
content not less than 0.005 molar. These values varied somewhat
depending on the grain size of the montmorillonite. Below a chlorinity
of 7.2 and a potassium concentration of 0.003 to 0.005 molar, the
amount of alteration was greatly reduced. No diagenetic alterations
were observed in either kaolinite or illite.

It is interesting to note that the limiting potassium contents
of 0.003 to 0.005 molar are about the same as Jonas' and Thomas'
threshold KCl concentration above which they got pronounced collapse
to 10 $\overset{o}{A}$. Jonas and Thomas used pure KCl solutions whereas Whitehouse
and McCarter used artificial sea water so the two systems are not
necessarily comparable. It seems to this writer that the charge
deficiency on the montmorillonites studied may have been such that
potassium fixation and chloritization progressed slowly with time.

Powers (1953) found a progressive decrease in expandable clay
minerals seaward from the Patuxent River, Maryland. He found more
illite and chlorite towards the sea and attributed the changes to
diagenesis.

Nelson (1958) attributed changes in the bottom sediments of
the Rappahannock River to diagenesis. He observed a progressive
decrease in the amount of collapsible clay seaward. Nelson (1960)

modified this interpretation after he observed what he considered authigenic feldspar in some of his downstream samples.

Weaver (1958 (a) and (b)) suggests that diagenetic changes are nearly nonexistent. His argument is based on a careful x-ray study of the variations in the morphology of illite and chlorite. He concludes that most ancient illites are of the 2M variety and are clastic fragments of muscovite formed at high temperature. The other varieties (1M and 1Md illite) represent low temperature forms produced by weathering and possibly diagenesis. He further states that most chlorites are trioctahedral and thus probably detrital. Diagenetic chlorites should be chiefly dioctahedral if derived from montmorillonites which are chiefly dioctahedral. One must be cautious here, however, because recently a large number of pseudo-chlorites produced from dioctahedral mica have been observed in soil profiles and aqueous sediments. These are discussed later.

Diagenetic modifications are suggested as a mechanism of glauconite formation by Burst (1958 a, 1958 b) and Hower (1961). Old glauconites contain more collapsed layers and fixed potassium than recent glauconites. Both Burst and Hower hypothesize that ferrous iron replaces aluminum in the octohedral position of the expandable clay layers, thus increasing their charge deficiency. With the increased charge deficiency, the tendency is to fix potassium and collapse to 10 $\overset{\circ}{A}$.

In conclusion it may be stated that potassium fixation by
potassium deficient clays with a high charge deficiency occurs in
the marine environment. This fixation is accompanied by a collapse
from 14 $\overset{o}{A}$ to 10 $\overset{o}{A}$ but no change in the constitution or charge
deficiency of the 2:1 layer units. It is this writer's opinion that this
change is not truly diagenetic. The structural modifications of
glauconite hypothesized by Hower (1961) and Burst (1958a, 1958b) are
truly diagenetic changes. It is probable that similar changes occur
in clay minerals other than glauconites and that illite-like minerals
tend to develop from expandable 2:1 layer clays with time. These
changes progress very slowly even on a geological scale, and certainly
do not affect the engineering properties of sediments. On the other
hand, clay mineral collapse produced by potassium fixation is a
fairly rapid process which may have a large effect on the engineering
properties of a clay deposit.

D. The Role of Aluminum

It has been known for some time that most clays contain some
adsorbed aluminum. For example, Carroll and Starkey (1960) suggest
that acid treatment of their clays resulted in the adsorption of
Al^{3+} which was not exchangeable by Ca, Mg, and Na in their titration
experiments. The role that aluminum plays in restricting both expansion
and collapse of clay minerals is described later in the discussion of
the experimental results.

III. METHODS OF MINERALOGICAL ANALYSIS

Consistent methods of analysis have been developed for the
mineralogical investigations of the vermiculitic soils under con-
sideration. The following tests have been run:

1. X-ray analyses by film patterns and diffraction traces.

2. Differential thermal analyses.

3. Cation exchange capacities by x-ray spectrometer.

4. Total potassium by x-ray spectrometer.

5. Glycol retentions.

6. Extractable aluminum and iron determinations.

The methods of analysis are briefly described below. The
reader is referred to Appendix A for any additional details.
Emphasis is placed on a "barium x-ray spectrographic analysis"
used for determining the cation exchange capacities.

A. X-Ray Analyses

Most of the x-ray work presented in the thesis was performed
with an x-ray diffractometer complete with geiger scaler and
automatic recorder. Copper radiation generated at 40 kilovolts and
15 milliamps was used for all of this work. The diffraction
equipment is located in the Department of Geology and Geophysics.

Oriented samples were prepared by dispersing a sample in
distilled water using an ultrasonic vibrator and then centrifuging
the suspension for about twenty minutes at 2000 r.p.m. over a
porous ceramic plate. During this time, all of the water was drawn
through the plate leaving a highly oriented, glossy layer of clay.
The sample can be x-rayed wet, air dry, or glycol saturated.

Powder patterns were obtained by x-raying a level surface of clay powder. A rectangular depression cut in a ceramic plate was filled with powder, scraped off level, and x-rayed.

Some of the initial x-ray analyses were performed using a film camera in the Soil Engineering Division, Department of Civil Engineering. Some of the films were run through a light intensity meter for presentation as an x-ray trace. (See M21, Batches 1 and 2, Appendix B.)

B. Differential Thermal Analyses (D.T.A.)

Clay samples to be thermally analyzed were air dried and ground down to 100 mesh. The clays were then brought into equilibrium with an atmosphere of about 50 per cent relative humidity. This was done by placing the clay over a saturated solution of hydrous calcium nitrate for at least seven days. The relative humidity of the oven was not controlled. Additional equipment data are given in Appendix A.

The purpose of equilibrating the clays with an atmosphere at 50 per cent relative humidity is to get a water peak of some significance. Unpublished data by Martin (M.I.T.) indicates that the size of the water peak is related to the cation exchange capacity and glycol retention of the clay. Any changes in cation exchange capacity due to cation fixation should be reflected in the size of the water peak.

C. Cation Exchange Capacities (C.E.C.)

Clay minerals having high charge deficiencies tend to fix certain sized cations. Degraded micas and illites, similar to the soil being studied, have the greatest fixing powers because of their

high charge deficiency. The ammonium cation fixes in this type of soil, so that if the usual ammonium exchange capacity method is used, cation exchange capacity values which are too low are obtained. Sawhney, Jackson, and Corey (1959) discuss the relationship between exchange capacity and fixation of certain cations.

For this reason, it was decided that a barium x-ray spectographic method of analysis should be used. The method involves washing the clay in barium chloride until it is homoionic in Ba^{++}. The sample is washed free of excess salt and placed in an x-ray spectrometer. The amount of adsorbed barium is determined by comparing the size of the barium $K\alpha$ peak with peaks obtained on previously prepared standards. The cation exchange capacity is expressed in milliequivalents of barium per 100 grams of clay (m.eq./100g.).

The details of this technique are given in Appendix A. The procedure was worked out with the assistance of Dr. Martin of the Soil Engineering Division and Dr. Hower of the Department of Geology and Geophysics.

D. Potassium Analyses

Total potassium was determined using the same x-ray spectrometer that was used for the cation exchange capacity determinations. The details of the method are described in Appendix A.

E. Glycol Retentions

The retention of ethylene glycol by clays is a useful indicator of soil properties and possibly surface area. The method used was that of Dyal and Hendricks (1950) as modified by Martin (1955). The method will not be discussed further in this report.

F. Extraction of Aluminum and Iron

Interlayer aluminum and iron were extracted by the sodium
citrate method of Tamura (1958). The method involved boiling a clay
sample several times in one Normal sodium citrate and decanting the
supernatant after centrifuging. Aluminum and iron were determined
spectrographically from strips of filter paper immersed in the
extracts and air dried.

An earlier method of extraction involved washing a clay sample
in one Normal NaCl brought to pH 3 with HCl. Aluminum and iron were
determined colorometrically. This extraction procedure was un-
successful.

IV. LOCATION OF SOIL PROFILE

The clay used for engineering testing was obtained from the
upper sixteen inches of a soil profile developed in a New England
glacial till. The soil profile itself, which is typical of the
"Brown Podzolic Group", was studied mineralogically to a depth of
55 inches. The profile occurs about ten feet down the side of a
large drumlin known as Orient Heights, located in Northeast Boston,
Massachusetts. The slope of this point is free of an organic cover.

V. RESULTS AND DISCUSSION

The locations of the samples taken from the soil profile and
fractionated for testing are shown in Fig. I-1. Although the samples
are not all of the same equivalent grain size, it is felt they are
comparable with one another.

A. Soil pH, Total Potassium, and Cation Exchange Capacity Results

Visual inspection of the soil profile indicated that the soil was brown and completely oxidized throughout the depth studied. The bleached "A" horizon extended to a depth of no more than six inches. The "B" horizon extended to a depth of about 24 inches and the "C" horizon beyond the depth explored. Although precipitated iron was observed in soil fissures down as deep as 50 inches, the greatest concentration occurred between 20 and 24 inches giving the clay a patchy appearance.

Soil pH values are given in Fig. I-1, which shows that the ground waters are more acid near surface. Two pH profiles representing different methods of measurement are shown. The higher values (lower acidity) were obtained by soaking and stirring the soil samples in demineralized water for about 45 minutes, and taking a pH reading of the clear supernatant with a Beckman Zeromatic pH meter. The lower values (higher acidity) were taken on the same soil-water mixes after enough $CaCl_2$ had been added to bring the concentration to 0.01 molar. The results are quite significant, as they indicate the presence of considerable adsorbed hydrogen. This hydrogen is probably present as hydronium, H_3O^+. The addition of $CaCl_2$ results in the exchange of the hydronium by Ca^{++}, giving an increase in the H ion concentration and a lower pH. One natural moisture content determination gave a value of 12 per cent. The soil pH was determined using this value for all samples. A pH of 3.9 to 4.0 was obtained in the upper part of the soil profile, increasing to about 4.7 with depth.

The total potassium contents of the soil samples are quite low (average 3.0% K) throughout the profile. (See Table I-I and Fig. I-1) However, there does seem to be a decrease from about 3.3 to 2.8 per cent K towards surface. The cation exchange capacities of the natural soil samples are very low for such low values of total potassium. There does appear to be an increase in exchange capacity towards surface; the lower four samples average 23 m.eq./100g. and the upper two average 32 m.eq./100g. These low C.E.C. values are caused by adsorbed aluminum and iron and are discussed in detail later.

All samples in Table I-I were given five washes with 1 N KCl over a period of 24 hours. They were then made homoionic in barium by the procedure described in Appendix A. In all but one case, there was a small increase in per cent K. The exchange capacity was expected to drop as a result of this treatment. It can be seen from Table I-I that all but one sample remained the same or showed a slight increase in C.E.C. Batch 3, which picked up 0.5 per cent K, showed a drop in C.E.C. from 35 to 27 m.eq./100 g. It is believed that adsorbed aluminum may have been replaced by K in some of the samples. Lin and Coleman (1960) and Coleman, Weed, and McCracken (1959) found that potassium is one of the better neutral salts for displacing adsorbed aluminum. Making the natural clay homoionic in barium probably did not remove any aluminum. After the 24-hour KCl treatment, some of the potassium which had replaced the aluminum was probably exchangeable, hence the increase in C.E.C.

Batches 3 and 4 from the upper part of the profile were given 14-day 1N KCl treatments, which involved about eight changes of solution. It was hoped that fixation would occur through diffusion. In both cases the C.E.C. increased greatly and the total K decreased. Once again these changes are attributed to the removal of Al by the strong KCl solutions.

B. X-Ray Analyses

1. Typical Diffraction Traces

X-ray diffraction traces of two powder samples of M21, Batch 3 (0-16 inches) are shown in Fig. I-2. The most obvious feature of both curves is the very low intensity of the (00ℓ) reflections compared with the (h k 0) reflections. This possibly is due to random interlayering, which can reduce the size of the (00ℓ) peaks. The 10 $\overset{o}{A}$ illite peak is slightly better defined in the potassium clay. The presence of a broad 3.50 $\overset{o}{A}$ peak and the absence of a 3.66 $\overset{o}{A}$ peak suggest a 2M rather than a 1M polymorphic crystal form. The slope of the 2.57 $\overset{o}{A}$ peak downward towards the 2.59 $\overset{o}{A}$ spacing is also indicative of a 2M structure. (The 2.59 $\overset{o}{A}$ peak is stronger than the 2.57 $\overset{o}{A}$ peak in 1M mica.) The (060) reflection at 1.501 $\overset{o}{A}$ indicates that the bulk of the clay is dioctahedral.

Patterns of centrifuge oriented, glycol saturated clay (M21, Batch 3), homoionic in sodium and potassium, are shown in Fig. I-3 and 1-4. The trace in Fig. I-3 indicates that illite and a vermiculite-like mineral (10.15 $\overset{o}{A}$ and 14.26 $\overset{o}{A}$) are very abundant constituents.

Fig. I-4 shows that a marked reduction in the vermiculitic phase
has been produced by the presence of interlayer potassium. The high
order reflections are close to being at integral values of the (001)
peaks. The two peaks at 4.29 Å and 4.11 Å are difficult to explain.
It is possible that they represent some high order reflection of a
regularly interlayered mineral phase. The potassium treatment
(Fig. I-4) had little effect on these two peaks, whereas it caused a
large reduction in the high order vermiculite peaks. This suggests
that chlorite and illite may be the interlayer constituents. **Lambe**
and Martin (1955) describe similar, strong, high order reflections
at different d values, and ascribe them to regularly interstratified
illite-chlorite mixtures. These two peaks were observed to be just
as strong or stronger in Batch 4 (0-6 inches). In Fig. I-5, a dif-
fraction trace of a potassium saturated sample from a depth of
18 inches is presented. The two peaks are barely visible in this
trace indicating that the interlayer complex is characteristic of
the upper part of the profile only.

The 7 Å peaks are stronger than the 14 Å peaks in both
Fig. I-3 and I-4. This suggests that either kaolinite or **iron** chlorite
is present in the samples. The very weak 3.55 Å peak after KCl
treatment (Fig. I-4) indicates that if kaolinite is present, it is
a very minor constituent.

2. KCl Treatments

The effect of 24-hour, 1 N KCl treatments on the clay samples
are shown in Figures I-6 and I-7. The samples were made homoionic to
barium and potassium and x-rayed air dry (Fig. I-6), and glycol
saturated (Fig. I-7). Although barium tends to collapse vermiculites
in the air dry state (Barshad, 1950), these clays were x-rayed because
they had already been used for the C.E.C. determinations.

The barium clay contains considerable 14 $\overset{o}{A}$ mineral, as shown in
Fig. I-6. Upon K saturation, this peak largely disappears, except for
a pronounced hump or shoulder on the 10 $\overset{o}{A}$ peak, in all samples from a
depth of greater than 17 inches. The KCl treatment had little if any
effect on Batch 4 from the upper 6 inches and only partially collapsed
the Batch 3 clay taken from 0 to 16 inches.

Fig. I-7 shows similar trends for these same samples after
saturation with glycol. The only difference is that the 14 $\overset{o}{A}$ peaks
may be slightly better developed with less background between the
14 and 10 $\overset{o}{A}$ peaks.

If one compares the 14 $\overset{o}{A}$:10 $\overset{o}{A}$ peak height ratios (Table I-II),
taken from the traces in Figures I-6 and I-7, the collapse produced
by potassium saturation is again obvious. For the air dried samples,
the ratio is 57 per cent smaller with potassium as the exchange ion
in the four samples from 17 inches to 55 inches depth. The upper two
samples show much less collapse, the decrease amounting to only
23 per cent and 40 per cent for Batches 4 and 3 respectively. Similar
trends were found in the glycolated samples.

Samples of Batches 3 and 4 which were KCl treated and then washed out with either NaCl or $BaCl_2$, had very strong 14 $\overset{o}{A}$ peaks, indicating that most of the potassium was exchangeable and not fixed. The 14-day KCl treatments actually produced less collapse than the 24-hour treatments. This is in accordance with the C.E.C. values, which also increased with the 14-day treatment. Additional data in this regard are presented in Appendix C on M21, Batch 3.

3. Heat Treatment

A sample of M21, Batch 3 (0-16 inches) was heat treated and x-rayed at successively higher temperatures. The results are shown in Fig. I-8. The 100° and $200^\circ C$ treatments were for half an hour each. The 350° and $500^\circ C$ treatments involved heating the specimen in an oven as the oven temperature rose, and removing it when the required temperature was reached. The hot samples were put in a desiccator containing silica gel and carried to the diffractometer. X-ray time was about 15 minutes, so that sufficient time was available for the re-expansion of any expanding minerals.

Air drying seems to have caused a great deal of collapse in a randomly interlayered phase, producing a high background between 14 $\overset{o}{A}$ and 10 $\overset{o}{A}$. This is in part caused by having sodium as the adsorbed cation (Barshad, 1950). The 100°, 200°, and $350^\circ C$ treatments caused the 14 $\overset{o}{A}$ peak to decrease in size until it was completely gone at $350^\circ C$. This gradual collapse is probably caused by the loss of hydronium water and hydroxyls from interlayer aluminum. Apparently this aluminum also prevented the re-expansion of the vermiculitic phase by water adsorption

during x-raying. Tamura (1956) reports progressive water losses and structural collapse with incremental heat treatments on a similar clay. These factors are discussed later.

The 500°C treatment resulted in the sudden development of a double peak at 13.8 $\overset{o}{A}$ and 12.3 $\overset{o}{A}$ while the 7.1 $\overset{o}{A}$ (002) peak nearly vanished. The shift of the (001) peak to a lower d value and an increase in its intensity relative to the (002) peak are characteristics of iron chlorite (Martin, 1955).

Some interesting color changes accompanied the heat treatments. The sample of clay was a medium yellow brown in the air dry and 100°C states. At 200°C it changed to a dark chocolate brown and at 350°C it became a very dark chocolate brown. This color change is attributed to the crystallization of amorphous iron (see D.T.A. discussion). At 500°C, the sample had changed to a dark golden brown color.

X-ray diffraction traces were obtained from several size fractions of the soil used to prepare M21, Batch 4 (0-6 inches). These are shown in Fig. I-9. The two fine fractions ($<$0.2 micron and $<$0.1 micron) are more poorly crystallized than the next two coarser fractions. They also appear to contain more expandable clay. The 5-2 micron clay and the 2-0.2 micron clay have very sharp 14 and 7 $\overset{o}{A}$ peaks. They also contain less potassium than the smaller than 0.2 micron clays. (See Table D-I, Appendix D.) This and the relative strength of the 14 and 7 $\overset{o}{A}$ peaks suggest that the coarser fractions may be more highly

chloritized than the finer fractions. Jackson (1960) suggested that the coarser fractions should have a greater charge deficiency than the smaller fractions because they are not so intensely weathered. Aluminum would tend to fix in these coarser, freshly cleaved micas, blocking open the layers and enabling faster leaching of potassium from the coarse fractions. This is probably what has happened here.

C. Differential Thermal Analyses

Differential thermal curves for homoionic clays (Batches 3 and 4) at 50 per cent relative humidity are given in Fig. I-10. The curves are all quite similar. One interesting feature is the flatter slopes of the high temperature side of the water peaks. This suggests a progressive loss of water as was observed in the "heat treatment—x-ray" study. The dip in the curve at 300° to $340^\circ C$ may represent the final dehydration of the vermiculitic phase of the clay. The 600° hydroxyl peak is characteristic of illite and also iron chlorite which was identified in the x-ray patterns. A pseudochlorite produced by the fixation of interlayer aluminum during weathering may also be present. A consistent dip in the differential thermal curves at 690° to 700° may be caused by this mineral.

A more distinctive water peak might have been obtained from a clay sample homoionic in Ca or Mg. According to Barshad (1948), both Ba and Na tend to give one water peak for vermiculite whereas Mg and Ca give two distinctive peaks.

The small exothermic hump at 350 to 400°C is probably due to crystallization of amorphous iron. Pronounced color changes at 350°C in the heat treated, x-ray samples support this theory. It was hoped that the stability of the hydroxyl groups would be affected by potassium fixation. Because the interlayer aluminum blocked the entrance of potassium, this idea could not be checked. Two thermograms of Batch 4 clay are shown in Fig. I-10. The Ba sample is quite similar to the Batch 3 curves. The KCl treated clay, however, has a pronounced hump at 800°C followed by a dip. Barshad (1948) presents somewhat similar curves for vermiculites. It is not known why only the KCl treated clays show this hump.

Additional D.T.A. curves for M21, Batches 2, 3, and 4 may be found in the Appendices.

D. Glycol Retentions

The glycol retention results on Batches 2, 3, and 4 are discussed in the Appendices. It will only be mentioned here that all of the values were quite low, just as were the C.E.C. values. Adsorbed interlayer aluminum and chloritization of the 2:1 layer clays are thought to be the explanation.

E. Aluminum and Iron Extractions

Aluminum and iron extractions were performed on the Batch 3 clay (0-16 inches). This clay was selected because much of the engineering testing was done on it. Also it only partially collapsed in KCl, did not fix potassium, and was known to contain some chlorite of unknown origin.

The 1N sodium chloride treatments at pH 3 were unsuccessful in removing iron and aluminum. Only 0.1 per cent aluminum and 0.002 per cent iron were removed. The cation exchange capacity did not increase and the clay did not fix potassium.

Using Tamura's Na citrate procedure (1958), 0.2 per cent Al and 18.4 per cent Fe were removed in 8 extracts over a two-day period. These percentages correspond to 7.0 m.eq./100g. and 330 m.eq./100g. of clay respectively. Most of the iron removed was probably amorphous material. As a result of the extractions, the C.E.C. rose from 35 to 60 m.eq./100 g. of clay.

X-ray traces were obtained on the clay to see if any changes were brought about by the extractions. Traces of the clay homoionic in Ba and K are shown in Fig. I-11. The Ba clay traces have very strong 14 $\overset{o}{A}$ peaks although some collapse is noticeable in the air dry sample. The K clay, both air dry and glycolated, has very small 14 $\overset{o}{A}$ peaks indicating that the interlayer aluminum has been successfully removed. The collapse resulting from potassium saturation indicates that the chloritized clay is vermiculite or degraded mica. The peak intensities are less for the Ba clay because barium tends to cause flocculation which prevents a high degree of orientation by centrifugation.

It should also be noted that the extraction has enabled some of the glycol saturated, Ba clay to expand from 14.3 $\overset{o}{A}$ (See Fig. I-7) to 16.4 $\overset{o}{A}$.

The weak 14.2 $\overset{o}{A}$ peak and the much stronger 7.1 $\overset{o}{A}$ (002) peak indicate that much iron chlorite still exists in the sample. No tests

were run on the clays from deeper in the soil profile to see if
they also contained iron chlorite. It is possible that iron may
have chloritized some of the 2:1 layer clays just as the aluminum
did. If this is the case, it was not removed by the sodium citration
extractions.

F. Discussion

Chloritized clay mineral complexes consisting of 2:1 layer
clays with interlayer aluminum have been described recently by a
number of authors (Brown (1953), Rich and Obenshain (1955),
Tamura (1956, 1957, 1958), Klages and White (1957), Sawhney (1958, 1960),
Rich (1958, 1960), Tamura, Hanna, and Shearin (1959), Nelson (1960),
and Brydon, Clark, and Osborne (1961)). In some cases the chloritized
complex was formed from montmorillonitic soils (Tamura (1958),
Tamura, Hanna, and Shearin (1959), and Brydon et al. (1961)). In
other cases, weathered, potassium deficient micas or illites were
chloritized into a non-expanding, non-collapsible complex (Rich and
Obenshain (1955), Rich (1958), Klages and White (1957), Tamura (1956)).
In all cases, chloritization occurs in the upper part of the soil
profile where aluminum and iron become fairly soluble in the low pH
ground water. Adsorbed hydrogen and hydronium no doubt assist in the
development of these complexes. The relationship of the clay
mineralogy to the soil profile is discussed in the next section.
Some of the similarities between the findings of this study and
those of other authors are presented in this discussion.

Although potassium was not observed to fix permantly in the
soil studied, it did cause the vermiculitic phase from depths greater
than 17 inches to collapse to 10 $\overset{o}{A}$. Potassium treated clays above
this depth showed decreasing tendencies to collapse towards surface;
the clay from 0—6 inches showing almost no collapse. Rich and
Obenshain (1955) and Tamura (1956) report similar collapse of clays
taken from different parts of Podzolic soil profiles. The vermiculite
at depth showed pronounced collapse and potassium fixation properties,
whereas the chloritized clays near surface showed little or no
collapse. They attribute the differences to interlayer aluminum in
the surface clays.

The potassium content was observed to decrease towards the top
of the soil profile studied. An increase in C.E.C. accompanied this
decrease. Klages and White (1957) observed a similar decrease in
potassium from the C to A horizons, but the C.E.C. remained fairly
constant throughout. The increase in C.E.C. reported for this profile
may be related somewhat to the smaller sizes of the Batches 3 and 4
clays compared to the deeper samples. Klages and White concluded
that a gibbsite sheet of poor quality was the interlayer constituent
of their clays.

It was mentioned that the glycol retentions of the clays
studied seemed abnormally low. Rich (1960) reports that the glycol
retention of vermiculites was reduced greatly when aluminum was
artificially fixed. Experimental fixation of aluminum in vermiculites
is reported by Sawhney (1960) and Rich (1960). Fixation was accompanied

by a large decrease in C.E.C. in each case. The low C.E.C. values in the soil profile studied can be explained logically by aluminum interlayers in the 2:1 layer clays.

Tamura (1956, 1958) has discussed the effects of interlayer aluminum on 2:1 layer clays in considerable detail. Chloritization resulted in a stable 14 $\overset{o}{A}$ mineral which would not collapse in KCl and would not expand in glycol. The heat stability of his clays was similar to that of the clay described in this thesis. Tamura (1958) reports that the dithionite-citrate treatment for the removal of iron oxides (Aguilera and Jackson, 1953) did not remove the interlayer aluminum. Tamura's Na citrate procedure (1958) was therefore used in this work. The method was quite successful.

VI. RELATIONSHIP OF CLAY MINERALOGY TO THE SOIL PROFILE

As mentioned previously, the ground water pH increased from about 3.9 at surface to 4.7 with depth. At pH values around 4, aluminum becomes quite soluble, as indicated by the solubility curve in Fig. I-12. It is probable, therefore, that aluminum is quite mobile in the soil profile studied.

Probably pH values as low as 4 are not required to mobilize the structural aluminum. As long as H^+ or H_3O^+ are adsorbed on the clay, there is probably a strong tendency for aluminum to migrate from the broken edges of the clay particles to the interlayer position. Soil pH values of 5.8 to 6.4 were reported by Tamura (1956) for the soil profile in which his aluminum clays were formed.

The adsorption of H^+ or H_3O^+ on to the clay particles would
produce a much higher acidity at the clay surface than in the ground
waters. Barshad (1960) suggests that H^+ displaces Al^{3+}, Mg^{2+}, and Fe^{2+}
from the octahedral position during weathering. The Fe^{++} would
probably oxidize and precipitate. The Al^{3+} would probably complex
as an hydroxide and precipitate unless the ground water is very
acid. The Mg^{++} would tend to replace the adsorbed H^+ and H_3O^+.

Both aluminum and ferric iron are somewhat soluble in low pH
ground waters such as exist in the upper 20 inches of the soil
profile studied. Both of these elements probably adsorb on the
clay surfaces as complex cations (Al and Fe hydroxides). Jackson
(1960) discusses the role aluminum plays in the profile, and
suggests that it exists in an acid environment as monomeric
aluminohexahydronium with a positive charge of about 0.65.

Coleman and Craig (1961) found that their artificial hydrogen
clays altered rapidly and spontaneously to aluminum clays, especially
if the system was warm.

Fig. I-13 is a reproduction of Fig. 6.9 from Dapples (1959).
It illustrates the weathering conditions existing in Podzolic soil
profiles. The hydrolysis curve represents the exchange of cations
by hydrogen and indicates that the adsorbed alkalies and alkaline
earths are essentially removed from the "A" and "B" horizons.
Oxidation, and solution of the carbonates are also relatively complete
in the "A" and "B" horizons. Because hydrolysis is complete in the

upper two horizons, the soil water is able to become very acid,

and aluminum and iron hydroxide go into solution. Once in solution

as complex cations, they displace some of the previously mentioned

hydronium. If adsorbed as monomeric aluminohexahydronium, they are

probably exchangeable. If complexed into clusters and semicontinuous

gibbsite sheets, they are non-exchangeable except under very acid

conditions. This complexing into gibbsite sheets results in the

chloritization of previously expanded 2:1 layer clays. It is believed

that this mechanism is responsible for the chlorite found in the

upper part of the soil profile studied. If mica or illite is stripped

free of potassium and then complexed in this fashion, dioctahedral

chlorites develop.

VII. CONCLUSIONS

The previously described study was undertaken to see why the

potassium deficient clay did not collapse in KCl. It may be concluded

that interlayer aluminum and iron complexed and chloritized the 2:1

layer clays, satisfying the charge deficiency and preventing both

expansion and collapse. Additional conclusions which can be drawn

from the study are listed below:

1. The potassium content of the clays decreases toward
   surface where weathering is more complete.

2. The soil pH decreases towards surface where hydrolysis
   is nearly complete, thus mobilizing aluminum and iron.

3. Chloritization occurs near the top of the soil profile only, where the pH is about 4.

4. Potassium saturation of the clays below 17 inches depth results in the collapse of the 14 $\overset{o}{A}$ vermiculite. Little or no collapse results in the chloritized material near surface.

5. Cation exchange capacity values were usually the same or slightly higher after 24-hour, 1N KCl treatments. Barium saturation apparently did not replace the adsorbed aluminum. The 24-hour KCl treatments apparently did remove some aluminum. This new potassium was then partly exchangeable by barium, hence the increase in C.E.C.

6. 14-day 1N KCl treatments tended to replace some of the fixed aluminum in the chloritized clays, resulting in marked increases in exchange capacity (e.g. Batch 4, 0—6 inches, C.E.C. increased from 28 to 36 m.eq./100g.).

7. 1N sodium citrate extractions removed much of the interlayer aluminum , resulting in an increase in C.E.C. from 35 to 50 m.eq./100g. in the Batch 3 clay from 0—16 inches depth.

8. Potassium saturation of the extracted sample resulted in collapse of the previously uncollapsible mineral.

9. It would have been better to have used soil from deeper in the soil profile for the engineering study described in Part Two. The deeper soil showed much greater collapse in KCl solutions than the batches of clay which were tested.

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TABLE I-I: MINERALOGICAL DATA, SOIL PROFILE STUDY

Sample Description				Before KCl Treatment			After 24 hour KCl Treatment			After 14 day KCl Treatment		
Sample No.	Depth (in)	Equiv. Size (microns)	Other	C.E.C.	%K	Glycol	C.E.C.	%K	Glycol	C.E.C.	%K	Glycol
106Ba	0-6	0.2	M21, Batch 4	28	2.7	71	28	2.8	69	36	2.6	73
64	0-16	0.4	M21, Batch 3	35	3.1	64	27	3.6	61	37	3.15	62
85	17-19	1	Soil Profile Study	21	2.7	-	23	2.8	-	-	-	-
86	26-28	1	"	28	3.0	-	28	2.9	-	-	-	-
87	42-44	1	"	22	3.4	-	22	3.9	-	-	-	-
88	55	1	"	21	3.2	-	25	3.2	-	-	-	-

C.E.C. in m.eq./100 g. of clay   (obtained spectrographically)

Glycol retentions in mg./g. of clay   (run on Ba clays)

%K obtained spectrographically.

TABLE I-II: 14Å:10Å PEAK HEIGHT RATIOS   (Showing the Effect of 24 hour KCl Treatment)

Sample Depth (inches)	Air Dried (from Fig. I-6)			Glycol Saturated (from Fig. I-7)		
	Homoionic Ba	Homoionic K	% Decrease	Homoionic Ba	Homoionic K	% Decrease
0-6	0.56	0.43	23	0.64	0.47	27
0-16	0.55	0.33	40	0.47	0.33	30
17-19	0.80	0.35	56	1.09	0.49	55
26-28	0.67	0.28	58	0.70	0.38	46
42-44	0.74	0.32	57	0.81	0.38	53
55	0.60	0.26	57	0.65	0.38	41

PODZOLIC SOIL PROFILE STUDY
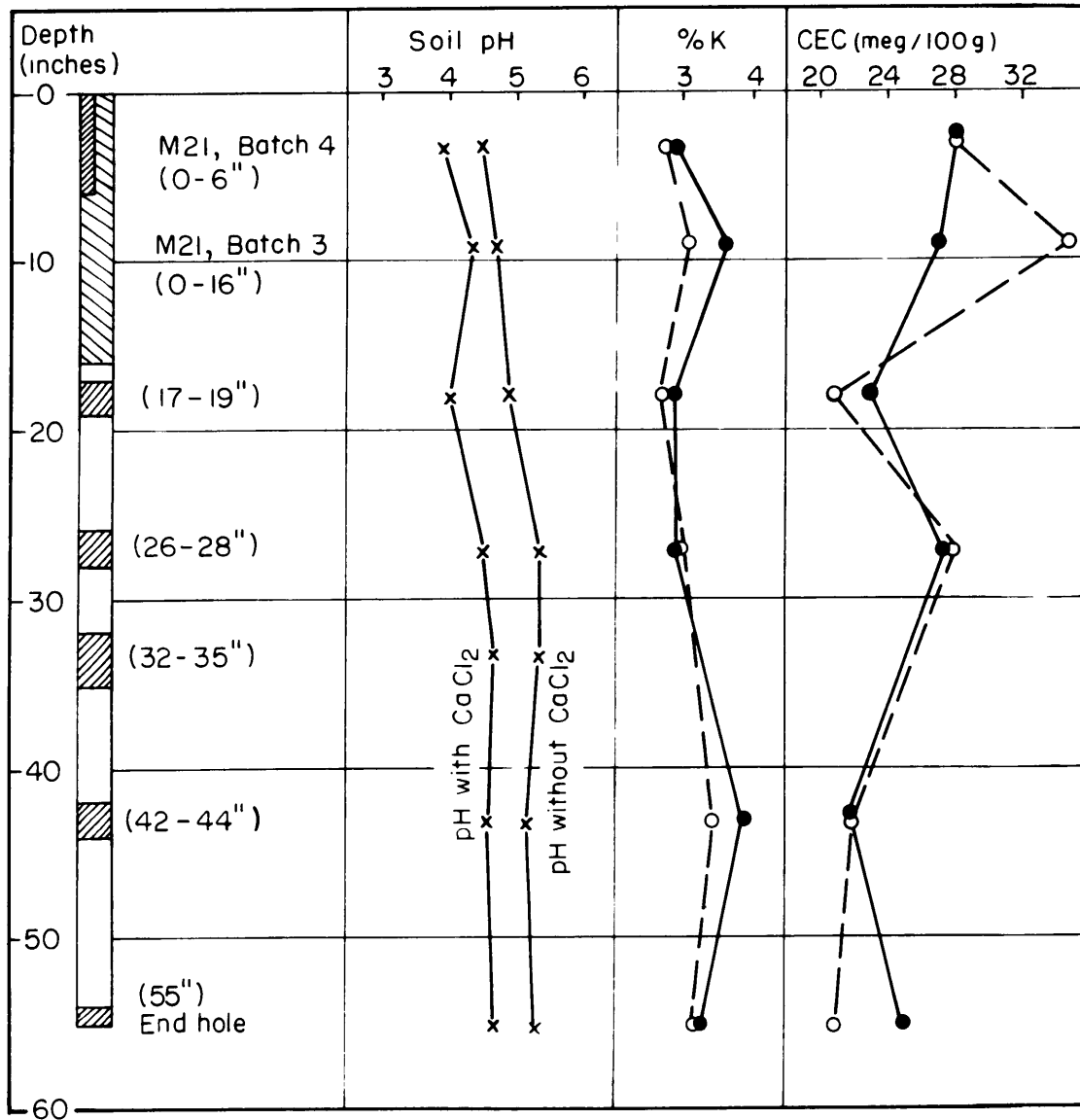
Composite plot showing sample locations, soil pH values, potassium content, and cation exchange capacity values in the soil profile studied.

O K and CEC values of Ba clay

● K and CEC values of Ba clay after 24 hour KCl treatment

FIGURE I-I

X-RAY DIFFRACTION TRACES
M21, BATCH 3 USED FOR ENGINEERING TESTS
(POWDER PATTERNS)
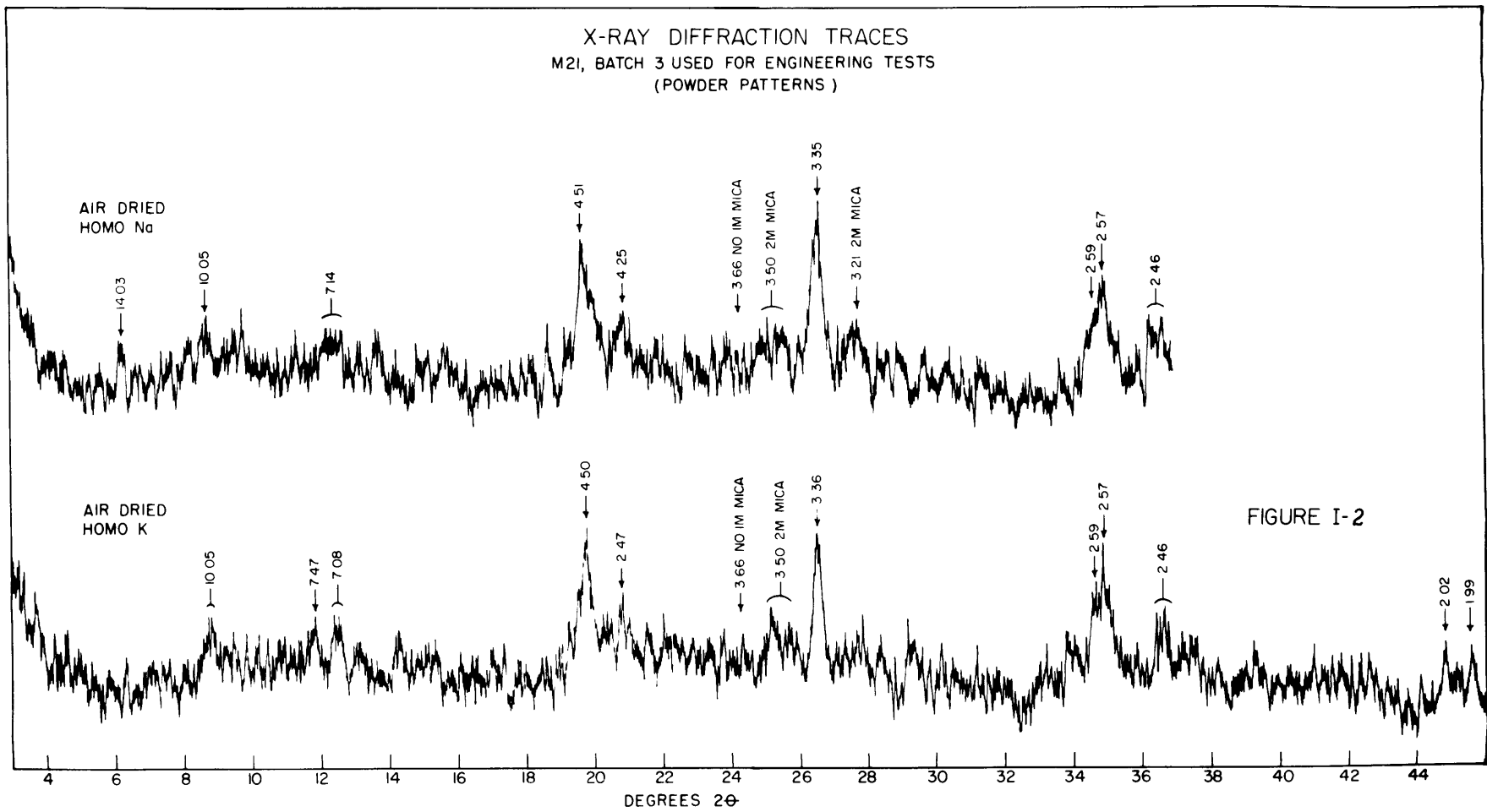
AIR DRIED
HOMO Na

AIR DRIED
HOMO K

FIGURE I-2

DEGREES 2θ

X-RAY DIFFRACTION TRACE
M21, BATCH 3 USED FOR ENGINEERING TESTS
CENTRIFUGE ORIENTED
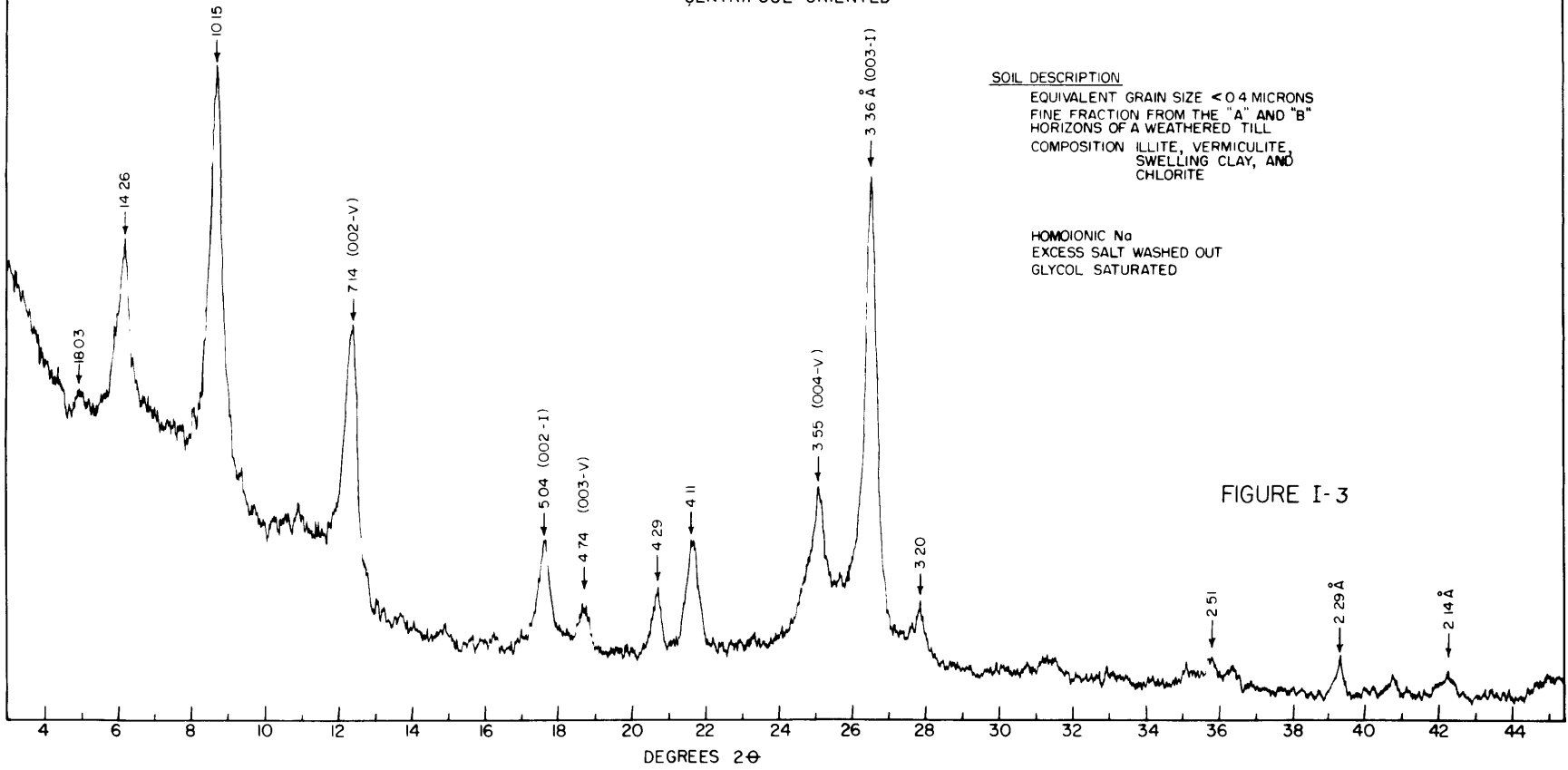
FIGURE I-3

SOIL DESCRIPTION
EQUIVALENT GRAIN SIZE < 0.4 MICRONS
FINE FRACTION FROM THE "A" AND "B"
HORIZONS OF A WEATHERED TILL
COMPOSITION ILLITE, VERMICULITE,
SWELLING CLAY, AND
CHLORITE

HOMOIONIC Na
EXCESS SALT WASHED OUT
GLYCOL SATURATED

DEGREES 2θ

X-RAY DIFFRACTION TRACE
M21, BATCH 3 USED FOR ENGINEERING TESTS
(CENTRIFUGE ORIENTED)

SOIL DESCRIPTION
EQUIVALENT GRAIN SIZE <0.4 MICRONS
FINE FRACTION FROM THE "A" AND "B"
HORIZONS OF A WEATHERED TILL
COMPOSITION ILLITE, VERMICULITE,
SWELLING CLAY, AND
CHLORITE

HOMOIONIC K
EXCESS SALT WASHED OUT
GLYCOL SATURATED

FIGURE I-4

14.26   10.05   7.1   5.01   4.74   4.27   4.09   3.52   3.35   3.20

DEGREES 2θ

64.
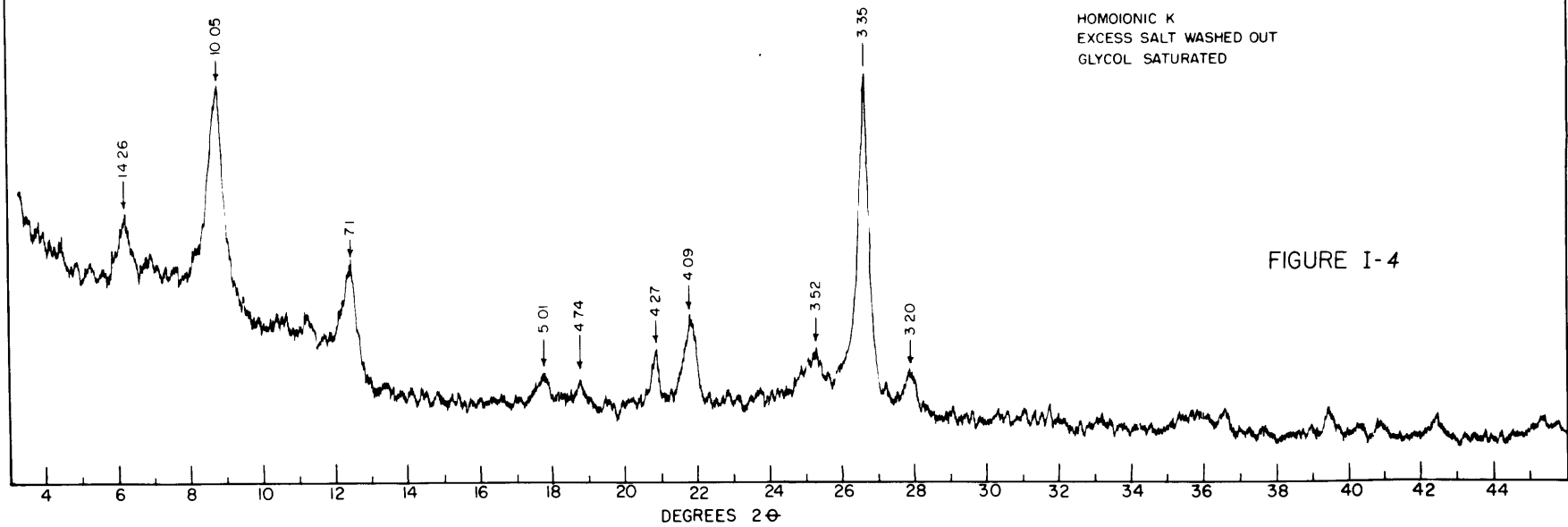
X-RAY DIFFRACTION TRACES
CLAY FROM 17-19"
(Centrifuge oriented)

Soil Description:
    Equivalent grain size 1 micron
    Sample from bottom of "B" horizon
    Composition: Illite
                 Chlorite

Homoionic K
All vermiculite collapsed
Air dry, no excess salt

DEGREES 2 θ
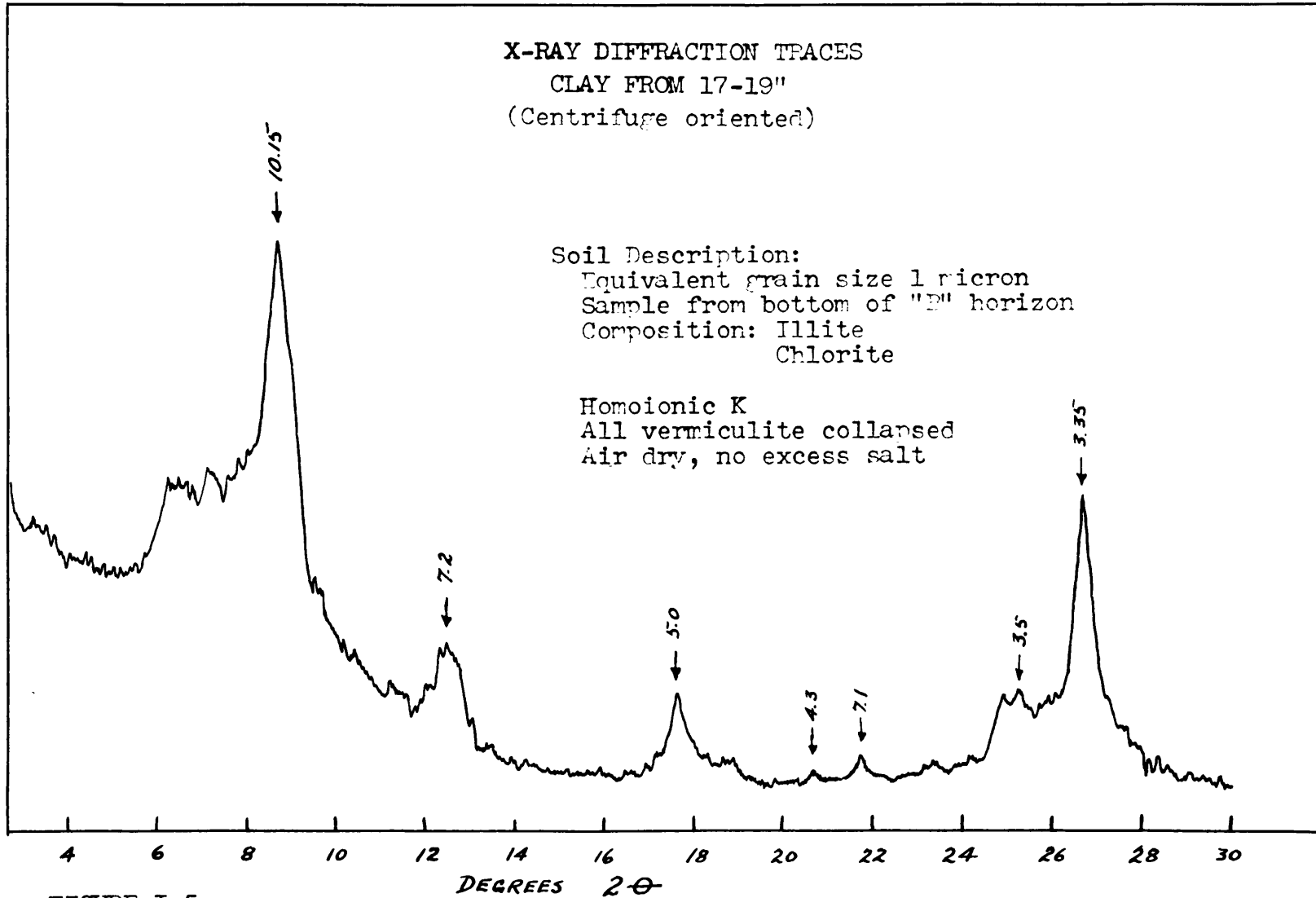
FIGURE I-5

X-RAY DIFFRACTION TRACES OF CLAYS FROM
SOIL PROFILE SHOWING EFFECT OF KCl TREATMENT

(ALL SAMPLES CENTRIFUGE ORIENTED AND AIR DRIED)
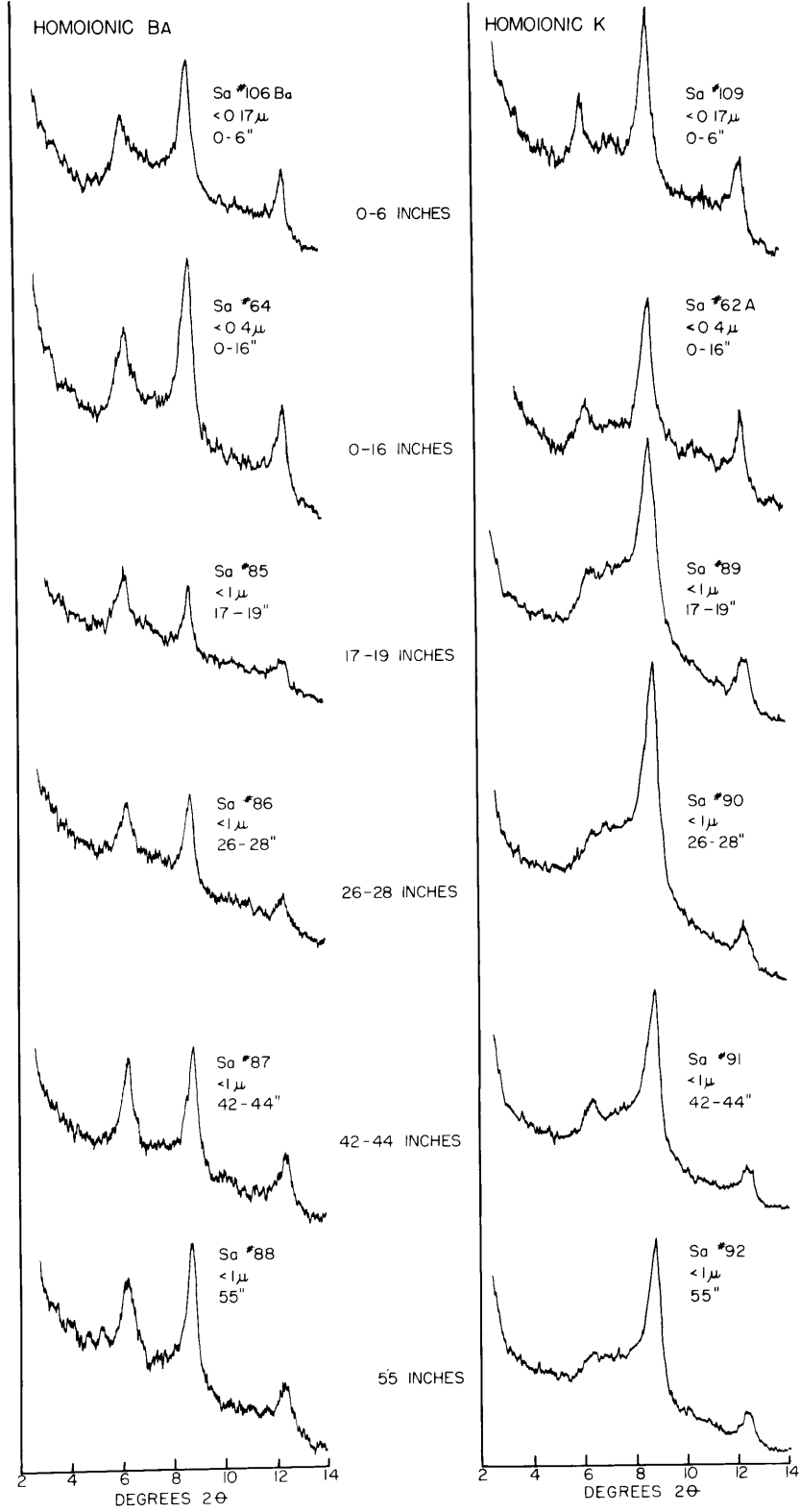
FIGURE I-6

X-RAY DIFFRACTION TRACES OF CLAYS FROM
SOIL PROFILE SHOWING EFFECT OF KCl TREATMENT

(SAMPLES CENTRIFUGE ORIENTED AND GLYCOL SOLVATED)

HOMOIONIC Ba

HOMOIONIC K

Sa #106 Ba
<0 17μ
0 – 6"

Sa #109
<0 17μ
0-6"

0-6 INCHES

Sa #64
<0 4μ
0-16"

Sa #62 A
<0 4μ
0-16"

0-16 INCHES

Sa #85
<1μ
17-19"

Sa #89
<1μ
17-19"

17-19 INCHES

Sa #86
<1μ
26-28"

Sa #90
<1μ
26-28"

26-28 INCHES

Sa #87
<1μ
42-44"

Sa #91
<1μ
42-44"

42-44 INCHES

Sa #88
<1μ
55"

Sa #92
<1μ
55"

55 INCHES

DEGREES 2θ

DEGREES 2θ
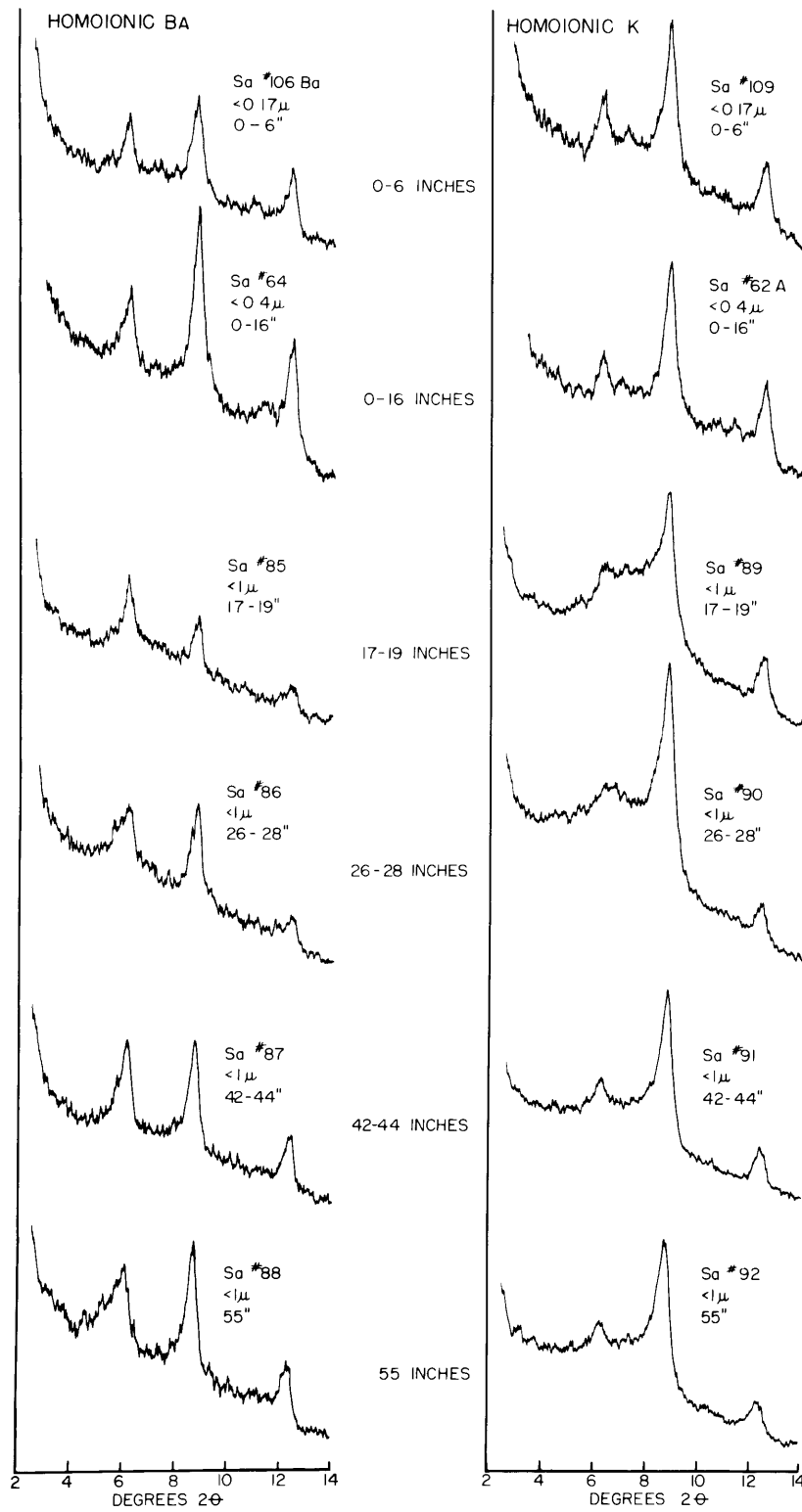
FIGURE I-7

X-RAY DIFFRACTION TRACES OF HEATED M21, BATCH 3

NOTE ALL TRACES FROM ONE CENTRIFUGED ORIENTED SAMPLE
HOMOIONIC IN Na (BOTTLE 61A) THE 500°C TREATMENT TESTS
FOR CHLORITE

FIGURE 1-8

a. 20→5 MICRONS HOMOIONIC Ba — Bottle 103 Ba
b. 5→2 MICRONS HOMOIONIC Ba — Bottle 104 Ba
c. 2→.2 MICRONS HOMOIONIC Ba — Bottle 105 Ba
d. <0.2 MICRONS HOMOIONIC Ba — Bottle 106 Ba
e. <0.1 MICRONS HOMOIONIC Ba — Bottle 107 Ba
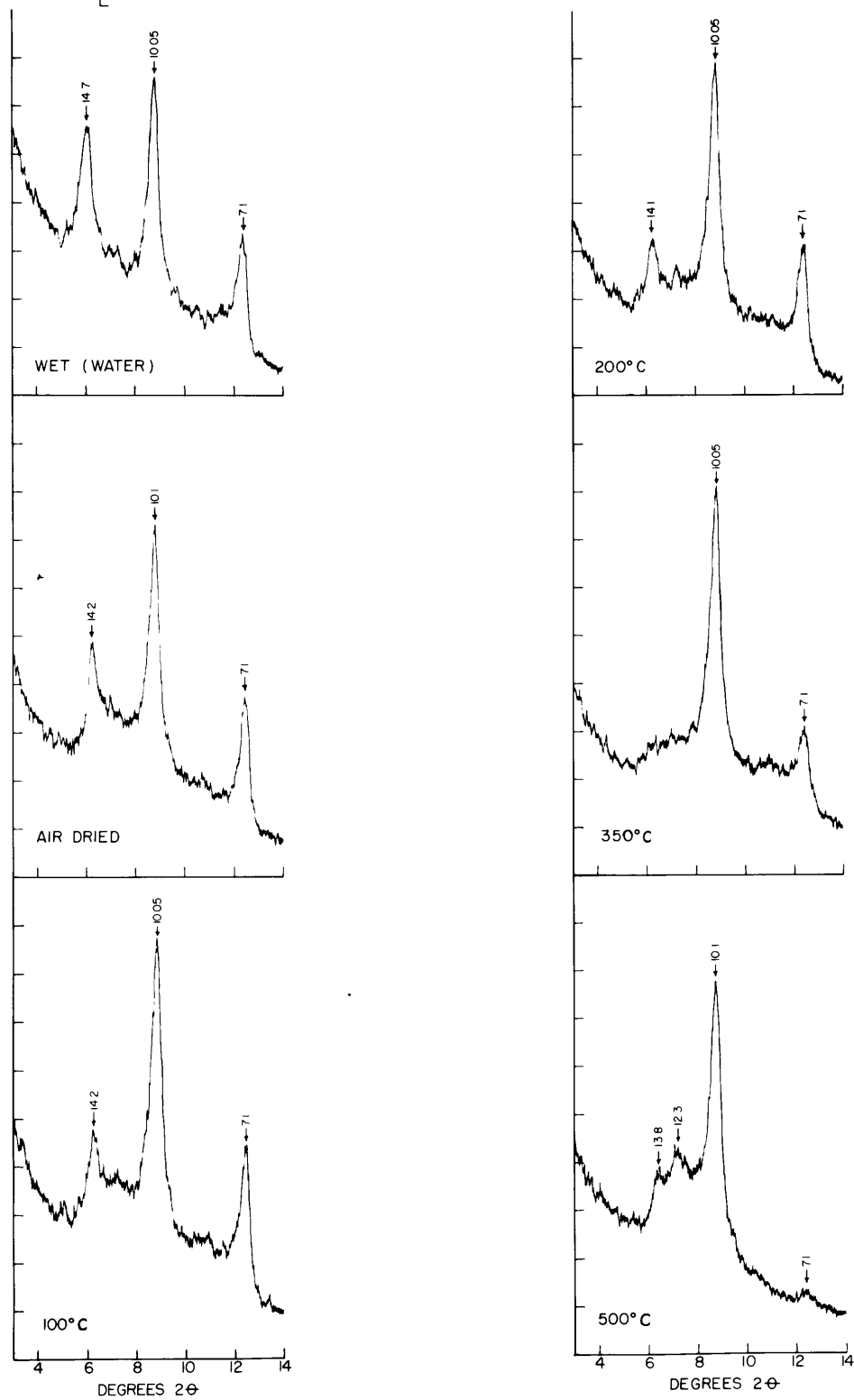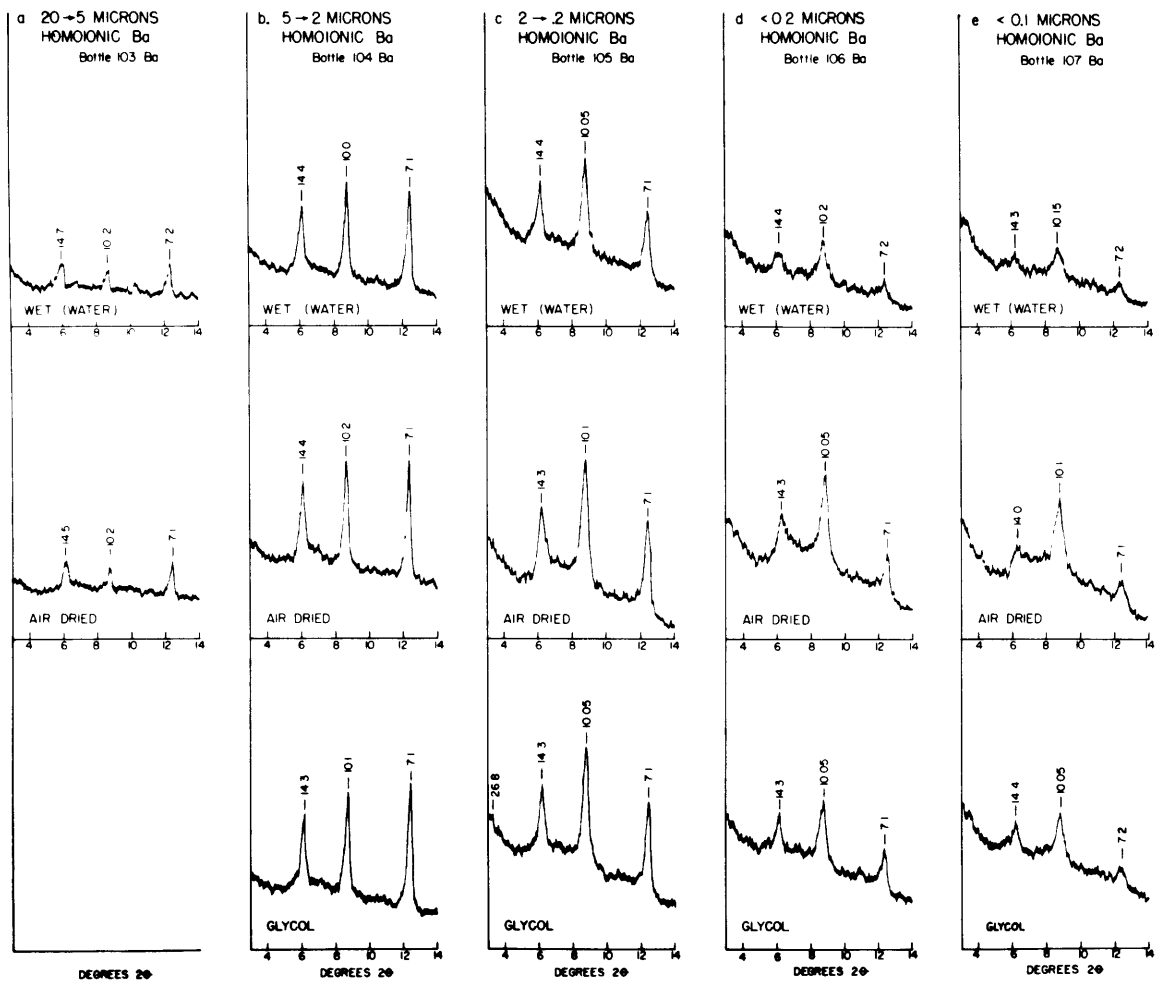
X-RAY DIFFRACTION TRACES

CENTRIFUGE ORIENTED SPECIMENS

VARIOUS SIZE FRACTIONS OF WEATHERED TILL USED TO PREPARE M21, BATCH 4

SOIL DESCRIPTIONS

EXCESS SALT WASHED OUT
ALL SAMPLES HOMOIONIC Ba
SEVERAL FINE FRACTIONS OF WEATHERED GLACIAL TILL FROM THE "A" HORIZON
CLAY MINERALS PRESENT
    ILLITE
    VERMICULITE
    SWELLING CLAY
    CHLORITE
LABORATORY SOIL M21

NOTE
THE d SPACINGS ARE INDICATED ABOVE THE DIFFRACTION PEAKS

INSTRUMENT DATA
PHILLIPS DIFFRACTOMETER
COPPER RADIATION
40 KV, 15 MA,
SCALE FACTOR · 8
TIME CONSTANT · 4
SCANNING RATE · 1°2θ/MIN

FIGURE I-9

DIFFERENTIAL THERMAL ANALYSES
M21, BATCHES 3 AND 4
(SAMPLES IN EQUILIBRIUM WITH R.H.≈50% BEFORE HEATING)
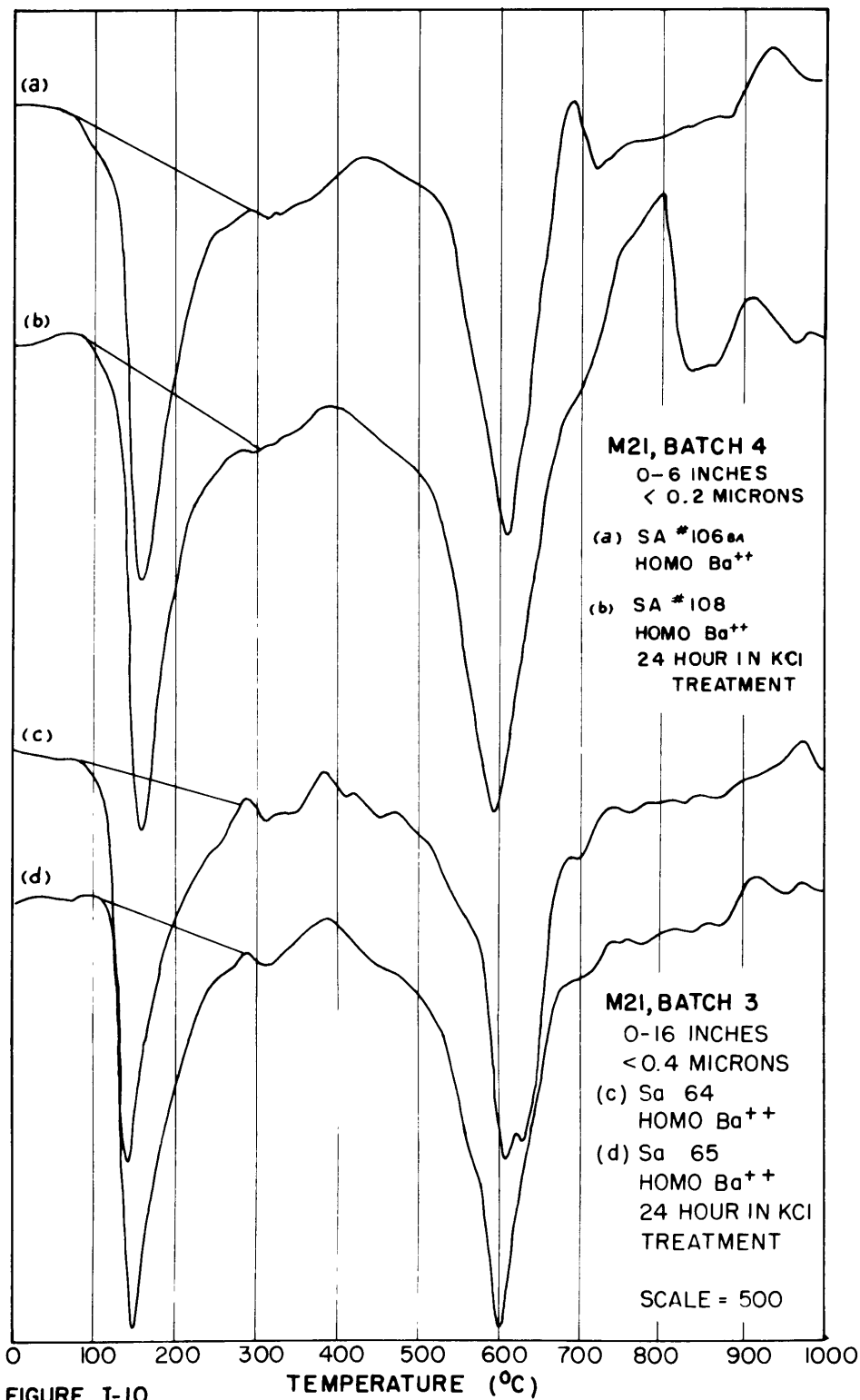
FIGURE I-10

X-RAY DIFFRACTION TRACES
SODIUM CITRATE EXTRACTED CLAY
M21, BATCH 3 (0-16")

HOMOIONIC BA

13.8   10.1   7.1

AIR DRY

16.4   14.3   10.1   7.1

GLYCOL

HOMOIONIC K

10.0   14.2   7.1

AIR DRY

14.2   7.1

GLYCOL

DEGREES 2θ

DEGREES 2θ
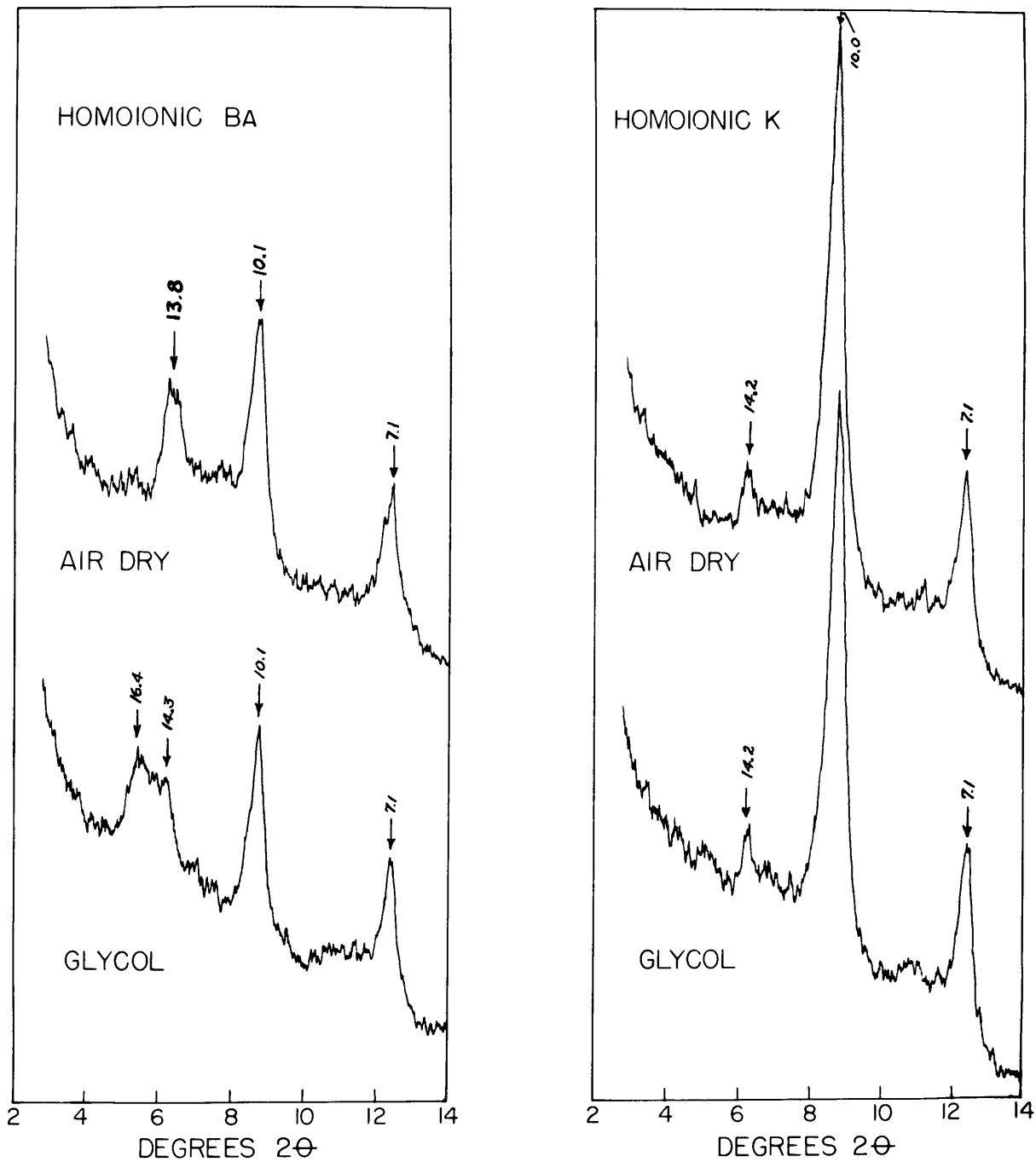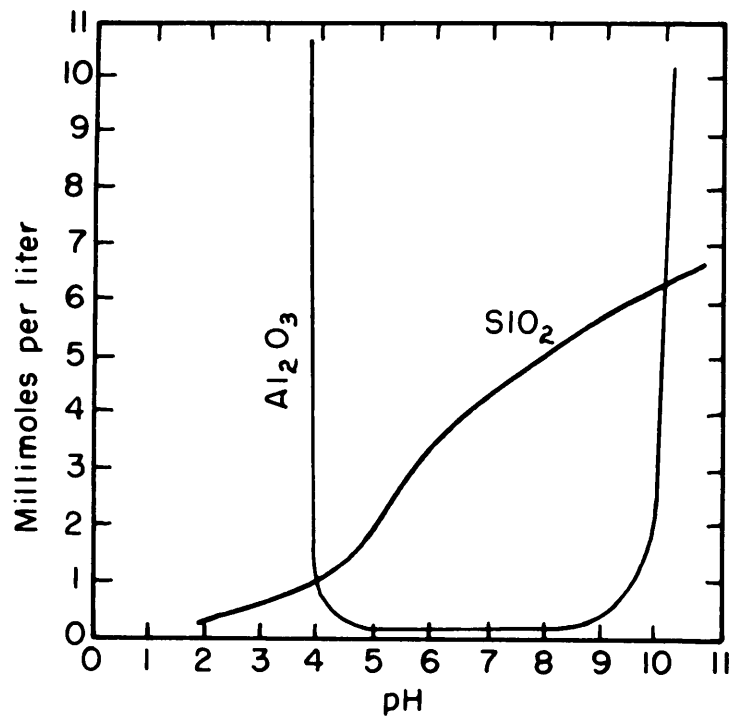
FIGURE I-11

FIGURE I-12   GRAPH SHOWING SOLUBILITIES OF
Al_2O_3 AND SiO_2 IN MILLIMOLES PER
LITER vs pH. After Correns, 1949 and
Keller 1958

Soil horizons — Intensity of physical process — Intensity of chemical process

"A"
"B"
"C"
Bedrock

Action of organisms
Frost action
Unloading

Colloid formation particularly iron and aluminum hydroxides
Solution of silica
Hydrolysis of silicates
Solution of carbonate
Oxidation

Depth below surface
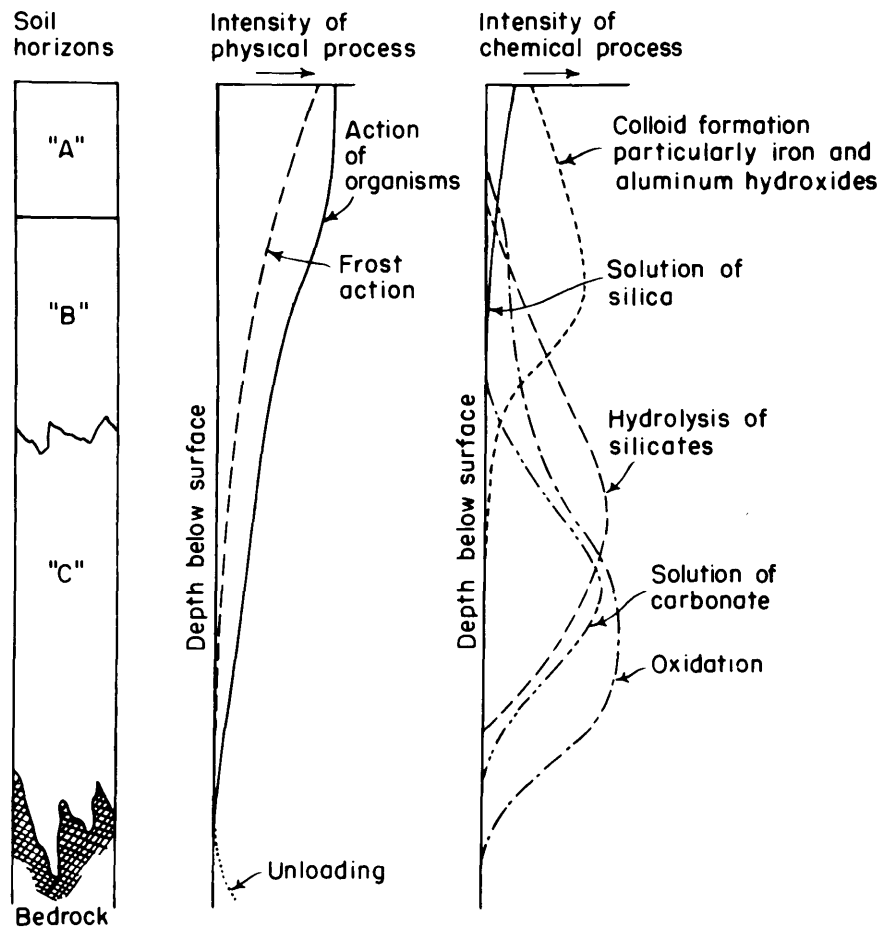
Idealized concept of the intensity of soil-forming processes in the common soil profile. Downward migration of the positions of greatest intensity of chemical processes proceeds as each soil horizon increases in thickness.

(Dapples, 1959, Fig. 6.9)

FIGURE I-13   SOIL FORMING PROCESSES IN THE COMMON SOIL PROFILE

PART TWO

ENGINEERING ANALYSES

I. INTRODUCTION

In Part One, some of the geological implications of potassium

fixation were discussed. Clay mineral diagenesis, as it is related

to potassium fixation and clay mineral collapse in the marine en-

vironment, was included in the discussion.

In this part of the thesis, the results of the engineering

tests performed on the clay batches are presented in detail. A con-

siderable amount of chemical and mineralogical control was required

for each batch of clay in order to interpret some of the test results.

Additional mineralogical data for the clay batches, not found in

Part One, may be found in Appendices B, C and D. Wherever possible,

the results of the fabric study in Part Three have been used to

interpret the engineering test results.

II. SCOPE OF THIS INVESTIGATION

A. Purpose

The ultimate purpose of this investigation was to determine

the effects of rapid mineralogical changes on the engineering

properties of clay soils in a marine environment. The immediate

purpose was to determine the effects of potassium fixation in

controlled salt environments consisting of pure NaCl and KCl. The

effects of ordinary cation exchange are also a question of considerable

interest.

Several size fractions of the clay mineral products of podzolic weathering have been studied in detail. These fractions contain variable amounts of collapsible and non-collapsible clay mineral components. Some work was also performed on a sample of interlayered illite-montmorillonite from California.

The clays were all made essentially homoionic in sodium, dispersed, and then sedimented in NaCl solutions. The sedimented samples were then leached with either NaCl or KCl before consolidation and subsequent strength testing. Two reactions take place as a result of KCl leaching: 1) Cation exchange of Na^+ by K^+ and 2) potassium fixation and mineral collapse. The effects of both of these reactions have to be determined and separated from one another where possible.

B. Previous Work

A greal deal of geological research has been done on the mechanisms of diagenesis in marine clays. Some of the most comprehensive contributions on the subject are by: Weaver (1958a and 1958b), Powers (1957), Whitehouse and McCarter (1958). This work was described in Part One in considerable detail and will not be repeated here.

Much work has also been done on potassium fixation and release from micaceous soils, especially with regard to agricultural problems. Some of this work has been summarized in Part One.

Very little work has been done to correlate the mineralogical changes with changes in engineering properties. However, considerable experimental work has been reported on the effects of cation exchange. The data in the Cornell Soil Stabilization Report (1951) were used to help develop a working hypothesis upon which the experimental work was planned for this study.

A composite plot of some of the Cornell data is given in Fig. II-1. The plot shows changes in undrained shear strength with water content for montmorillonite, illite, and kaolinite. The hatched or dotted areas enclosed by solid curves represent the range of values produced by different cations. All of the Cornell clays were electrodialyzed, neutralized with different bases to make a homoionic clay, and then mixed with distilled water. As a result of the electrodialysis method employed, the clays probably contained considerable aluminum on the exchange sites. Coleman and Craig, 1961, showed that hydrogen clays alter spontaneously to aluminum clays very rapidly, particularly at higher temperatures. This aluminum would not be removed during neutralization by the bases. The shear strengths apparently were determined by consolidated undrained triaxial tests although this is never clearly specified. The clays were mixed at a fairly high water content and consolidated to the required pressure. This preparation procedure is quite different from the sedimentation-leaching procedure used for the research in this thesis, and must have produced different soil fabrics and engineering properties.

On the basis of Fig. II-1, one would expect any mineralogical changes to outweight vastly the effects of ion exchange at high water contents. Using Fig. II-1, one might make a few hypotheses. Start with vermiculite or montmorillonite at 80 per cent water content (Point A), change it to illite by potassium fixation, and one of two things might happen. The clay may either consolidate to Point B on the illite curve and have about the same strength as before, or it may remain at the same moisture content and show a loss in strength (Point C).

Figure II-2, which is a partial reproduction of a plot from the Cornell report, shows that illite is stronger with potassium than sodium as the exchange cation. A similar plot showed the same trend for montmorillonite but is not included here. The potassium illite appears to be about 80 psf (35%) stronger than sodium illite between water contents of 50 and 80 per cent.

On the basis of these results, one might hypothesize that replacement of sodium by potassium (at constant water content) would increase the shear strength of both illite and montmorillonite. On the other hand, if potassium fixation occurred, producing a change from vermiculite to illite and a corresponding drop in cation exchange capacity, one might expect the opposite to occur. The amount of collapsible material present would determine which of the two reactions would be more important.

Rosenqvist (1957) reports the results of index tests on montmorillonite and illite, homoionic in various monovalent cations. The results of his liquid limit tests are reproduced in Fig. II-3. He relates the liquid limit to the polarizability of the exchange cations, the polarizability being induced by the force field between adjacent clay particles. The polarizability, α , is partly controlled by the dielectric of the medium, but chiefly by the size of the cation. Large cations are more easily distorted to produce an induced dipole than smaller cations.

Rosenqvist (1955) seems to suggest that the polarizable cations induce an attraction between particles. It may be that the attraction between the positive edges and the negative faces increases as the polarizability of the adsorbed cations increases. More water would, therefore, be required in a potassium clay to reduce the interparticle forces to the same level as in a sodium clay. If we assume that the net forces at the liquid limit are the same in Na and K clays (i.e., they have the same strength), the K clay will have the higher moisture content (the higher liquid limit).

During a seminar series at M.I.T. in the fall of 1960, and in a recent publication (Moum and Rosenqvist, 1961) Rosenqvist explained the shape of the montmorillonite curve in Fig. II-3, as being a function of the amount of interlayer (infracrystalline) water. For K, Rb and Cs clays, the amount of interlayer water is about the same so that the liquid limit is a straight line function of the polarizability as in illite. On the other hand, Li and Na adsorb a greal deal of water

because they have very high ionic potentials. This gives these cations very large hydrated radii and the montmorillonite swells to large d values. The hatched area in Fig. II-3 represents this interlayer water.

In his seminar series, Rosenqvist also described a group of experiments designed to study the effects of interlayer water and interparticle water on the shear strength of sodium and potassium clays. (This work has been presented recently at the Fifth International Conference on Soil Mechanics, 1961). Illites and montmorillonites, artificially sedimented and consolidated in 35%.NaCl, were subjected to KCl leaching for a period of 26 months before strength testing.

The illites, which were nearly completely leached by KCl, had undisturbed undrained strengths about 1.6 times greater than the corresponding Na illites. In the remolded state, the K illite was about 2.1 times stronger than the Na illite. The Na and K illites had sensitivities of 7.5 and 4.5 respectively. The shear strength envelopes are replotted in Fig. II-4 for the illites. Rosenqvist explains the higher strengths of the K illites in terms of the polarizability of the cations just as he did for the liquid limit values.

The results of strength tests on the montmorillonite are shown in Fig. II-5. The leaching was incomplete so the K (Na) curve was extrapolated to 100% potassium content. Once again the K clay is stronger than the Na clay in the undisturbed state. In the

remolded state, the Na clays were stronger than the K clays. The reason for this may be related to the expulsion of interlayer water during KCl leaching. Although no K fixation occurred, x-ray patterns indicated that the (001) reflection decreased from 20.1 to 16.35 $\overset{o}{A}$ as a result of the leaching. This water was found to correspond to about 18% of the volume of the mineral phase. This water became part of the interparticle pore water upon expulsion and although it appears not to have affected the undisturbed strength much, it seems to have greatly reduced the remolded strength.

These changes reflect themselves in the sensitivity of the clay. Sensitivities of 4 and 14 were obtained on the Na and K montmorillonites respectively.

When Rosenqvist's data are plotted as undrained strength versus water content, the KCl leached clays are stronger than the Na clays at a given water content.

C. Clay Soils Studied

The details of the mineralogy of the clay batches are presented in Appendices B, C and D. Approximate compositions for each batch are given below for easy reference. The simple chemical and engineering tests results are also given.

1. M21, Batches 1 and 2: (90% smaller than 2 microns)

Before K Fixation (0.154N NaCl)	After K Fixation (0.154 N KCl(+NaCl))
60% illite	70% illite
15% vermiculite	0-5% vermiculite
5% chlorite	5% chlorite
20% quartz	20% quartz
C.E.C. = 19 m.eq./100g.(av)	C.E.C. = 14 m.eq./100g (av.)
K = 3.0%	K = 3.4%

The x-ray results presented in Appendix B, showed that the vermiculite collapsed from its 14 $\overset{o}{A}$ d spacing to 10 $\overset{o}{A}$ illite in the KCl leaching solutions. This collapse was permanent for the most part and accompanied by an increase in fixed potassium. The cation exchange capacity (C.E.C.) also dropped from about 19 to an average value of 14 m.eq./100g. Although the glycol retention did not show a decrease with the increase in fixed K it is believed that there was some decrease in surface area. The removal of fixed aluminum by the KCl treatment, as discussed in Part One, may have had some effect also, tending to bring the glycol retention back up.

2. M21, Batch 3 (smaller than 0.4 microns)

    60% illite
    15% vermiculite
    20% chlorite
    5% quartz
  C.E.C. = 35 m.eq./100g.
     K = 3.1%

The detailed mineralogical studies for this batch are given in Appendix C. The x-ray results showed that some collapse did occur in the 14 $\overset{o}{A}$ vermiculite component. Glycol retentions on Na, K, and Ba clays showed that the K clay had the smallest glycol retention probably due to a decrease in surface area as a result of the collapse. Long term KCl treatments did not cause K fixation; rather the C.E.C. increased and the K content remained fairly constant. KCl proved to be a good neutral salt for displacing fixed aluminum as discussed in Part One.

3. <u>M21, Batch 4</u> (smaller than 0.17 microns)

    65% illite
    10% vermiculite
    25% chlorite
    trace of quartz

The detailed mineralogical studies for this batch are presented in Appendix D. KCl treatment resulted in little collapse because the vermiculite content was so low. The C.E.C. increased with time under KCl treatment as the fixed aluminum was removed. This material was highly chloritized in the soil profile as discussed in Part One.

4. <u>California Illite-Montmorillonite</u> (smaller than 2 microns)

    Interlayed illite-beidellite

    From shales of Santa Monica area, California

This clay was not studied in detail. X-ray film data indicated that KCl treatment caused a marked increase in intensity of the 10 $\overset{o}{A}$ illite peak resulting from collapse of the beidellite. The Atterberg Limit data presented later, showed that considerable interlayer water was expelled by this collapse. The surface area of the clay probably decreased a great deal also but no glycol retentions were run to check this.

In summary it may be stated that the vermiculite or beidellite components of the clay batches did collapse in KCl solutsions. Usually this collapse was reversible, the clays re-expanding when the KCl was washed out by either NaCl or $BaCl_2$. M21, Batches 1 and 2 showed evidence of permanent fixation and collapse.

One layer of water is expelled during collapse of the
vermiculite and the surface area must decrease. Collapse of the
montmorillonite in the California clay probably involved the expulsion
of many layers of water when Na was replaced by K.

D. Engineering Tests and Experimental Methods

A series of consolidation, permeability, and strength tests
have been performed on several of the batches of clay. In general,
the following procedure was employed. The clay was washed in 1 or
2 Normal NaCl depending on the batch, brought into equilibrium with
a 9%.NaCl(0.154N) solution by washing, dispersed 10 minutes in a
mixer or blender, deaired, and syphoned into a lucite sedimentation
chamber. The clay would then flocculate freely without "matting"
and settle into the consolidation chamber at the base of the sedi-
mentation column. If the flocs matted because the clay suspension
was too thick, the suspension was diluted and sedimented in two
portions. After a 3 day settling period, the clay was subjected to
a small seepage force for a day or two (10 cm. head). A thin porous
stone was then allowed to settle directly onto the soil. A little
clay slurry was always lost up the sides during this step. The clay
rapidly consolidated next to the stone, the slurry was cleaned out
above the stone, and clear NaCl or KCl solution was added to the
chamber. A 20 cm. head was then applied and seepage was carried
on over an 8 or 9 day period. During this time, 1 to 3 soil volumes
of solution passed through the clay sample. The leached clay sample
was then consolidated under increasing increments of load. The con-
solidated samples were usually about 3/4 inches thick.

Filters of silt and sand were used in the early consolidation tests, but were abandoned in favor of the method described above. Particles from the filters caused the lucite pistons to stick erratically producing large experimental erros.

Figure II-6 contains photographs showing samples of clay at various stages of sedimentation and consolidation.

About one part per million of mercuric chloride was added to all of the samples from Batches 1 and 2, to prevent any biological activity. None was added to Batches 3 and 4 and no detrimental effects were observed.

Falling head permeability tests were conducted on the clays at the end of each load increment in many of the tests. These were discontinued towards the end of the year because the values computed from the consolidation data gave similar trends.

Unconfined compression tests were performed on soil samples from Batches 1 and 2. Miniature samples were taken from the consolidated clay by means of a tiny tube sampler and extruder. The samples were approximately 1/2 inches long by 1/4 inches in diameter. A sensitive pan balance was used to load and fail the tiny specimens. An approximate measure of strain was obtained by recording the deflection of the stylus. This procedure was discontinued after Rosenqvist visited M.I.T. in the fall of 1960. His work on similar Na and K clays had shown differences in sensitivity depending on the exchange ion. The degree of disturbance produced by tube sampling was probably different for the Na and K clays making the strength data difficult to interpret.

A vane testing procedure was adopted and used during this past year. A miniature vane measuring 1/4x1/4 inches was made and mounted on a Wykeham Farrance stand. The vane was lowered into the clay and turned by means of a Water's watch gauge measuring torque in ounce inches. Strain could not be measured by this device. Time to failure was kept short to minimize drainage during shear. Failure was usually reached in about 1/2 minute. A photograph of the apparatus is shown in Fig. II-7. Another photograph in Fig. II-32, shows two vane tested samples which, when oven dried, split naturally along horizontal planes.

Drained direct shear tests were performed on M21, Batches 2 and 3 to obtain the effective stress envelopes. A small mold, 1 3/4 inches square, was used because only a small amount of clay was available. The clay samples were 3/8 to 1/2 inches thick at failure. The rate of strain at failure was about 2.7×10^{-4} inches per minute (about 0.9% per hour) for the tests giving adequate time for 100 per cent consolidation.

Determinations of the sodium to potassium ratio in the KCl leached samples were made on several samples. The extent of leaching turned out to be an extremely important consideration in the interpretation of the engineering test results. A Baird flame photometer was used to make the analyses.

Atterberg limits were obtained on several samples before and after KCl treatment. Although the tests were run at widely spaced intervals, it is felt that they are all comparable with one another.

III. ENGINEERING TEST RESULTS

A. Index Tests:

Atterberg Limits were run on several of the soil samples after strength testing. The results are listed in Table II-V.

For M21, Batches 1 and 2, KCl leaching caused the liquid limit to increase similar to Rosenqvist's illites. This suggests that cation exchange is the dominant reaction rather than interlayer collapse, at least as regards the liquid limit. The plastic limit also increased a little so that the plasticity index tended to remain the same.

For Batch 3, the liquid limit was larger with K than Na as the exchange cation, just as in Batches 1 and 2. The plastic limits, however, are nearly the same so that the K clay had a larger plasticity index. It will be seen later that despite this greater plasticity, the K clays had higher friction angles.

The California illite-montmorillonite showed very different trends. With 0.154N KCl as the pore fluid, the liquid limit was slightly lower, and the plasticity index much lower than with 0.154N NaCl. When the KCl concentration was increased to about 0.6N, the liquid limit and the plasticity index showed a very large decrease. These changes and differences from the M21 clays were caused by much greater layer lattice contraction and expulsion of interlayer water as discussed by Rosenqvist. Apparently this clay collapsed a great deal more in the stronger KCl solution.

The specific gravity of M21, Batches 1 and 2 was computed to be 2.71 on the basis of the mineralogical composition. A value of 2.85 was used for Batch 3 on the basis of one specific gravity test. These values were used in the computations for the engineering tests.

B. Consolidation Tests

1. M21, Batch 2

The samples of M21, Batch 2 were saturated with sodium by washing in 2 Normal NaCl. The excess salt was washed down to 9‰ NaCl (0.154 Normal) before sedimentation. Typical consolidation curves are shown in Fig. II-8. The dashed curves are for the sodium clays and the solid curves for the KCl leached clays. Although the curves are quite similar in shape, the potassium clays exist at a higher void ratio than the sodium clays at any given consolidation pressure within the range studied. The Na curves lie quite close together whereas the K curves are somewhat separated. It was originally thought that this spread was just an experimental error. Later determinations of the K:Na ratio (degree of leaching) indicated that the most completely leached clays showed the greatest separation from the Na curves. This is discussed in more detail later. It is sufficient to note here that the upper curve (Consol. No. 11) has a higher K:Na ratio than Consolidation No. 19. The c_v curves for the clays are also plotted on this figure. The K clays have slightly higher c_v values than the Na clays.

All of the above described clays were deposited in 9‰ NaCl in an expanded form (i.e., containing 15% vermiculite), so they all had the same fabric before leaching. The maximum seepage force on the clay was about 40 psf at the bottom of the samples. This is about the same as the first static load shown on the e-log p curves. At this load, the K clays existed at higher void ratios than the Na clays, so apparently greater consolidation was produced by NaCl leaching than KCl leaching. The K clay appears to have "set-up" as a more rigid structural network. Unfortunately volume changes were not measured during leaching.

Volume changes were measured on Batch 1 clays and reported in Publication 105, Soil Engineering Division, M.I.T., 1960. The clays were deposited in NaCl and leached at very high void ratios (about 10) with KCl. At these high void ratios, collapse of the vermiculite and expulsion of the interlayer water resulted in a 3 dimensional shrinkage and a 10 to 15 per cent reduction in void ratio. This of course is opposite to the effects observed in the previously described consolidation tests.

The potassium leached clays were completely collapsed at the end of the consolidation tests as indicated by the x-ray film data in Figs. B-1 and B-2 in Appendix B.

As it was not known whether potassium fixation or cation exchange played the predominant role in the changes described, two consolidation tests were run on clays which had been collapsed prior

to sodium saturation and sedimentation. The clays were washed twice in 0.1 Normal KCl, sitting overnight in the second wash. The clay was then washed twice in 2 Normal NaCl, sitting overnight in the second wash. The excess salt was then removed by three washes in 9‰ NaCl and the clay sedimented as previously described. Consolidation tests 17 and 18 were leached with 9‰ NaCl and 11.5‰ KCl respectively, before consolidation. The consolidation curves obtained are shown in Fig. II-9. The two curves lie very close together rather than spread apart as before. However, the KCl leached clay is still on top. Consolidation 18 was checked by Consolidation 21 which was absolutely identical. Consolidation 17 was not checked. Unfortunately, the K:Na ratio was not obtained for either Consolidation 18 or 21. This may not be too important as the leaching time, soil quantities, etc. were the same for all of the tests. A K:Na ratio of about 2.5:1 is probable for this clay, just as in Consolidation 11.

It should be mentioned here that the collapsed clay in Consolidation tests 17, 18 and 21 are partially re-expanded by the strong NaCl treatment prior to consolidation. This is shown by the x-ray film data in Fig. B-3. Some of the vermiculite remained collapsed as indicated by the x-ray data and the cation exchange capacity data (Table B-I, Appendix B).

In Fig. II-10, the consolidation curves for the collapsed and uncollapsed clays are compared.

Curve 1

>   Average of Consolidation 11 and 19
>   Clay deposited in expanded form
>   Collapsed by KCl leaching after deposition but before consolidation.

Curve 2

>   Average of Consolidation 10 and 20
>   Clay deposited in expanded form
>   NaCl leached and consolidated in expanded form.

Curve 3

>   Consolidation 18
>   Clay collapsed before sedimentation in NaCl
>   KCl leached after deposition but before consolidation.

Curve 4

>   Clay collapsed before sedimentation in NaCl
>   NaCl leached and consolidated in semicollapsed form.

We may conclude that KCl treatment prior to sedimentation produces a different result than KCl leaching after sedimentation. It may be that the partially collapsed clay flocculates differently than the expanded clay thus producing a different soil structure. If the Na collapsed and Na expanded curves (4 and 2 respectively in Fig. II-10) are extended to the left, it appears as though the collapsed clay has flocculated and settled to a smaller void ratio than the expanded clay. Judging from the shape of the curve, it appears as though the initial flocculated fabric and structure may play nearly as great a role as leaching. At any rate, potassium fixation by a clay containing as little as 15 per cent collapsible vermiculite produces measurable changes in the consolidation characteristics.

2. M21, Batches 3 and 4

Air dry samples of this clay were given two consecutive washes

in 1 Normal NaCl, a blender or mixer being used to break up the clay

lumps. The salinity was then brought down to 9‰ NaCl by 3 washings,

dispersed in a mixer for 10 minutes, desired, and sedimented in

9‰ NaCl. The clay for all consolidation tests except Consolidation 34

was prepared from air dry, powdered clay and tested for about the

same length of time. A shortage of clay made it necessary to use the

clay from Consolidation 33 for Consolidation 34. In Part One of this

report, it was suggested that exposure to neutral salt solutions over

an extended period of time caused the removal of some fixed aluminum.

By the end of Consolidation 34, the clay had undergone about 3 months

of exposure to solutions of NaCl and KCl and some serious changes

no doubt took place.

The consolidation curves for the six tests run on Batch 3 are

shown in Fig. II-11. The KCl leached clays all have e-log p curves

which lie above a close grouping of NaCl curves. Tests 30 and 31

were pilot runs on smaller amounts of clay than used for the rest of

the tests. Consolidation 31 was, therefore, more completely leached

than the others. K:Na ratios of 7.3:1 and 1.5:1 were obtained for

Consolidation 31 and 35 respectively. Poorly leached Consolidation 35

lies much closer to the Na curves than Consolidation 31. A K:Na ratio

was not obtained on Consolidation 34, but at first glance its position

suggests that it is well leached. On the other hand, this clay was

used twice as mentioned earlier. Any decrease in fixed aluminum would

probably cause an increase in exchange capacity which would also tend to shift the curve upwards.

Two consolidation curves for Batch 4 are shown in Fig. II-12. The KCl leached clay had a K:Na ratio of 9.7:1 at the end of the test indicating fairly complete leaching. The effect of the leaching is the same as before.

In Fig. II-13, consolidation curves for M21, Batches 2, 3, and 4 are presented together. Batches 3 and 4 are quite similar, lying above Batch 2 because of their greater cation exchange capacity and smaller grain size.

Batches 3 and 4 could not be permanently collapsed before sedimentation because potassium would not fix in the interlayer position. NaCl washings after KCl treatments invariably washed out the new potassium. This meant that no assessment could be made of the relative effects of fixation and cation exchange.

In the fabric study in Part Three of this report, it was suggested on the basis of Fig. III-5, that the Na clays were better oriented at any given consolidation pressure than the K clays. This orientation, which is produced by the breakdown of the initial flocculated structure, seems to be more easily developed in the Na clays. This better orientation may explain why the Na clays lie below the K clays on the consolidation plots.

According to Rosenqvist (1957) the greater polarizability of the potassium ion would result in a greater attractive force between the edge to face contacts in a flocculated soil. The flocculated K clay

with closer particle to particle contacts and more rigid structure would be more difficult to compress than a similar Na clay. One could also explain the differences in terms of the size of the hydrated cations. Sodium with a larger hydrated radius than potassium, might have a dispersing or lubricating effect which could facilitate particle reorientation.

The presence of expanded minerals, which are somewhat free to glide along the basal planes through the interlayer water might also tend to facilitate particle reorientation.

3. California Illite-Montmorillonite

Consolidation curves for the California illite-montmorillonite are shown in Fig. II-14. The curves are nearly identical despite the KCl leaching. Only small amounts of soil were used for these two tests, so it is thought that a high K:Na ratio existed in the KCl leached sample. The c_v curve for the K clays lies above the Na clay as it did in M21.

In a montmorillonite, more of the water would be present as interlayer water with Na than K as the exchange cation. At a given void ratio, therefore, the Na montmorillonite had less interparticle pore water than the K montmorillonite. In effect, this says that at a given consolidation pressure, the K montmorillonite exists at a higher interparticle pore water content or void ratio than the Na montmorillonite, although the total water contents or void ratios are about the same. It makes these results more compatible with the

findings for M21, Batches 1 to 4. KCl treatment had two effects on
the montmorillonite. Greater edge-face attraction forces (Rosenqvist)
and a more rigid structure tend to cause an open structure with a
high void ratio. It also causes marked collapse, expulsion of inter-
layer water and a lower void ratio at a given consolidation pressure.
The two effects appear to have been about equal here so that the
consolidation curve of the K clay is the same as for the Na clay.

The montmorillonite had very pronounced secondary consolidation
characteristics. An attempt was made to see if any changes in the
secondary consolidation were produced by KCl leaching. In Fig. II-15,
the per cent settlement is plotted against log time for several load
increments. The secondary compression portion of the curves appear
in the 3rd cycle on this plot. Although the curves are quite similar,
a difference is noticeable between the Na and K clays: the Na clay
being slightly more compressible than the K clay. The per cent
settlement per log cycle averages 2.44 for the K clay and 2.95 for
the Na clay.

C. Permeability Tests

Falling head permeability values on M21, Batch 2 are plotted
against consolidation pressure in Fig. II-16. The plot shows that
the K clays are all more permeable than the Na clays regardless of
collapsing before sedimentation. The greatest spread occurs for
Consolidation 11 which has the higher of the two determined K:Na ratios.
The spread of these curves is rather similar to the spread of the con-
solidation curves, suggesting that the permeability is a function of
the void ratio.

In Fig. II-17, the permeability is plotted against void ratio for the same clays. At a given void ratio the K clays are only slightly more permeable than the Na clays.

Permeability values for M21, Batch 3, calculated from the consolidation data, are shown in Fig. II-18. Only curves for Consolidations 30 and 31 are plotted because these represent the greatest spread. As before, the K clay is slightly more permeable than the Na clay.

In Fig. II-19, the permeability is plotted against void ratio for Batch 3. There seems to be very little, if any, difference between the Na and K clays.

Two permeability plots for the California illite-montmorillonite (Fig. II-20) show that the K clay has a greater permeability than the Na clay at any given consolidation pressure within the range studied. Fig. II-21 shows that the K clay is more permeable than the Na clay at any given void ratio within the range studied. Permeability values computed from falling head tests gave trends similar to those calculated from the consolidation data. The permeability results may be explained in the following manner. Considering the montmorillonite first: at a given void ratio, the expanded Na clay contains a great deal more relatively immobile, interlayer water than the partially collapsed K clay. At this void ratio the K clay contains more interparticle water which is free to flow and hence has the greater permeability. At a given consolidation pressure, the void ratios of the Na and K clays are about the same, so the same argument applies.

The batches of M21 did not show the same pronounced effects of collapse that the California clay did. At a given void ratio, the K clays were only slightly more permeable than the Na clays. This is probably because only a small amount of vermiculite (15% maximum) was present. Further only one water layer was expelled by the collapse. This means that only a very small percentage of the total water is bound up as interlayer water and the effects of collapse do not show up. At a given consolidation pressure the K clays were more permeable than the Na clays because they were at higher void ratios.

D. Strength Tests

1. M21, Batches 1 and 2 - Undrained Shear

The results of unconfined compression tests on Batches 1 and 2 are shown in Figs. II-22 and II-23. The test data are tabulated in Table II-1.

Figure II-22 shows that the sodium clay is stronger than the potassium clay at any given consolidation pressure within the range studied. All of the samples shown in Fig. II-22 were sedimented in the expanded form and subsequently treated with KCl. The scatter of the points for Batch 1 was caused by grains from the silt and sand filters producing erratically sticking pistons, variable degrees of KCl leaching, disturbance of the miniature unconfined samples during sampling, and partial rebound of the clay before strength testing.

Figure II-23 shows that the potassium clay is stronger than the sodium clay at any given water content within the range studied. The

vane strength data which are discussed later, indicated that the Na clays were more sensitive than the K clays. The strengths of the Na clays are probably too low compared to the K clay strengths for all unconfined compression tests.

Sample 21 (sedimented collapsed and KCl leached) is stronger than sample 19 (sedimented expanded and KCl leached) even though both have nearly the same water content. This difference is probably related to different soil fabrics produced during initial flocculation. Layer lattice collapse in sample 19 may have had some effect.

In Fig. II-24, vane shear strength results are compared with the unconfined results. The vane test data may be found in Table II-II. Samples 20 and 19 were deposited in the expanded form and subsequently leached with NaCl and KCl respectively. Once again the Na clay is stronger than the K clay. The actual strength values, however, are much higher than for the unconfined tests. Samples 17 and 21, shown in the same figure, were collapsed with KCl prior to sedimentation and subsequently leached with NaCl and KCl respectively. The vane strengths indicate that the K clay is now stronger than the Na clay at the consolidation pressure under consideration.

Rosenqvist's work indicated that K illites are stronger in undrained shear than Na illites at a given consolidation pressure. As discussed previously, he attributed the greater strength to greater edge to face bonding forces when the more polarizable K cations replaced the Na cations. Samples 17 and 21 were essentially all illite

when they were deposited, having been collapsed in KCl. The results
on these two samples are in agreement with Rosenqvist's data. However,
when the clays were deposited in the expanded form (i.e., 15%
vermiculite) and subsequently leached, the opposite trend developed;
the expanded Na clay being stronger than the collapsed K clay. During
KCl leaching of the expanded Na clay, a certain amount of K fixes in
the interlayer position resulting in an expulsion of interlayer water.
This causes some of the expanded packets to shrink along the "c" axis,
producing an increase in the interparticle water and a decrease in
interlayer water. The liquid limit results discussed previously
suggested that this effect was minor compared to the effects of cation
exchange. Probably the explanation is related to the soil structure
modified by the type of cations present. Samples 21 (K) and 17 (Na),
both deposited collapsed, have similar e-log p curves and probably
similar interparticle arrangements. The K sample, however, may have
stronger edge to face bonding forces (Rosenqvist) or in effect greater
mineral to mineral contact stresses and hence greater resistance to shear.

Samples 19(K) and 20(Na), both deposited expanded, have different
e-log p curves; the K samples having the more open or flocculated
structure. The fabric study on Batch 3, strongly suggested that the
Na clays had greater horizontal parallelism than the K clays. The
vane cut across the fabric at right angles so that during shear more
reorientation was required in the Na than the K clays. It is possible
that this effect is more important than the greater contact stresses

in the K clay, thus forcing the strength of the Na clay up relative to the K clay.

The previous explanations are somewhat speculative. Undrained triaxial tests with pore pressure measurements are really required to explain the data. These tests would give some idea of the vector curves and "A" factors characteristic of the different clays. It is probable, however, that a clay showing much greater collapse would be needed for good, easily interpretable test results.

Sensitivity values of about 2.9 and 2.0 were found for the Na and K clays respectively, regardless of their state when sedimented.

2. M21, Batches 1 and 2 - Drained Shear

The results of a series of drained direct shear tests performed on M21, Batch 2 are, tabulated in Table II-III, and shown in Fig. II-25. The collapsed K clay and expanded Na clay were found to have drained friction angles (ϕ_d) of 26° and 20° respectively. Three points lying on a straight line were considered adequate to define the envelopes. The undrained vane strength envelopes are also plotted on the figure. Two tests are plotted here that were not plotted in Figs. II-23 and II-24. They are plotted in Fig. II-26 where they are more easily interpretable. It is believed that the Na clay strength from Consol. 22 is too low. The Na clay envelope probably should pass through or above the origin. This is the reason the two points were not plotted on the other figures. The undrained envelopes are for clays deposited in an expanded form.

It is interesting to note that the drained envelope of the
Na clay has a cohesion intercept of about 100 p.s.f. while the
envelope of the K clay passes through the origin. Although it is
a little strange for a normally consolidated clay to have a cohesion
intercept, similar data for Batch 3 suggest it is real.

In Fig. II-26, drained shear strength is plotted against water
content. We can see from this and the previous plot, that at a given
normal pressure ($\overline{V}_{ff}$), the K clay has a higher drained strength and
a higher water content than the Na clay.

Figure II-26 also contains the undrained vane strength results
on the clay. On this plot the curves of strength versus water content
show a pronounced curvature. On a semi-log plot (Fig. II-27) the
test gives two distinct trends rather than one unique slope. It is
believed that these two trends reflect differences in structure
between the undisturbed ., vane tested samples, and the direct shear
samples which were remolded before consolidation. More evidence of
this is presented later for batch 3 on which more results were obtained
and further discussion is withheld until then.

Interpretation of the pore pressure build up from the drained
and undrained envelopes in Fig. II-25 is very difficult because of
suspected fabric differences in the Na and K clays. The shape of the
vector curves which are greatly affected by the soil structure can
only be roughly estimated so no attempt has been made here to infer
pore pressures at failure. It is probably safe to say, however, that
greater particle reorientation was produced by vane shear of the Na clay.

3. M21, Batch 3

Undrained and drained shear strength data for this batch are given in Tables II-II and II-IV. The shear strength envelopes obtained on M21, Batch 3 are shown in Fig. II-28. There is very little, if any, difference between the undrained envelopes of the Na and K clays. An average undrained friction angle, ϕ_{cu} of 12° was obtained. One reason for the similarity of the curves may be that KCl leaching was incomplete (K:Na=1.5:1 or less). Another reason may be fabric differences in the two clays. The fabric study in Part Three of the report indicated that the Na clays developed more particle orientation during consolidation than the K clays. As the vane cuts across this fabric at right angles, it is possible that the strength of the Na clay has been forced up relative to the K clay.

In the upper corner of Fig. II-30, the undisturbed and remolded vane strengths are plotted. The two upper K points are off the page. On both curves the K clays are stronger than the Na clays at a given water content.

The sensitivities of the Na and K clays average 5.2 and 3.2 respectively. It was hoped that this batch of clay would contain enough collapsible vermiculite to produce large differences in undrained strength. Obviously this did not occur. The increase in sensitivity produced by collapse of Rosenqvist's montmorillonites after KCl leaching was not observed in these clays either. Part of the reason for this is that Rosenqvist's clays were KCl leached after consolidation.

He thus probably retained most of the Na clay fabric while replacing
the Na by K. In the tests performed here, the original Na fabric
probably has been largely destroyed by the consolidation after leaching.

Drained shear strength envelopes for the clay with three
different K:Na ratios are shown in Fig. II-28. The drained friction
angle increases from 16° for the Na clay to 23° for the K clay. In
pure KCl solution, the cohesion intercept for this clay dropped from
150 p.s.f. to about 75 p.s.f. The correction made to the point on
the pure KCl envelope is justified as it straightens out the e-log
p curve shown in Fig. II-31, making it similar to the others.

The effect of the K:Na ratio is strikingly illustrated in
Fig. II-29 where the drained shear strength is plotted against water
content. At a given water content the strength increases as the
K:Na ratio increases. This may be explained in terms of Rosenqvist's
cation polarizability or the strength of hydration of the two cations.
At a given water content the Na cations would have a much larger
disruption effect on the oriented water than would the K cations,
because of their greater ionic potential and larger hydrated radius.
It could also be hypothesized that the K clays have higher particle
to particle contact stresses ($\overline{\overline{\sigma}}$) than the Na clays and hence
greater frictional resistance.

All of the strength versus water content data are plotted in
Fig. II-30. Once again it is obvious that the strength void ratio
curve is not unique. Although the difference in test procedures might

appear to be the most obvious answer, it is felt that fabric has played a large role. The K:Na ratio produced a large spread in strength in drained shear whereas the undisturbed vane strength curves lie very close together. This suggests that something other than the K:Na ratio has affected the undrained strengths. It is known that consolidation produced pronounced orientation in both the Na and K clays with the Na clay showing greater horizontal parallelism. The vane strengths are probably peak strengths characteristic of the structural rigidity of the clay rather than the void ratio. This would make them appear high on this plot. The undisturbed K(Na) clay curve lines up reasonably well with its associated drained strength curve (K:Na=1.5:1). The Na clay curve appears to be shifted too far to the right, as a result of the clay's greater horizontal parallelism.

The drained strength data shown in Fig. II-29 are replotted in Fig. II-31 on semi-log paper. The straight line curves show a marked convergence. If the strength curves are extended downwards, it appears as though they will meet and cross one another at a water content between 30 and 40 per cent. The water content versus log $\overline{\tau}_{ff}$ show a similar crossing at $\overline{\tau}_{ff} \approx 6000$ psf and water content of about 50 per cent. This reversal of the strength relationship of the K and Na clays appears to be characteristic of the water content plot only. Figure II-28 shows that K clays will remain stronger than the Na clays at any given $\overline{\tau}_{ff}$.

IV. CONCLUSIONS

A. **M21, Batches 1 and 2**

1. These two batches of clay contain about 10 per cent of permanently collapsible vermiculite.

2. The liquid limit is higher for the clay in 0.154 N KCl than in 0.154 N NaCl. This suggests that cation exchange has a greater effect than the layer lattice collapse in this clay.

3. When the clays were deposited in NaCl in their semi collapsed form after KCl treatment:

   a) The e-log p curves were very similar for the Na and K clays.

   b) At a given consolidation pressure, the K clay was stronger in undrained shear than the Na clay at about the same water content.

   c) This may be explained by Rosenqvist's polarizability of cations; potassium being more polarizable than sodium, hence larger edge to face bonding forces with potassium as the exchangeable cation.

   d) An equally plausible explanation is that potassium with its lower ionic potential is much less hydrated than sodium. Sodium with its higher ionic potential adsorbs a great deal of water around it which may have a lubricating effect on the system. One may also think of the K clay as having higher particle to particle contact stresses and hence a higher shear strength.

4. When the clays were deposited in NaCl in their <u>expanded form</u>:

   a) The KCl leached clays had e-log p curves considerably above the Na clay curves.

   b) At a given vertical consolidation pressure within the range studied, the Na clays were significantly stronger than the K clays.

   c) At a given water content within the range studied, the K clays were stronger than the Na clays. In other words, at a given consolidation pressure, the Na clay had a slightly higher undrained strength and a lower water content.

   d) When the clay is deposited in an expanded form and KCl leached, the vermiculite collapes to illite, the interlayer water becomes interparticle pore water and a strength decrease should result. The liquid limit data, however, suggested that cation exchange had a larger effect than collapse so it is possible that something else has caused the Na clay to be stronger than the K clay at a given consolidation pressure. Different flocculated soil structures may have developed in the clays deposited in collapsed and expanded forms and may have had some effect on the results. A greater degree of particle reorientation during consolidation may also have given the Na clay a greater strength.

5. The drained shear strengths show that at a given effective stress on the failure plane, the K clay has a higher strength and a higher water content than the Na clay.

B. **M21, Batches 3 and 4.**

1. These two batches of clay contain no permanently collapsible vermiculite but do contain clay which collapses in KCl solutions.

2. Liquid limits of batch 3 were higher in KCl than in NaCl suggesting that interlayer water effects are minor, as in Batch 2.

3. Consolidation curves for the clay deposited in NaCl, and later leached by NaCl or KCl, showed a strong dependence on the K:Na ratio or the degree of leaching. The well leached K clays had e-log p curves further separated from the Na clays than those which were poorly leached.

4. The x-ray diffraction study suggested that the Na clays had better developed parallelism perpendicular to the con-solidation pressure than the K clays.

5. At a given consolidation pressure, the K clays are a little more permeable than the Na clays because they exist at a higher void ratio. At a given void ratio, the permeabilities are about the same although the K clays may be very slightly more permeable.

6. The Na and K clays have about the same strength in undrained shear at a given consolidation pressure. At this consolidation

pressure, the K clay has the higher water content. The high degree of parallelism may have a greater effect on the strength than the type of cation. The Na clay strength may have been forced up by its greater parallelism because the vane had to cut across this fabric. An average undrained friction angle, ϕ_{cu}, of $12°$ was obtained from the vane tests.

7. Drained friction angles varying from $16°$ for the Na clay to $23°$ for the K clay were obtained from direct shear tests.

8. The K clay is stronger than the Na clay at a given water content in both undrained and drained shear. The strength differences in drained shear are very dependent on the K:Na ratio.

9. The strength versus water content plots show a marked con‑ vergence on semi-log paper suggesting that the Na clay may become stronger than the K clay at lower water contents and higher pressures.

10. The effects of collapse and cation exchange could not be separated in any way as they were in Batch 2. Batch 3 did not fix potassium and therefore could not be collapsed before sedimentation.

C. <u>California Illite-Montmorillonite</u>:

1. The active clay showed collapsing tendencies in pure KCl solutions.

2. The liquid limit in 0.154 N KCl was less than in 0.154 N NaCl. When the KCl concentration was increased to 0.59 N, the liquid limit decreased greatly. These changes are attributed to the expulsion of interlayer water during partial layer lattice collapse. The effects of this collapse are much larger than the accompanying effects of cation exchange.

3. The e-log p curves are about the same for the Na and K clays.

4. The secondary consolidation characteristics of the two clays are different; the Na clay having a slightly greater secondary compression than the K clay. This probably is related to the greater hydrated radius of sodium.

5. At a given consolidation pressure, the K clay has a higher permeability than the Na clay. At a given void ratio, the K clay has the greater permeability. At a given void ratio some of the water in the Na clay is tied up as interlayer water so that the amount interparticle water is less than in the K clay. This is probably the reason why the permeability is lower for the Na clay.

6. No strength tests were run on this clay.

In conclusion it may be stated that cation exchange of sodium
by potassium has produced significant and consistent changes in
engineering properties. The effects of potassium fixation and mineral
change could not be very accurately assessed because most of the clay
would not collapse. Aluminum and iron fixation in the soil profile
during weathering chloritized the degraded mica preventing collapse .
Most of the changes in engineering properties can be related to the
hydratability of the cations or cation polarizability as discussed by
Rosenqvist. The K clays can also be thought of as having greater
particle to particle contact stresses. Where these explanations do
not work, the changes in properties appear to be related to the
expulsion of interlayer water as a result of collapse of the expandable
clay minerals.

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TABLE II-I: UNCONFINED COMPRESSION STRENGTH DATA (M21, Batches 1 and 2)

Consol. No.	Salt	K:Na	Soil Volumes KCl through	σ_c (psf)	e_f	w_f (%)	1/2 unconfined compressive strength (psf)	c/p	Remarks
M21, Batch 1:									
1	NaCl	-	0	665	2.18	80.7	64	.10	Filter
2	NaCl (+KCl)	?	?	637	2.35	86.8	47	.07	Filter
3	KCl	?	~1	958	2.02	74.5	103	.11	Sloping Filter
4	NaCl	-	0	578	2.17	80.6	68	.12	No filter
5	KCl	?	?	967	2.11	78.0	86	.09	Filter
6	NaCl	-	0	976	1.96	72.3	111	.11	No filter
M21, Batch 2:									
10	NaCl	-	0	1422	1.60	59.2	128	.09	No filter
11	KCl	2.5:1	~3.5	1424	1.76	65.2	117	.08	No filter

TABLE II-II: VANE SHEAR STRENGTH DATA   (M21, Batches 2 and 3)

Consol. No.	Salt	K:Na	Soil Volumes KCl through	∇_c (psf)	e_f	w_f (%)	Vane Strength Undisturbed (psf)	Remolded (psf)	S_t	c/p	Remarks
Batch 2, Deposited in Expanded Form:											
20	NaCl	-	0	1024	1.66	61.4	185	63	2.9	.18	
22	NaCl	-	0	539	1.805	66.6	88	30	2.9	.16	
19	KCl	2.3:1	?	1023	1.85	68.1	175	88	2.0	.17	
23	KCl	2.9:1	~2	528	2.00	73.9	94	44	2.1	.18	
Batch 2, Deposited in Collapsed Form:											
17	NaCl	-	0	1025	1.80	66.3	164	61	2.7	.16	
18	KCl	?	?	1027	1.82	67.2	173? Disturbed	77	2.2?	.17?	←Dropped Sample
21	KCl	?	~1.3	1024	1.81	66.8	207	110	1.9	.20	
Batch 3:											
32	NaCl	-	0	1012	2.80	98.2	221	44	5.0	.22	
33	NaCl	-	0	2000	2.405	84.4	425	77	5.5	.21	
34	KCl	?	~1.5	1012	3.02	106.0	188	58	3.2	.19	#33 reused.
35	KCl	1.1:1	~2.0	2000	2.47	86.7	425	130	3.3	.21	

TABLE II-III: DRAINED DIRECT SHEAR STRENGTH RESULTS   (M21, Batch 2)

Test No.	Soil from Consol. No.	Salt	K:Na	$\overline{\sigma}_{ff}$ (psf)	τ_{max} (psf)	Displacement (inches)	$\Delta \ell/L_o$ (%)	Water Content (%)			
								Top	Middle	Bottom	Average
1	22	NaCl	-	1117	482	0.08	4.6	-	-	-	-
2	"	"	-	2117	848	0.07	4.0	43.2	40.2	42.1	41.8
6	"	"	-	3117	1172	0.04	2.3	36.3	33.7	35.7	35.2
3	23	KCl	2.9:1	1117	535	0.09	5.1	-	-	-	-
4	"	"	"	2117	1038	0.08	4.6	-	-	-	-
5	"	"	"	3117	1530	0.07	4.0	39.1	36.8	42.8	39.6
Collapsed by KCl Treatment:											
8	24	NaCl	-	2000	791	0.08	4.6	-	-	-	-
11	"	"	-	1500	625	0.08	4.6	45.9	44.6	45.6	45.4
12	"	"	-	3117	1095	0.04	2.3	38.0	36.4	38.5	37.6

TABLE II-IV: DRAINED DIRECT SHEAR STRENGTH RESULTS   (M21, Batch 3)

Test No.	Soil from Consol. No.	Salt	K:Na	$\overline{V}_{ff}$ (psf)	τ_{max} (psf)	Displacement (inches)	$\Delta\ell/L_o$ (%)	Water Content (%)				Remarks
								Top	Middle	Bottom	Average	
13	31	KCl	7.3:1	3000	1276	0.09	5.1	66.8	66.0	65.7	66.2	Fabric Study
14	32	NaCl	-	1000	431	0.10	5.7	72.7	70.5	72.8	72.1	-
15	"	"	-	2000	716	0.06	3.4	61.8	65.4	64.7	64.0	-
16	"	"	-	3000	1000	0.08	4.6	58.3	59.6	56.2	58.0	-
17	35	KCl	1.5:1	1000	522	0.07	4.0	78.4	79.0	80.2	79.2	-
18	"	"	"	2000	868	0.08	4.6	67.1	68.5	66.3	67.3	-
19	"	"	♥	3000	1240	0.07	4.0	59.9	63.3	60.6	61.3	-
20	31 & 35	KCl	100%K	1000	495	0.08	4.6	93.7	92.5	97.3	94.5	K content increased by washing 4 times in .154N KCl
21	"	"	"	2000	790	0.07	4.0	80.7	88.2	81.3	83.4	
22	"	"	"	3000	1306	0.08	4.6	66.8	68.4	63.9	66.4	

TABLE II-V: INDEX TESTS ON CLAY BATCHES STUDIED

CLAY BATCH	SPECIFIC GRAVITY
M21, Batches 1 and 2	2.71 (computed from composition)
M21, Batch 3	2.85 (measured)
M21, Batch 4	2.85 (estimated)

CLAY BATCH	SOIL TREATMENT	LIQUID LIMIT	PLASTIC LIMIT	PLASTICITY INDEX
M21, Batch 1	Consol. 1, 0.154N NaCl.	68	34	34
" "	Untreated, Demin. water.	72	35	37
M21, Batch 2	Consol. 10, 0.154N NaCl.	62	27	35
" "	Consol. 11, 0.154N KCl, (K:Na - 2.5:1)	72	33	39
" "	Consol. 24, 0.154N NaCl. (previously collapsed)	63	28	35
M21, Batch 3	Consol. 33, 0.154N NaCl.	99	40	59
" "	Consol. 35, 0.154N KCl + NaCl, (K:Na=1.5:1)	118	43	75
" "	Direct shear 20, 21, 22. 0.154N KCl.	120	47	73
California Illite-Mont-morillonite	Consol. 15, 0.154N NaCl	270	38	232
"	Consol. 12, 0.154N KCl	250	69	181
"	0.154N KCl	138	59	79

SHEAR STRENGTH vs WATER CONTENT

MONTMORILLONITE
ILLITE
KAOLINITE

(After Cornell Report, 1951)

FIGURE II-I

SHEAR STRENGTH vs WATER CONTENT

ILLITE

SHOWING EFFECT OF TYPE OF ADSORBED CATION
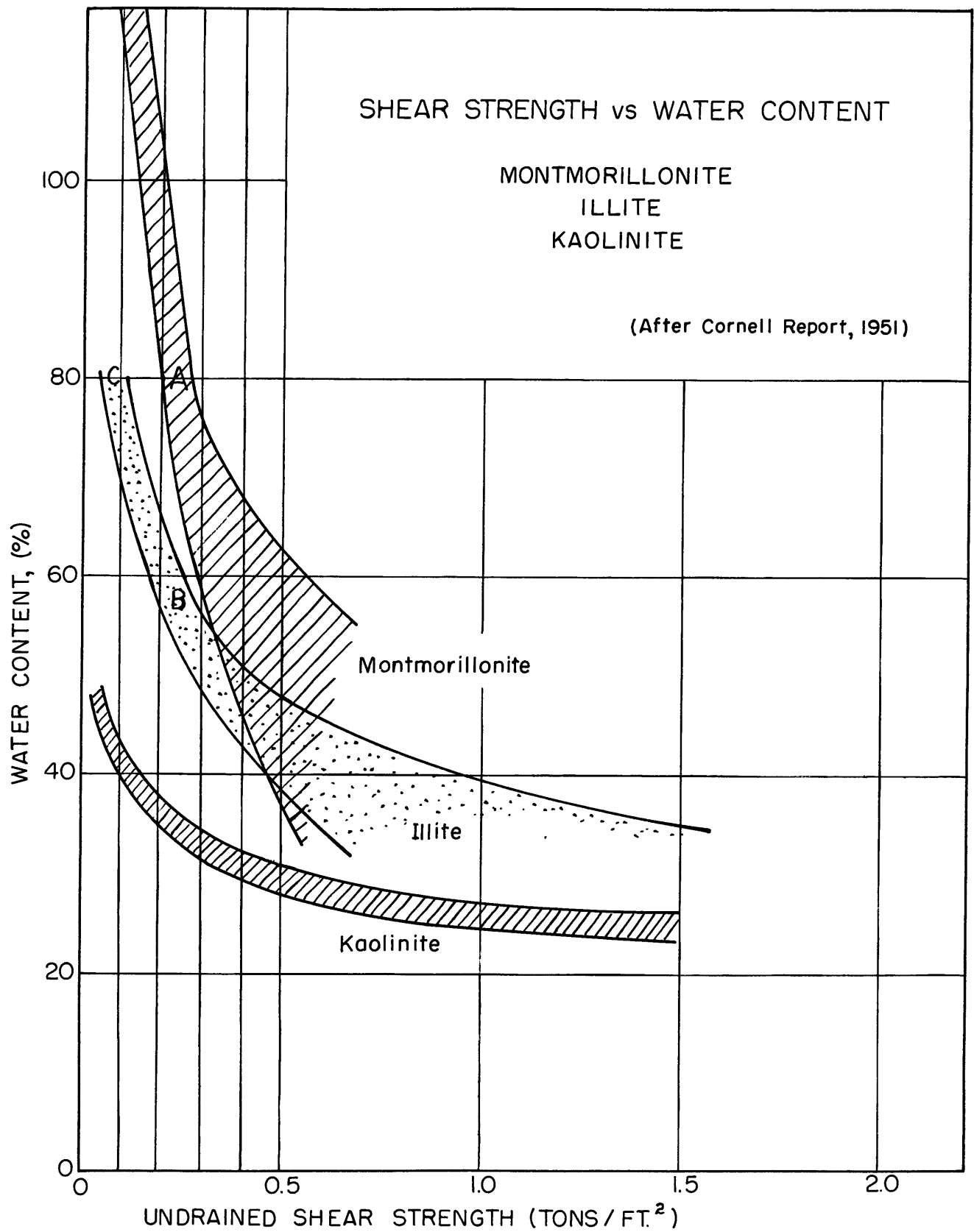
(After Cornell Report, 1951)
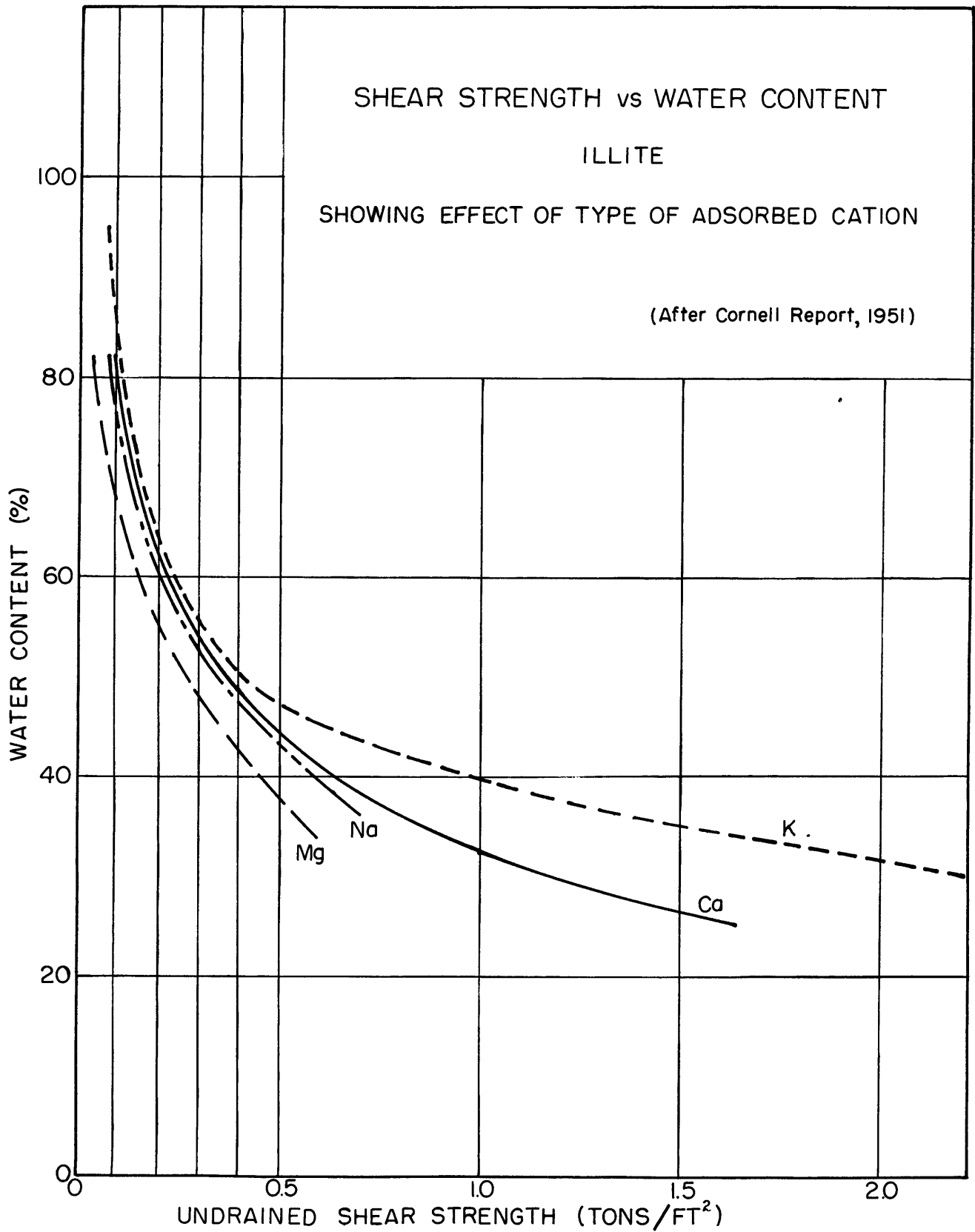
FIGURE II-2

VARIATION IN LIQUID LIMIT WITH VARIOUS CATIONS

(After Rosenquist, 1957)

Interlayer water

Montmorillonite
CEC = 110 meg/100 g

Li
Na
K
Rb
Cs

≈ 90% Illite
CEC = 30 meg/100 g

Na
K

≈ 40% Illite
CEC = 17 meg/100 g

Li
Na
K
Rb
Cs

LIQUID LIMIT ⟶

$\alpha = \dfrac{\epsilon - 1}{\epsilon + 2} R^3 \ (\overset{\circ}{A}{}^3)$

FIGURE II-3

UNDRAINED STRENGTH ENVELOPES
(NORWEGIAN ILLITE)

(After Rosenquist, 1961)

FIGURE II-4

UNDRAINED STRENGTH ENVELOPES
(HUNGARIAN MONTMORILLONITE)

(After Rosenquist, 1961)
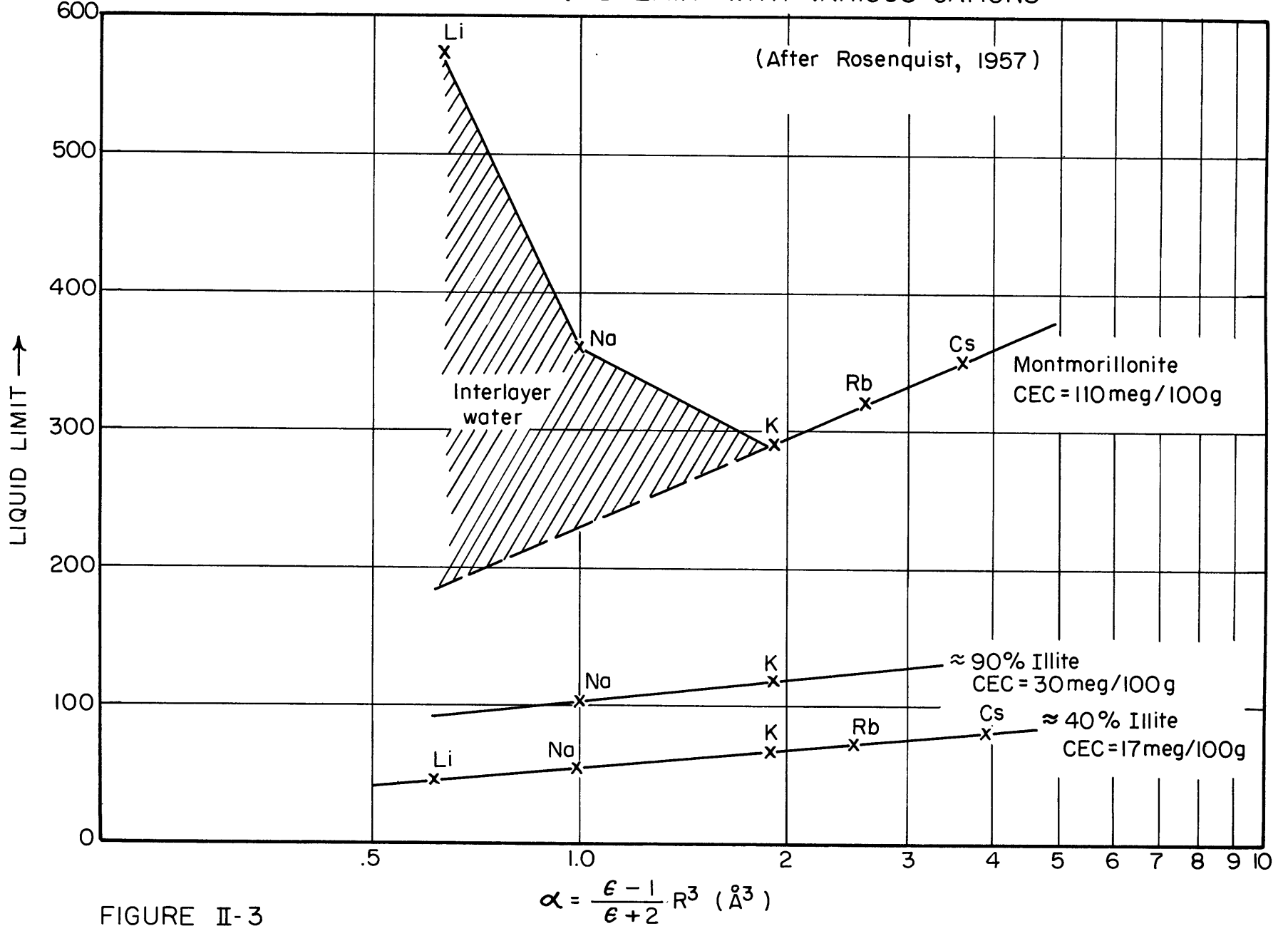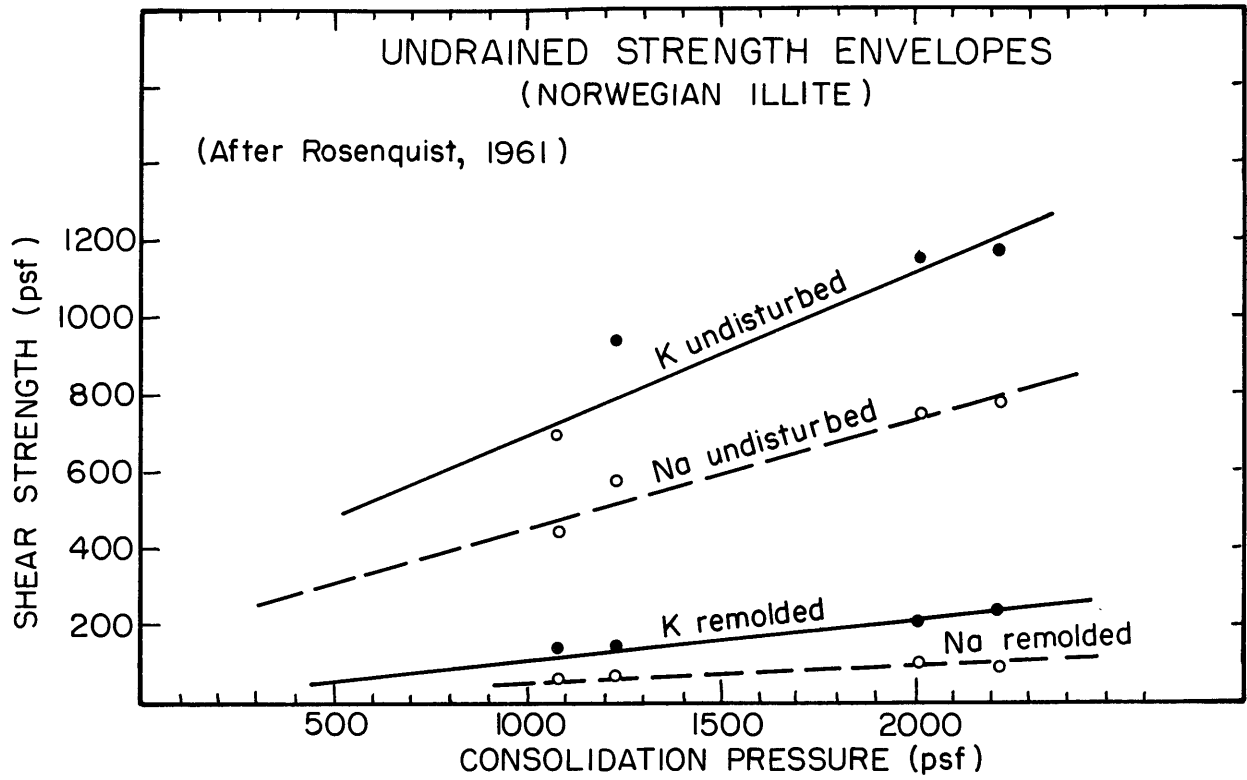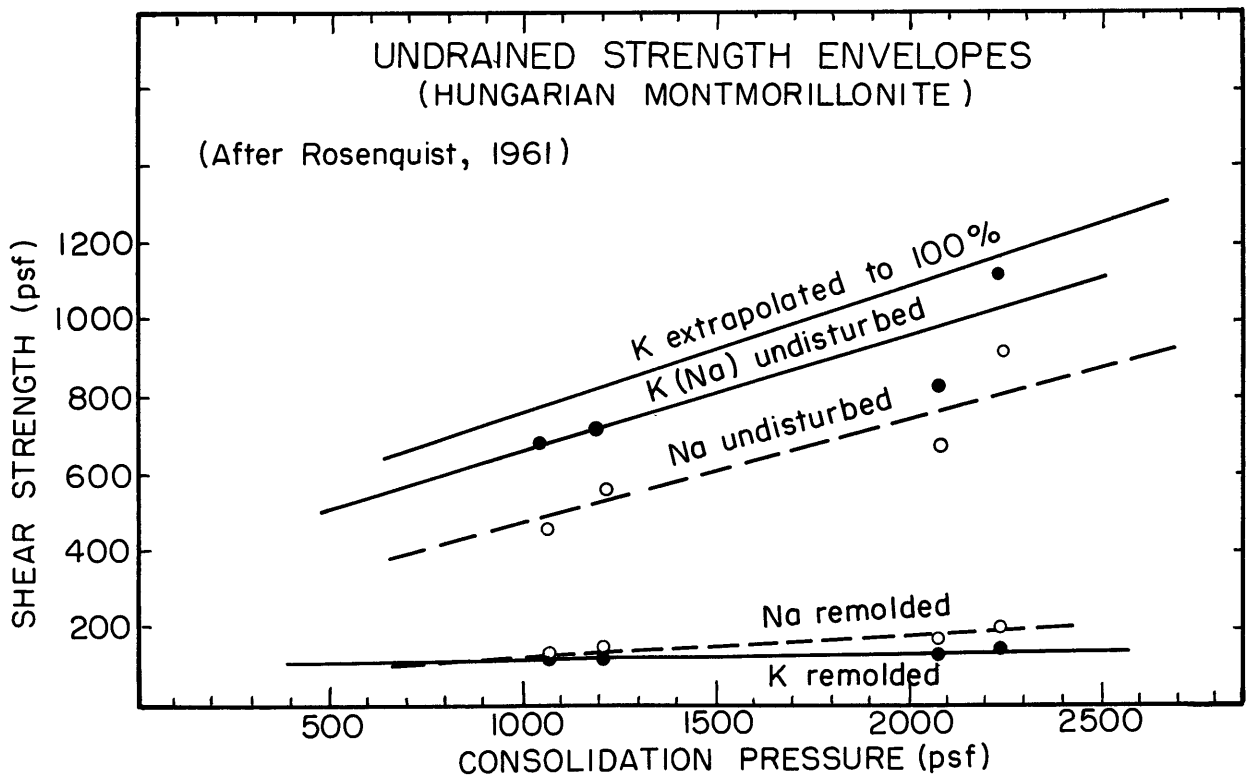
FIGURE II-5

Photograph of sedimentation chambers
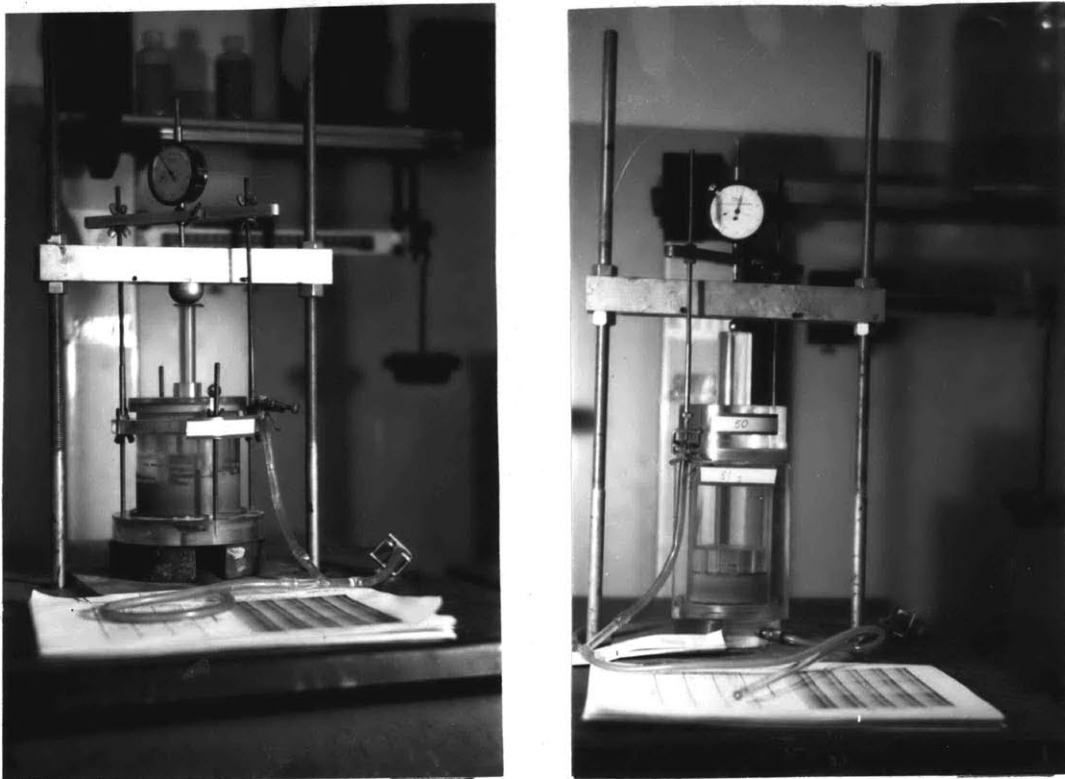
Note the two types of consolidation chamber

FIGURE II-6   PHOTOGRAPHS OF CLAY SAMPLES AT VARIOUS
STAGES OF SEDIMENTATION AND CONSOLIDATION

FIGURE II-7   PHOTOGRAPH OF VANE STRENGTH
TESTING APPARATUS

CONSOLIDATION CURVES
(M21, BATCH 2)

LEGEND

□ Consol 10 ⎤   NaCl 9‰ = 0.154 N
△ Consol 20 ⎦   (NaCl leached before consolidation)

■ Consol 11 ⎤   KCl (+NaCl) = 0.154 N
▲ Consol 19 ⎦   (KCl leached before consolidation)

Consol 11   K/Na = 2.5/1
Consol 19   K/Na = 2.1/1

Leached at this pressure

VOID RATIO

C_v (cm^2/sec × 10^{-3})

CONSOLIDATION PRESSURE (psf)

FIGURE II-8

CONSOLIDATION CURVES
(M21, BATCH 2)
COLLAPSED

LEGEND

○ Consol 17 NaCl 9‰ = 0.154 N
(NaCl leached before consolidation)

● Consol 18 KCl 11.5‰ = 0.154 N
(KCl leached before consolidation)

Clay collapsed in KCl, then Na
saturated and sedimented in NaCl

VOID RATIO

C_v (cm^2/sec x 10^{-3})

CONSOLIDATION PRESSURE (psf)

FIGURE II-9

CONSOLIDATION CURVES
(M21, BATCH 2)

Legend

(1) Average of Consol 11 & 19 KCl

(2) Average of Consol 10 & 20 NaCl

(3) Consol 18 & 21 (collapsed) KCl

(4) Consol 17 (collapsed) NaCl

Note:

(1) & (2) deposited in expanded form

(3) & (4) deposited in collapsed form

VOID RATIO

C_v (cm^2/sec x 10^{-3})

CONSOLIDATION PRESSURE (psf)

FIGURE II-10

CONSOLIDATION CURVES
M21, BATCH 3

Legend

o Consol 30 ⎤
□ Consol 32 ⎦ Leached with 0.154 N NaCl
△ Consol 33 ⎦ before consolidation

● Consol 31 ⎤ K Na = 7.5 : 1 ⎤
■ Consol 34 ⎦ K : Na = ?   ⎦ Leached with 0.154N KCl
▲ Consol 35 ⎦ K : Na = 1.5 : 1 ⎦ before consolidation

Note : All samples sedimented in 0.154 N NaCl
(Salinity = 9‰ = Brackish water)

VOID RATIO

VERTICAL CONSOLIDATION PRESSURE (psf)

FIGURE II-11

125.

CONSOLIDATION CURVES
M21, BATCH 4

- Consol 51   K/Na = 9.7/1
  (Leached with 0.154N KCl before consolidation)

- Consol 50   Pure NaCl (0.154 N)
  (NaCl leached before consolidation)

VOID RATIO

VERTICAL CONSOLIDATION PRESSURE (psf)

FIGURE II-12

CONSOLIDATION CURVES
(M21, BATCHES 2, 3, & 4)

Batch 4, Consol 51, K:Na = 9.7:1

Batch 4, Consol 50, 100% Na

Batch 3, Consol 31, K = Na = 7.3:1

Batch 3, Consol 30, 100% Na

Batch 2, Consol 11, K:Na = 2.5:1

Batch 2, Consol 10, 100% Na

VOID RATIO

VERTICAL CONSOLIDATION PRESSURE (psf)

FIGURE II-13

127.

CONSOLIDATION CURVES

CALIFORNIA CLAY
ILLITE - MONTMORILLONITE

LEGEND

● Consol No. 12   KCl 11.5‰=0.154N
(KCl Leaced before consolidation)

O Consol No. 15   NaCl 9‰=0.154N

VOID RATIO

C_v

$\left(\dfrac{cm^2/sec}{X10^{-5}}\right)$

FIGURE II-14   CONSOLIDATION PRESSURE (psf)

PER CENT SETTLEMENT vs LOG TIME

CALIFORNIA ILLITE - MONTMORILLONITE

LEGEND

● Consol No. 12 KCl 11.5‰ = 0.154N
(KCl leached before compression)

○ Consol No. 15 NaCl 9‰ = 0.154N

Number	Load Increment (psf)
1	41 → 76
2	76 → 198
3	405 → 673
4	673 → 1043
5	1043 → 1423
6	198 → 403
7	403 → 859

% SETTLEMENT (SETTLEMENT / ORIGINAL THICKNESS)

LOG TIME IN MINUTES

FIGURE II-15

PERMEABILITY vs
CONSOLIDATION PRESSURE
(M2I, BATCH 2, EXPANDED & COLLAPSED FORMS)

Note:
All values from falling head
permeability tests.

Legend

□ Consol 10
△ Consol 20 } NaCl = 0.154 N

■ Consol 11 } K:Na = 2.5:1
▲ Consol 19 } K:Na = 2.1:1 } KCl (+NaCl) = 0.154 N

○ Consol 17   Collapsed, NaCl
● Consol 18   Collapsed, KCl

VERTICAL CONSOLIDATION PRESSURE (psf)

PERMEABILITY (X10^{-7} cm/sec)

FIGURE II-16

PERMEABILITY vs VOID RATIO

(M21, BATCH 2)
EXPANDED AND COLLAPSED FORMS

FIGURE II-17

PERMEABILITY vs CONSOLIDATION PRESSURE
(M21, BATCH 3)

Note:
Permeability values calculated from consolidation test data

Consol 30, 0.154N NaCl

Consol 31, K:Na = 7.3:1
KCl (+ NaCl) = 0.154 N

VERTICAL CONSOLIDATION PRESSURE (psf)

PERMEABILITY (X 10^{-7} cm/sec)

FIGURE II-18

FIGURE II-19

PERMEABILITY vs VOID RATIO

M21, BATCH 3

Legend

○ Consol 30
□ Consol 32   — Leached with 0.154 N NaCl
△ Consol 33

● Consol 31
■ Consol 34   — Leached with 0.154 N KCl
▲ Consol 35

Note : Permeability values calculated from consolidation test data

VOID RATIO

PERMEABILITY (X10^{-7} cm/sec)

PERMEABILITY vs CONSOLIDATION PRESSURE

CALIFORNIA ILLITE – MONTMORILLONITE

LEGEND

● ▲ Consol No. 12   KCl 11.5‰ = 0.154 N
(KCl seepage before consolidation)

○ △ Consol No. 15   NaCl 9‰ = 0.154 N
(NaCl seepage before consolidation)

● ○ Computed From Falling Head
Permeability Tests

▲ △ Computed From The
Consolidation Tests

VERTICAL CONSOLIDATION PRESSURE (psf)

PERMEABILITY (X10^{-7} cm/sec.)

FIGURE II-20

PERMEABILITY vs VOID RATIO

CALIFORNIA ILLITE – MONTMORILLONITE

FIGURE II-21

UNDRAINED SHEAR STRENGTH
vs
MAXIMUM PAST PRESSURE

(M2I, BATCHES I & 2)

Legend

o   □   NaCl only

●   ■   KCl treated

Numbers above symbols indicate consolidation test number.

Batch 2

Batch I

FIGURE II-22

UNDRAINED SHEAR STRENGTH
vs
WATER CONTENT
(M21, BATCHES 1 & 2)

Legend

10 11
□ ■ Unconfined strengths ⎤ Deposited in
20△ 19▲ Vane strengths ⎦ expanded form

17○ 21● Vane strengths ⎤ Deposited in
                        ⎦ collapsed form

Numbers above symbols indicate consolidation
test number

FIGURE II-23

UNDRAINED SHEAR STRENGTH
vs
MAXIMUM PAST PRESSURE

(M21, BATCHES 1 & 2)

Legend

○ Deposited expanded, NaCl leached
● Deposited expanded, KCl leached
□ Deposited collapsed, NaCl leached
■ Deposited collapsed, KCl leached

Batch 2
Vane strengths

Batch 1 & Batch 2
Unconfined compression
From Figure II-22

NaCl only

KCl treated

NaCl

KCl

FIGURE II-24

SHEAR STRENGTH ENVELOPES

M21, BATCH 2

Soil: Fractionated, < 2 Microns
        Illite ~ 60%
        Vermiculite ~15%
        Quartz ~20%

Solid lines = 0.154 N KCl, collapsed clay, K:Na=2.9:1
Dashed lines = 0.154 N NaCl, expanded clay

$\phi_d = 26°$

$\phi_d = 20°$

Drained direct shear

$\phi_{cu} = 10°$

Undrained vane

SHEAR STRESS (psf)

$\overline{\sigma}_{ff}$ (FOR DIRECT SHEAR) & $\overline{\sigma}_c$ (MAX. PAST PRESSURE, VANE SHEAR) (psf)

FIGURE II-25

SHEAR STRENGTH
vs
WATER CONTENT

M21, BATCH 2

Undrained vane strengths

Soil: Fractionated, <2 Microns
        Illite ~60%
        Vermiculite ~15%
        Quartz ~20%

Solid lines = 0.154 N KCl Pore Fluid
                Collapsed clay K:Na ≈ 2.5:1

Dashed lines = 0.154 N NaCl Pore Fluid
                 Expanded clay

Drained direct shear tests

FIGURE II-26

SHEAR STRENGTH AND CONSOLIDATION PRESSURE
vs
WATER CONTENT
(M21, BATCH 2)

FIGURE II-27

SHEAR STRENGTH ENVELOPES

M21, BATCH 3

Soil: Fractionated, <0.4 Microns
Illite, Vermiculite, Swelling clay

Salt concentration in all tests = 0.154 N

Note: This point assumed to lie on a straight line envelope. Other curves adjusted accordingly. See text.

$\phi_d = 23°$ Drained direct shear

$\phi_d = 20°$

$\phi_d = 16°$

Pure KCl

KCl: NaCl = 1.5:1

Pure NaCl

$\phi_{cu} = 12°$

Undrained vane

SHEAR STRESS (psf)

$\overline{\sigma}_{ff}$ (DIRECT SHEAR) & $\overline{\sigma}_c$ (MAX. PAST PRESSURE, VANE SHEAR) (psf)

FIGURE II-28

142.

DRAINED SHEAR STRENGTH
vs
WATER CONTENT
(M21, BATCH 3)

FIGURE II-29

SHEAR STRENGTH
vs
WATER CONTENT
(M21, BATCH 3)

FIGURE II-30

DRAINED STRENGTH AND **EFFECTIVE STRESSES**
vs
WATER CONTENT
(M21, BATCH 3)

FIGURE II-31

FIGURE II-32 PHOTOGRAPHS OF OVEN DRIED, VANE TESTED
CLAY SPECIMENS, SHOWING MARK LEFT BY
THE VANE

PART THREE

MEASUREMENT OF SOIL FABRIC USING
X-RAY TECHNIQUES

I. INTRODUCTION

The importance of soil structure on the engineering properties of clay soils has been recognized for many years. Much engineering testing has been reported in the literature showing the effects of remolding on the engineering properties. These changes are attributed to the breakdown of the natural soil structure by remolding.

More recently, the full significance of soil structure has been brought out by detailed studies on leached marine clays and compacted clays. Semiquantitative visual methods for determining fabric have been developed and the results successfully correlated with the engineering properties.

Soil structure consists of two components: 1) particle to particle arrangement on a large and small scale, i.e., fabric, and 2) the nature and strength of the linkage between particles. In this part of the thesis, a method for determining average particle to particle arrangement over a fairly large area by x-ray diffraction is described.

It is not intended that this discussion be a complete resume on fabric. Rather, it is hoped that this work will initiate a long-term program of study on soil fabric using x-ray methods. Soil fabric has been a subject of great interest to the Soil Engineering Division

for several years, and has been intensively studied using direct
optical methods of anaylsis and less direct engineering tests.
The use of the x-ray techniques described here were developed
incidental to the major portion of this research project. The
results, however, proved to be quite significant despite the make-
shift fashion in which the studies were carried out.

II. PREVIOUS WORK

The breakdown of the structure of a soil, by remolding or dis-
turbance during sampling operations, produces large changes in
engineering properties. Casagrande (1932) stresses the importance
of structure by showing the effects of remolding on the consolidation
and strength characteristics of clay soils. He also recognizes that
considerable geologic time is required to develop a rigid structure
and that once destroyed it probably can never be regained.

Hvorslev (1938) provided reasonably good visual evidence of
particle orientation. Thin slices of dry, anisotropically consolidated
clay were immersed in water. The slices disintegrated into fracture
patterns that showed particle orientation perpendicular to the con-
solidation pressure. Isotropically consolidated clays showed no
preferred orientation. Hvorslev also attributes strength loss upon
remolding to particle reorientation. Unconfined compression tests
on clay samples with preferred orientation showed interesting but
inconclusive results.

More recently, the work of Lambe (1953, 1958a, 1958b),
Mitchell (1956), Pacey (1956), Rosenqvist (1955, 1959) and Seed
and Chan (1959) have shown the full importance of the role fabric
plays in the interpretation of the engineering behavior of clays.
Lambe (1953) discusses soil structure in terms of soil chemistry
and interparticle forces. Figure III-1, which is reproduced after
Lambe, shows his concept of the effects of remolding. Presumably,
the particle parallelism produced by remolding would also occur in
the shear zone on an undisturbed flocculated clay. Positive evidence
of this is presented in this thesis.

Lambe (1958a, 1958b) applied his fabric concepts to compacted
clays. These two papers and one by Seed and Chan (1959) illustrate
the important role that fabric plays in the engineering behavior of
compacted clays.

Direct measurements of clay particle fabric are rather
difficult to obtain. Mitchell (1955, 1956) and Pacey (1956) used an
optical method of analysis that involved the impregnation of a clay
sample with wax. The sample was then cut into thin sections and
observed in polarized light with a petrographic microscope. Mitchell
found preferred orientation in natural clays and in artificially
consolidated clays. He was also able to correlate soil fabric with
the engineering properties of compacted clays.

Quigley (1956) observed highly developed particle orientation
in thin sections of varved clays from the Connecticut Valley. Salas

and Serratosa (1953) mentioned the use of a petrographic microscope
and thin sections of clay to study the parallelism produced by
anisotropic consolidation. Rosenqvist (1955), who also used an im-
pregnation technique to study thin sections of clay, found that
Norwegian quick clays consisted of randomly oriented clay particles.
Larger flakes of mica (about 10 microns) were also observed to be
in a subparallel arrangement, probably in the plane of the surface
of deposition. Rosenqvist (1959) extended his study of soil fabric
by means of the electron microscope. He proved quite conclusively
with electron photomicrographs that undisturbed marine clays have
a "card-house" structure which would appear quite random in thin
section.

The use of x-ray diffraction equipment to study fabric has
not been widely used. Silverman and Bates (1960) used an elaborate
x-ray device to study clay particle orientation in shales. Their
method involved the preparation of thin sections cut perpendicular to
the bedding planes. They worked out a method for determining the
degree of orientation independent of the amount of clay present.

Fairbairn (1949) discusses the use of x-ray diffraction in
the study of fabric in micaceous rocks.

Buessem and Nagy (1953) report the use of x-ray diffraction to
measure clay fabric. This is the only article found in which x-ray
methods are reported to have been used on a soil. Buessem and Nagy
studied changes in particle orientation in samples subjected to unconfined com-
pression between two lubricated plates. The clay was free to flow

laterally between the plates. They used the intensity of the x-ray diffraction peaks, as recorded on film, to measure the degree of orientation. Their samples were prepared by rolling Georgia kaolin into balls and cutting a block out of the center. The clay in the block was randomly oriented according to the x-ray data, while the clay near the surface of the balls was oriented parallel to the surface. The compression-flow tests, which they performed on the clay blocks, produced marked particle orientation perpendicular to the axis of compression.

III. EXPERIMENTAL PROCEDURE

A. Equipment

A Phillips x-ray diffractometer complete with a geiger scaler and a Brown recorder were used for this work. Copper radiation was used in all of the studies.

B. Preparation of Fabric Extremes

Maximum parallelism was obtained by high speed centrifugation of a dispersed clay suspension onto a porous ceramic plate. A small amount of clay powder was first dispersed in distilled water using an ultrasonic vibrator. The clay was generally centrifuged at 2000 rpm for about 20 minutes. During this time, all of the water was drawn through the plate leaving a highly oriented, glossy layer of clay. Occasionally a tiny amount of NaOH was used to aid in the dispersion.

Minimum parallelism or a net randomness was obtained by x-raying a level surface of clay powder. A rectangular depression

was cut into a ceramic plate, filled with powder and levelled off. X-ray diffraction traces showing maximum parallelism and net random-ness are shown in Figs. III-3 and III-10.

C. Preparation of Soil Samples for X-Ray

Test specimens of soil which were to be x-rayed were generally cut into small blocks about 1" x 1/2" x 1/2" and allowed to air dry. The shrinkage produced by drying was sometimes recorded. The air dried samples were then carefully sanded down into smaller blocks, measured, and coated on 5 sides with a thin layer of general purpose epoxy. The 6th side was left exposed for x-raying. The epoxy pre-vented the dry clay from chipping at the corners when successive layers were ground off side 6.

The grinding procedure required a great deal of care to prevent misorientation of the sample in the x-ray machine. The makeshift method described below worked very satisfactorily.

An "L" shaped mount was made which could be clipped to the machine. One epoxy covered surface of the sample was sanded smooth and the block was secured to the "L" shaped mount by an elastic band. (See Fig. III-2) The sample was then ground down with fine sandpaper so that the surface was smooth and in exactly the same plane as one arm of the "L". The powder was blown or even wiped off the sanded surface depending on the density of the sample. The "L" mount was then clipped to the machine and the sample x-rayed.

IV. CLAY SOILS STUDIED

The fabric of four clay soils which had been subjected to a variety of engineering tests were studied. The compositions of these materials are briefly listed as follows:

1. M21, Batch 2

   Fractionated, 90% smaller than 2 microns
   Illite ~60%
   Vermiculite ~15%
   Quartz ~20%

2. M21, Batch 3

   Fractionated, less than 0.4 microns
   Chiefly illite, vermiculite and interlayered swelling clay

3. Georgia Kaolin

   Pure kaolinite
   Smaller than 2 microns

4. Vicksburg Buckshot Clay

   Chiefly montmorillonite and illite
   Large amount of silt plus a little fine sand.

V. SOIL FABRIC MEASUREMENTS

Because fabric is controlled by the stress-strain history of the samples, the following discussion will deal directly with the type of engineering tests performed and the effects of these tests on the soil fabric.

A. General Discussion of the Method

Differences in orientation of the clay platelets in a soil being x-rayed produce very large differences in the intensities of

the basal reflections. Samples with maximum parallelism, shown in Figs. III-3 and III-10, exhibit very large basal reflections and no (hkℓ) reflections. For a given area of x-rayed surface, the size of these (00ℓ) peaks should be proportional to the degree of particle parallelism.

In a powder pattern, the (00ℓ) peaks are about the same size as the (hkℓ) peaks. (Figs. III-3 and III-10). Generally, even a small amount of parallelism causes the (hkℓ) peaks to disappear.

In this study the area subjected to x-rays was kept constant, and the height of the (00ℓ) peaks was measured for various parallel surfaces within the sample.

B. Fabric of Clay Flocs (M21, Batch 3)

A sample of M21, Batch 3 was dispersed for 5 minutes in 35‰ NaCl using an ultrasonic vibrator. After the vibration, the suspension was allowed to flocculate and settle out on a ceramic plate. It was then centrifuged for 2.5 minutes at a maximum speed of 1,200 rpm. The x-ray diffraction pattern of the wet clay flocs is shown in Fig. III-3, Curve 2. The pattern is nearly identical to the random powder pattern shown in the same figure. The (00ℓ) peaks are slightly stronger than the (hk0) peaks, indicating that a small amount of orientation was produced by the 2.5 minutes of centrifugation. In a completely random pattern, the (00ℓ) and (hk0) peaks are about the same size.

The x-ray time was about 22 minutes and during this period
some drying occurred. Surface tensions apparently produced some
particle orientation parallel to the plates because the (00ℓ) peaks
intensified at the expense (hk0) peaks as shown by Curve 2a.

A. Fabric of Anisotropically Consolidated Clays (M21, Batch 3)

Small rectangular blocks were cut from the consolidated samples
of consolidation tests 31 through 35 (M21, Batch 3). Tests 32 and 33
were run on clays with 0.154 N NaCl as the pore fluid and tests 31,
34, and 35 on KCl leached clays. The details of the consolidation
tests are described in Part II of this thesis. In Table III-1, the
test data pertinent to the fabric study are presented.

The areas of the top surfaces x-rayed were all within 3% of
one another with the exception of test 31. The peak amplitudes are
roughly corrected for both scale factor and surface area for this
test. The amplitude of the peaks should all be more or less directly
comparable despite different absorption characteristics of the samples
depending on orientation, type of adsorbed cations, etc.

In Part II, it was pointed out that the extent of the KCl
leaching had a large effect on the e-log p curves. The well leached
potassium clays existed at higher void ratios than the sodium clays
at any given consolidation pressure. The more poorly leached the
sample, the closer its e-log p curve lay to the sodium curves. If
these differences are due to fabric differences, it is possible that
both the K:Na ratio and the consolidation pressure (σ_c) will affect
the degree of parallelism in the leached samples.

X-ray patterns were obtained on surfaces cut parallel and perpendicular to the vertical consolidation pressure. These surfaces are labelled side and top respectively in Table III-I. Two x-ray traces from the side and top surfaces of consolidation 31 are plotted in Fig. III-4 to show the different character of the curves. In the table, all of the important reflections which were obtained are entered. However, only the 3.4 $\overset{o}{A}$ (003) basal reflections and the 4.48 $\overset{o}{A}$ (hk0) reflections have been used for interpretation. In Fig. III-5, the peak height of these two reflections are plotted against log τ_c maximum. The plot shows quite definitely that particle orientation increases with increasing τ_c. The shrinkage data, obtained by air drying, also indicate pronounced orientation. Figure III-5 also suggests that better orientation has been developed in the sodium clays, however, the data are too preliminary to draw any final conclusions in this regard.

D. <u>Fabric Within Direct Shear Specimens</u>

Fabric studies were performed on two drained direct shear specimens after maximum shear stress had been reached. Moisture contents for the top, middle, and bottom of the specimens were obtained. Both samples were air dried before x-raying. The two tests, numbered 2 and 13, were run on M21, batches 2 and 3 respectively. The engineering test data are presented in Part II of this thesis.

In Test No. 2, the clay was remolded, pushed into the shear box and consolidated to 2117 psf. The shear displacement amounted to

0.115 inches. Moisture contents of 43.2, 40.2 and 42.1 percent were obtained from the top, middle, and bottom of the specimen respectively.

The x-ray results for this test are given in Fig. III-6. Two peaks, the 10 $\overset{\circ}{A}$ (001) peak of illite and the 7 $\overset{\circ}{A}$ (002) peaks of chlorite and vermiculite, are plotted against position within the sample. The first few measurements were taken too far apart. The measurements taken close together suggest a very complicated multiple slip system that may not be at the center of the specimen. In Fig. III-7, two sketches of the failure system in another similar direct shear sample are presented. The specimen was broken along sections A-A' and B-B'. An intricate, arcuate slip system was clearly visible as shown by the drawings.

In test No. 13, an undisturbed sample from consolidation test 31 was placed in the shear box and reloaded to 3000 psf. The previous maximum consolidation pressure was 16,000 psf. A drained shear strength of 1276 psf was obtained. The maximum shear displacement amounted to .087 inches. Water contents of 66.8, 66.0, and 65.7 per cent were obtained from the top, middle, and bottom respectively.

The x-ray diffraction results are plotted in Fig. III-8. The (001) and (003) peaks of illite and the (002) peak of vermiculite and chlorite are plotted against position within the sample. The orientation of the sample (i.e., which was top and bottom) was lost during

preparation for x-raying. Because the sample continued to consolidate during shear, it was assumed that the shear zone would have the lowest water content. The shear zone, which was clearly located by the x-ray results, is therefore assumed to be near the bottom of the sample.

Shrinkage amounted to about 20 per cent across the failure plane and 5 per cent in the other two directions.

E. Fabric in the Failure Zone of a Triaxial Sample

An air dried triaxial sample of highly flocculated kaolinite (smaller than 2 microns) was obtained from A. Wissa (1961). The specimen had been failed in undrained shear over a period of 50 hours. The shear displacement was of the order of 2 millimeters, and occurred in a shear zone about 2 millimeters wide. Sharply defined slip surfaces were clearly visible.

According to Wissa, (personal communication) about 80 per cent of the excess pore pressure built up during shear, was retained in the sample after the deviator stress was completely removed. This can be explained by hypothesizing particle reorientation inside the failure zone of the flocculated sample. Bjerrum (1961) described a series of tests on extremely sensitive, Norwegian quick clays which showed similar results. He hypothesized particle reorientation in the failure zone to explain his high "A" factors and his high residual pore pressures after removal of the deviator stress.

The results of x-ray diffraction tests on Wissa's sample are

plotted in Fig. III-9. The very pronounced increase in height of the

7 $\overset{o}{A}$ (001) kaolinite peaks indicates marked particle orientation within

the shear zone. The plot of the 4.35 $\overset{o}{A}$ (hk0) peaks also show a slight

increase in height. This may be due to an increase in density of the

kaolinite within the shear zone after air drying. The greater parallelism

permits greater shrinkage and hence a greater dry density.

In Fig. III-10, four diffraction traices of the same Georgia

kaolin are illustrated. Curve (a) represents maximum parallelism

produced by centrifugation as described previously. Curve (d) is a

powder pattern representing complete randomness. Curve (b) and (c)

were obtained inside and outside of the shear zone, respectively.

In all cases the area of sample exposed to x-rays was about the same.

It is obvious that although considerable particle orientation has

been produced by the shearing, it is not great when compared with

curve (a).

F. Additional Fabric Studies

A few additional fabric studies of a very preliminary nature

were performed on compacted kaolinite and Vicksburg Buckshot clay.

A few x-ray patterns were obtained from kaolinite compacted

about 2 per cent wet of optimum using static and kneading procedures.

Very little difference was observed in the patterns of the two samples.

The large surfaces subjected to x-rays showed about the same average

orientation. Mitchell's work, however, showed that pronounced

parallelism was prodoced over small areas in kneaded soils (1956). Small areas subjected to x-rays would probably show the same results.

Two series of tests were performed on failed specimens of Vicksburg Buckshot clay. The clay contained a great deal of silt and fine sand. One series of measurements was taken across the failure plane of an undrained triaxial test specimen. The other series was performed across the slickensided zone of a sample failed in undrained shear in Hvorslev's torsion apparatus. The latter test was performed by R. Harkness of the Soil Engineering Division.

No particle orientation was found in either series of tests. This, however, does not mean that particle orientation did not develop. It is the writer's feeling that a high degree of particle orientation may have been produced around the silt and sand grains, as observed by Mitchell in some of his thin sections. This type of orientation would tend to produce a random x-ray pattern over a large area.

VI. CONCLUSIONS

The fabric study, which has been described in this thesis, is of a very makeshift and preliminary nature. The results, however, have been very encouraging and in some cases significant. The following conclusions can be drawn:

1. X-ray diffraction procedures offer a rapid and reliable method for determining the average soil fabric over the area being x-rayed.

2. Silty soils are probably not adaptable to this method of analysis. The silt grains apparently tend to produce a "wavy" type of parallelism that shows up as a net randomness on an x-ray pattern. Whether these oriented areas can be identified by x-raying small surfaces is a matter for future study.

3. The fabric studies performed on the engineering test specimens gave the following results:

   a. Anisotropic consolidation produces marked particle orientation perpendicular to the direction of the consolidation pressure.

   b. The failure surface in direct shear specimens tend to be arcuate in shape, often with a multiple slip system.

   c. Parallelism is produced in the shear zone of flocculated clay samples failed in undrained shear.

   d. Samples containing small areas of marked parallelism may appear random when x-rayed over a large surface. The small areas of parallelism are important as they frequently control the engineering properties of the soil, (e.g., kneaded compaction sample). These particles may possibly be picked up by reducing the size of the area x-rayed.

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TABLE III-I: FABRIC OF ANISOTROPICALLY CONSOLIDATED CLAYS

Consolidation Test No.	Maximum (psf)	K:Na ratio	Shrinkage		Area Side Surface (in^2)	Area Top Surface (in^2)	Peak Heights (inches)			
			Parallel to ∇_c.	Perpendicular to ∇_c.			Side 2.56Å (hk0)	Surface 4.48Å (hk0)	Top 3.34Å (003)	Surface 4.98Å (002)
32	1012	Pure Na	38%	10.5%	.260	.260	1.55	2.1	4.3	1.4
33	1952	Pure Na	32%	9.5%	.259	.261	2.2	2.3	5.4	3.7
34	978	1:1?	-	-	.240	.267	1.55	1.7	4.4	1.3
35	2000	1.5:1	30.5%	9.5%	.262	.263	1.4	1.3	4.2	1.2
31	16000	7.3:1	-	-	.171	.166	1.8	*3.5	*7.0	2.1

*Corrected heights adjusted for small areas of x-ray.

164.
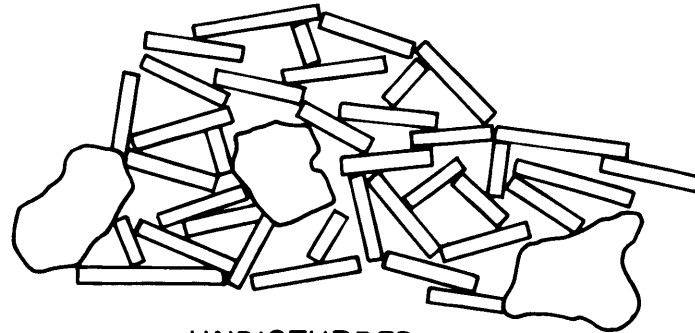
UNDISTURBED
Salt Water Deposit
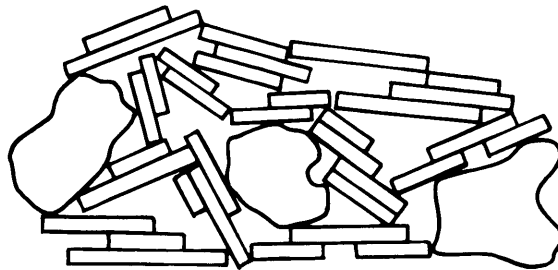
UNDISTURBED
Fresh Water Deposit
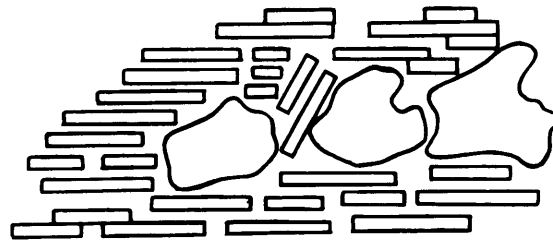
REMOLDED

FIGURE III-I   SOIL FABRIC AND EFFECTS OF
REMOLDING (After Lambe, 1953)

X-RAYS

FRONT VIEW

STIFF WIRE CLIP

SIDE VIEW

CERAMIC
EPOXY
GLASS PLATE

OBLIQUE VIEW
"L" SHAPED MOUNT

SAMPLE SURFACE
TO BE X-RAYED
EPOXY COATING
STIFF
ELASTIC
BAND

SIDE VIEW
SAMPLE MOUNTED FOR X-RAY
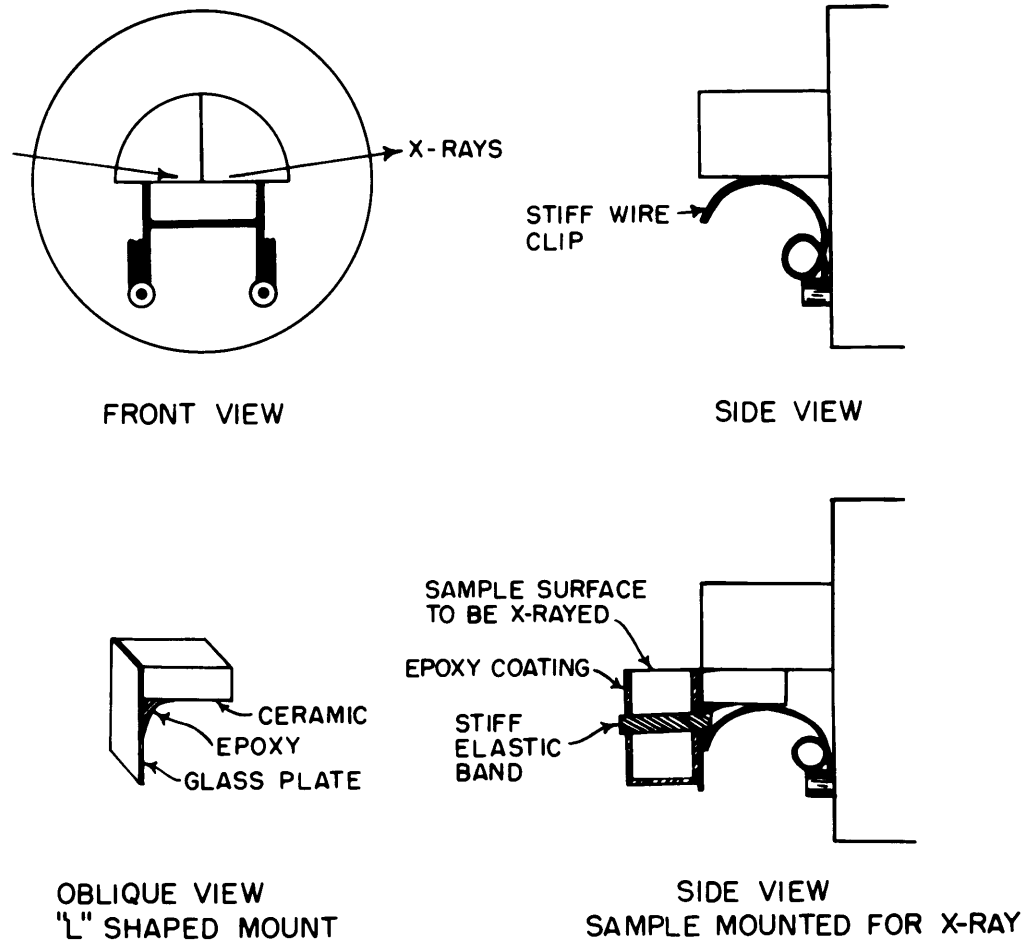
FIGURE III-2   SKETCHES SHOWING "L" SHAPED MOUNT
AND SAMPLE MOUNTING PROCEDURE

X-RAY DIFFRACTION PATTERNS
M2I, BATCH 3

① Maximum parallelism
Dispersed NaOH, centrifuged 40 min., 2000 rpm

② Very wet clay flocs, 35 ‰ NaCl

③ Completely random, powder pattern

FIGURE III-3

X-RAY DIFFRACTION TRACES

SHOWING PARALLELISM PRODUCED
BY ANISOTROPIC CONSOLIDATION

Consolidation Test 31
Originally highly flocculated
Consolidation pressure = 8 TSF

Soil: M21, Batch 3
Deposited in 9‰ NaCl
Leached 11.5‰ KCl
and consolidated

(a) Pattern from
horizontal plane
normal to ∇_c
(top surface)

(b) Pattern from
vertical plane
parallel to ∇_c
(side surface)

(a)

(b)

100Å (00ℓ)   7.1Å (00ℓ)   4.47Å (h,k,0)   3.36Å (00ℓ)   2.56Å (hk0)

DEGREES 2θ

FIGURE III-4

CLAY PARTICLE ORIENTATION PRODUCED
BY ANISOTROPIC CONSOLIDATION

$$\left(\begin{array}{c} \text{M2I, BATCH 3} \\ \text{CONSOL. TESTS 31-35} \end{array} \right)$$

Numbers beside points are
consolidation test numbers.

Black points = KCl leached
Open points = NaCl leached

3.34 Å (003)
Basal reflections
(Top surface)

4.48Å (hkO)
Reflections
(Side surface)

PEAK HEIGHT IN INCHES

MAXIMUM PREVIOUS CONSOLIDATION PRESSURE

1000   10,000

FIGURE III-5

FIGURE Ⅲ-6   PARTICLE ORIENTATION WITHIN A SHEARED
DRAINED DIRECT SHEAR SAMPLE (SAMPLE
AIR DRIED BEFORE X-RAY)

STIPPLED AREA = MARKS LEFT
BY TOP POROUS STONE

GOUGED OUT AREA USED
FOR WATER CONTENT
DETERMINATIONS

A-A' & B-B'
  SECTIONS ALONG WHICH DRY
  SAMPLE WAS BROKEN TO
  STUDY FABRIC

Scale X1

DIRECT SHEAR SPECIMEN

SECTION SHOWING STRUCTURE
WITHIN THE SHEARED SPECIMEN

Scale X2
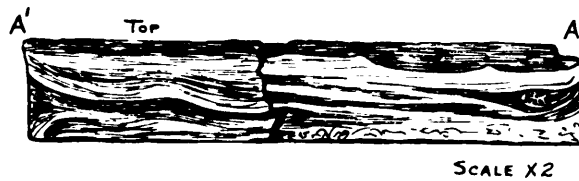
SECTION A'- A

SECTION SHOWING STRUCTURE
WITHIN THE SHEARED SPECIMEN

Scale X2

SECTION B-B'

FIGURE III-7   SKETCHES OF SHEAR ZONE WITHIN A DIRECT
               SHEAR SPECIMEN (SAMPLE AIR DRIED AFTER
               TESTING)
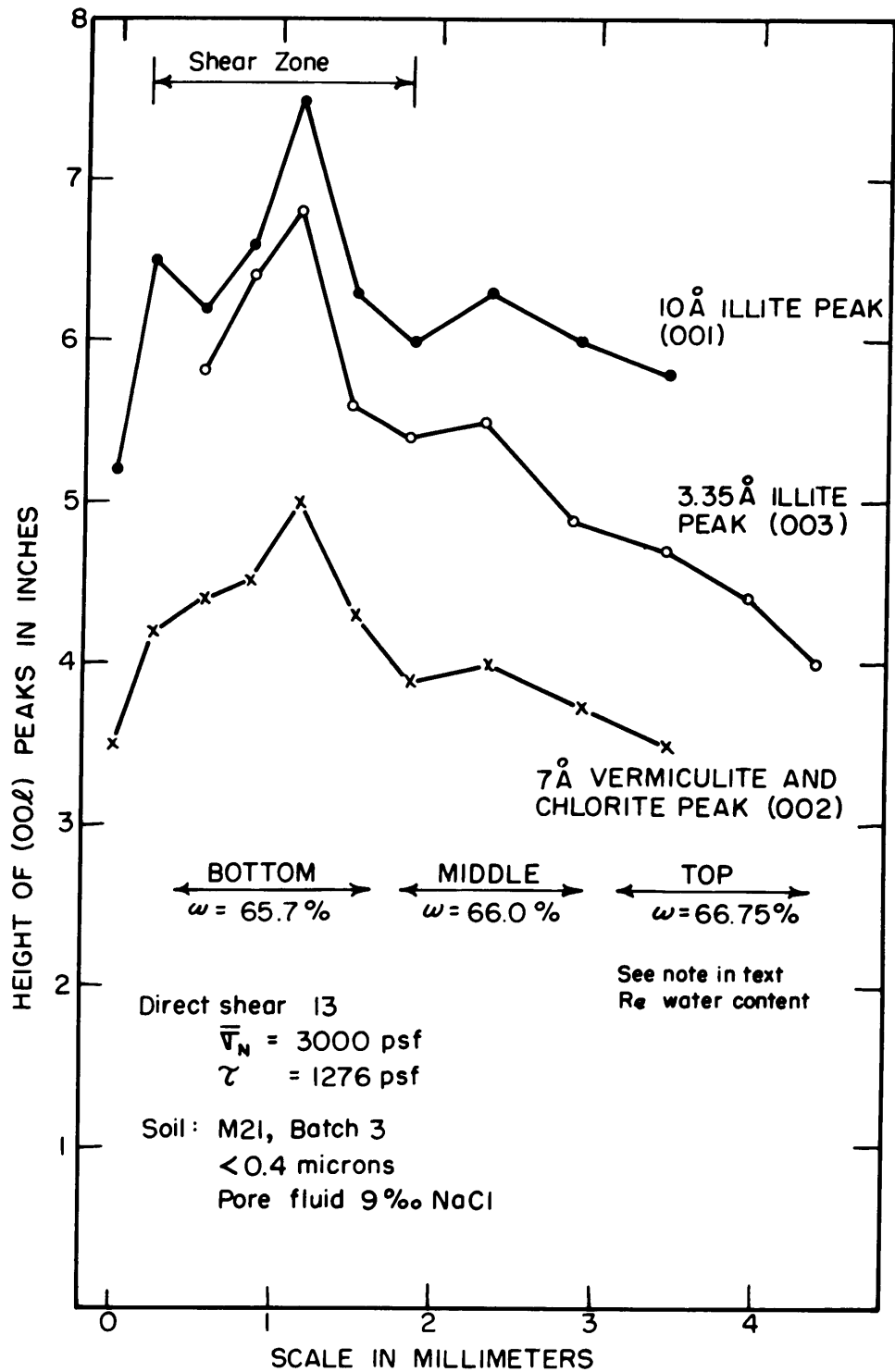
FIGURE III-8 PARTICLE ORIENTATION WITHIN A SHEARED
DRAINED DIRECT SHEAR SAMPLE (SAMPLE
AIR DRIED BEFORE X-RAY)
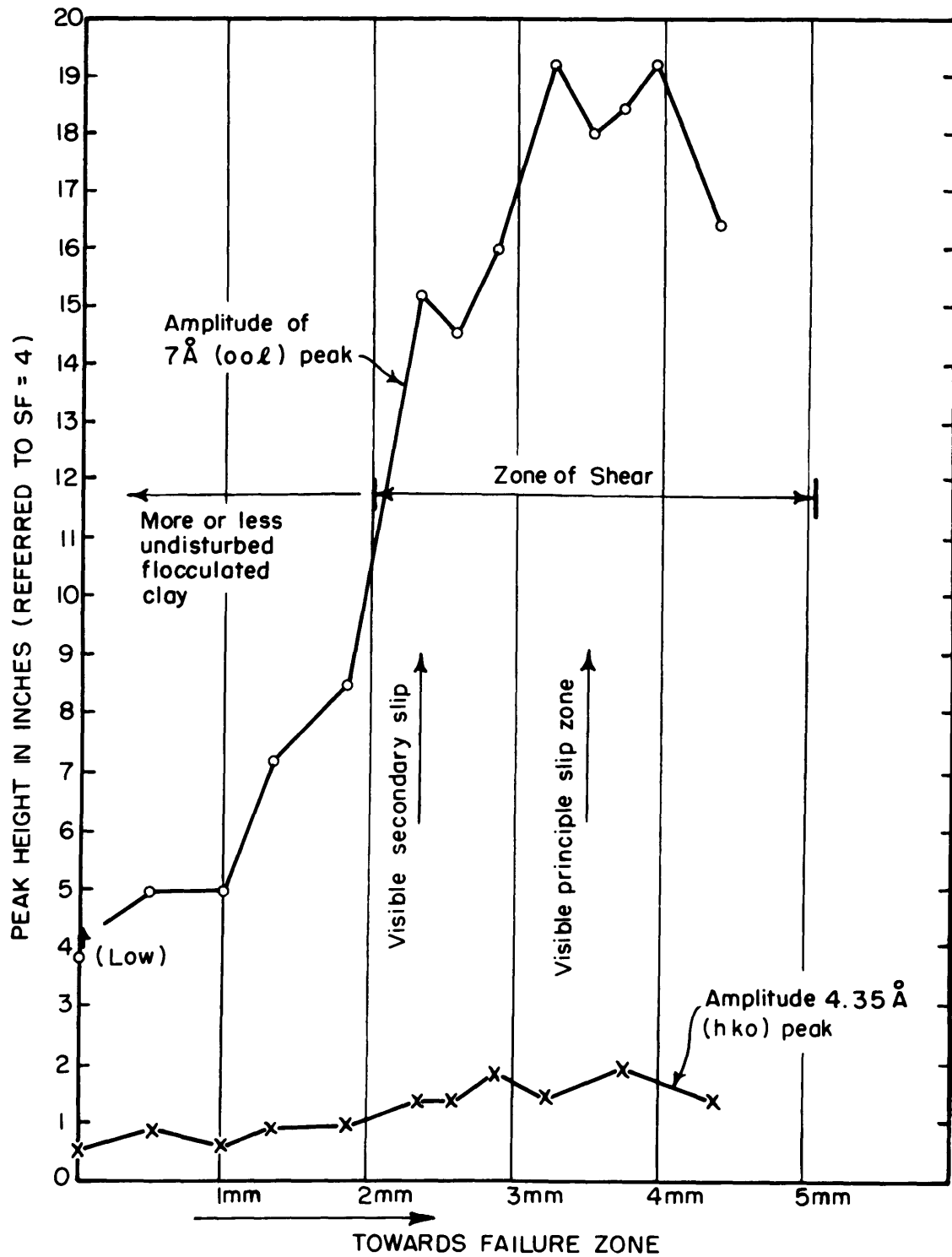
FIGURE III-9   CHANGE IN PARTICLE ORIENTATION AS A RESULT OF SHEARING ACTION

X-RAY DIFFRACTION PATTERNS OF KAOLINITE
SHOWING DEGREE OF PARTICLE ORIENTATION

(001)
7.2 Å

(a)

(002)
3.6 Å

a) Dispersed, centrifuged on porous
   plate 15 min. at 2,000 rpm

b) X-rayed surface of clay cut from
   failure plane of a test specimen.
   ie, surface in plane of
   movement.

c) Floculated kaolin from same
   sample as (b) but outside of
   failure zone

d) Random, powder pattern.
   Powder sprinkled on plate
   and X-rayed.

(003)
24 Å

Parallel

(b)

Semi - parallel

(c)

Random

(001)
7.2 Å

(hkℓ)

(002)
3.6 Å

(003)
2.4 Å

(d)

Random

8   10   12   14   16   18   20   22   24   26   28   30   32   34   36   38   40

DEGREES 2θ

FIGURE III - 10

RECOMMENDATIONS FOR ADDITIONAL WORK

Ideas for future work on the geological and engineering charact-eristics of marine clays are presented below. Most of these ideas have evolved from the present studies of potassium fixation and soil fabric.

1. Additional Studies of Potassium Fixation:

The work described in Parts One and Two of this thesis, showed that potassium saturation produced very little collapse of the degraded micas or vermiculites produced by acid weathering in the upper 16 inches of the soil profile studied. The mineralogical investigation showed that the clays were chloritized by interlayer aluminum and possibly iron, thus preventing fixation and collapse. The batches of clay used for engineering testing were obtained from the chloritized zone and hence showed little collapse. Therefore, most of the changes in engineering properties were produced by cation exchange and not collapse.

a) The soil profile study showed that below a depth of about 16 inches, the degraded clays were not chloritized and exhibited a marked collapse when potassium saturated. Additional engineering tests on clays from deeper in the soil profile might show some interesting effects of collapse. The x-ray data on the deeper clays suggested that some aluminum was present so it would probably be a good idea to clean them up (ie. remove this aluminum) before testing.

b) It is quite possible that potassium deficient tropical soils show pronounced potassium fixation characteristics. Aluminum and iron are not nearly so mobile in these soils because the ground water pH is higher. Some preliminary work might be started to see if this idea is correct.

c) Another way to produce a degraded mica would be to artificially leach the potassium out of an illite or fine grained mica. Leaching would not be accompanied by the drop in charge deficiency which seems to accompany weathering. Refixation of potassium would, therefore, probably be guaranteed.

d) A study of cation exchange effects on pure illite should be run in association with any additional work on degraded illites.

2. **Study Effects of Interlayer Water on the Properties of Montmorillonite:**

The purpose of this study would be to determine the effects of layer lattice contraction on the properties of montmorillonite which will not collapse completely. The object would be to extend the work done by Rosenqvist and relate the changes to those produced by potassium fixation.

For example, it was found in the present study that the salt concentration had a large effect on the Atterberg limits of the California illite-montmorillonite. Also the K:Na ratio had a large effect on the test results of the other clays studied. The effect of these factors on the layer lattice contraction and engineering properties would be studied.

a) The initial engineering tests would involve running Atterberg limits, which should be markedly affected by both the salt concentration and the K:Na ratio.

b) If large changes occur in the Atterberg limits, more comprehensive engineering tests could be started. Drained direct shear measurements should probably be obtained first, as this past year's

work has shown them to be highly sensitive to changes in the K:Na ratio.

3. Studies of Soil Fabric:

Part Three of this thesis showed that x-ray diffraction methods may be a useful tool in determining soil fabric. The following program of study hinges on the use of this method for measuring the fabric component of soil structure.

a) The first phase of the study would be to develop a more quantitative measure of fabric than was obtained in the preliminary study in Part Three.

b) Seminatural soil solidification could be studied by artificially precipitating iron hydroxide and calcium carbonate in clay soils. Both of these cementing agents precipitate naturally in the marine environment. Ferrous hydroxide precipitates as ferric hydroxide when it enters the marine environment. By controlling the pH and iron concentration, iron may be precipitated as a cementing agent. Preliminary tests have indicated that calcium carbonate may be precipitated by controlling the calcium ion concentration, partial pressure of CO_2 and pH. These reactions are similar to those in the tropics where changes in temperature and partial pressure of CO_2 affect carbonate precipitation.

c) The fabric of the cemented soils would be measured by the x-ray methods described.

BIOGRAPHICAL SKETCH OF THE AUTHOR

The author of this thesis, Robert M. Quigley, was born in Toronto, Ontario, Canada, on January 22, 1934. He attended the local public schools, graduating from Earl Haig Collegiate Institute in June, 1951.

The following September he entered the University of Toronto, taking a four year engineering course in Applied Geology. He received his Bachelor's degree with Honours in June, 1955 and his Master's degree in October, 1956. During his senior year he was president of the Coleman Geological Club. He obtained a scholarship from the Ontario Research Foundation to pursue his studies towards his Master's degree.

During the summer months between 1951 and 1956, the author worked at a variety of geological jobs in a variety of locations. He worked two summers on a geology bush party near Kirkland Lake, Ontario for the Ontario Dept. of Mines. He worked one summer underground at McIntyre Porcupine Mines, Ltd., Timmins, Ontario. In the summer of 1955 he worked as a geologist for Texaco Exploration Company, on a pack-horse party in the Rocky Mountains of Alberta. In the summer of 1956 he was employed by the Defense Research Board of Canada, as a member of an expedition to Baffin Island in the Canadian Arctic.

After obtaining his Master's degree, the author worked for nearly a year as a soil engineer for Geocon Ltd, out of Toronto.

In September 1957, the author entered upon a doctorate program in Geology and Soil Mechanics at M.I.T. from which he will graduate with a Doctor of Philosophy in September, 1961. During his stay at M.I.T. he was employed one year as a teaching assistant, two years as

a research assistant and this past year as an instructor. During

the summers away from M.I.T. he worked as a soil engineer for Geocon

Ltd. out of Toronto. After graduating he will rejoin Geocon as a

senior soil engineer and geological engineer, working out of

Montreal, Quebec.

The author was married just before starting M.I.T. in July, 1957,

to Marian Margaret Flack. He is deeply indebted to his wife for her

continued encouragement and patience during the past four years. While

at M.I.T. the author and his wife became parents of a son, Steven Robert.

The author is a registered member of the Association of Professional

Engineers of Ontario.

The author and Dr. R.T. Martin are presenting a paper entitled,

"Composition and Engineering Properties of Some Vermiculitic Products

of Weathering," at the 10th National Clay Conference in Austin, Texas

in October, 1961.

APPENDIX A

DETAILS OF MINERALOGICAL TEST PROCEDURES

I. FRACTIONATION PROCEDURES

The methods of soil fractionation were adopted from Jackson, 1956, "Soil Chemical Analysis - Advanced Course". The reader may refer to Jackson for the details not presented in this Appendix.

A. M21, Batches 1 and 2

The < 2 micron size clay used for these two batches was fractionated by ordinary settling procedures in 40 liter glass containers. The soil was dispersed in very dilute NaOH and after separation was flocculated with a spoonful of $CaCl_2$. The actual work was done by a graduate student and his exact procedures are not known. It is known, however, that Batch 2 sat around in 3 liter jars in its flocculated state for about 1 year after Batch 1 was air dried.

B. M21, Batch 3

To obtain the smaller than 0.4 micron clay for this batch, a combination settling and supercentrifuge procedure was used. The procedure is outlined below:

1. The -100 mesh soil was dispersed with a mixer in 2×10^{-3} Normal NaOH.

2. The dispersed soil was poured into 40 liter vats.

3. The 24 hour suspension was poured into large jugs for later centrifugation. (Suspension equivalent grain size < 2 microns approx.).

4. The sediment in the large vats was redispersed and the 24 hour setting repeated.

5. The < 2 micron clay suspension was passed through a Sharples Super-Centrifuge.

6. Super-Centrifuge Data:

Assumed soil specific gravity $\approx$ 1.65 = (Δs) (Submerged hydrated vermiculite).

Speed of revolution = 10,000 r.p.m. = (Nm).

Flow rate = 670 ml/min. = (F ml/min.).

Eqn: $F_{ml/min.} = 2.534 \times 10^{-5} \Delta s \, (Du)^2 (Nm)^2$.

(Du) = required equivalent grain size in microns = 0.4.

7. The fine suspension was flocculated with NaCℓ, air dried, and ground down to about 40 mesh.

8. Total preparation time (exposure to solutions) $\approx$ 9 days.

9. Obtained 390 grams of air dry clay for testing.

C. M21, Batch 4

Batch 4 was prepared by the same procedure as Batch 3. Only the different centrifuge data are presented below:

Speed of revolution = 20,000 r.p.m.

Flow rate = 47 ml/min.

Assumed specific gravity (Δs) = 1.65

Grain size obtained < 0.17 microns

Total preparation time (exposure to solutions) $\approx$ 10 days

Obtained 266 grams of air dry clay for testing.

II. X-RAY ANALYSES

Most of the x-ray work performed on M21, Batches 1 and 2, was film camera work. Samples of powdered clay were glycerol saturated and pressure oriented (GPO), mounted on glass rods, and

x-rayed under vacuum using chromium radiation. The pressure orientation intensifies the basal reflections and the glycerol saturation ensures maximum interlayer expansion. The basal spacings could not be accurately determined from the GPO samples without running powder patterns and correcting the GPO patterns. The approximate positions of the basal spacings are shown on the film traces from consolidation tests 10, 11, 17 and 18 in Figs. B-1 and B-3.

The film data can be presented in the form of prints from the negatives or light intensity traces. Both methods involve the loss of considerable film definition easily seen by eye. It was decided to run the films through a light intensity meter and plot the inverse of the meter readings. This gives a light intensity trace similar in shape to an x-ray diffraction trace. This method can only be used on light, clean film because a dark film will not transmit enough light, and dirt spots on the film produce erratic readings.

All of the x-ray work on Batches 3 and 4 was performed with an x-ray diffractometer complete with Geiger scaler and automatic recorder. Copper radiation generated at 40 kilovolts, and 15 milliamps was used for all of this work. The diffraction equipment is located in the Department of Geology and Geophysics at M.I.T.

Using this technique, the correct basal spacings could be obtained from oriented specimens without any corrections. Oriented samples were prepared by dispersing a sample in distilled water

using an ultrasonic vibrator and then centrifuging the suspension for about 20 minutes at 2000 r.p.m. over a porous ceramic plate. During this time, all of the water is drawn through the plate leaving a highly oriented, glossy layer of clay. The sample can be x-rayed wet, air dry, or glycol saturated.

Powder patterns were obtained by x-raying a level surface of clay powder. A rectangular depression cut in a ceramic plate was filled with powder, levelled off, and x-rayed. Typical patterns are shown in Figs. III-3 and III-10.

III. DIFFERENTIAL THERMAL ANALYSES

Clay samples to be thermally analyzed were air dried and ground down to 100 mesh before heating. The clay may be run in an air dried condition or at some specific relative humidity. All of the differential thermal analyses reported here were run on clays brought into equilibrium with an atmosphere of about 50 per cent relative humidity. This was done by placing the clay over a saturated solution of hydrous calcium nitrate. The relative humidity in the oven was not controlled.

The following additional information concerns the differential thermal analysis equipment used for this investigation:

Heating rate ~12.5 ^{O}C/min.

Thermocouples - Single Block, Pt-Pt (10% RH)

Sample size - Single block, 1.35 cc.

Pretreatment - > 7 days over saturated $Ca(NO_3)_2 . 4H_2O$ solution

Temperature control couple - in nickel steel block, temperatures are uncorrected.

Temperature calibration - Single block; quartz $\alpha \rightarrow \beta$ at ~ 571°C; $BaCO_3$ at 820° and 990°C.

The purpose of equilibrating the clays with an atmosphere at 50 per cent relative humidity was to get a water peak of some significance. Unpublished data by Martin (M.I.T.) indicates that the size of this water peak is related to the cation exchange capacity and glycol retention of the clay. Any changes in cation exchange capacity due to cation fixation should be reflected in the size of the water peak.

IV. CATION EXCHANGE CAPACITY DETERMINATIONS

The detailed procedure for the barium x-ray spectrographic analyses is presented below. A general outline was presented in Part One.

A. Experimental Procedure

1. Approximately one gram of clay solids is washed 5 times in 1N $BaCl_2 \cdot 2H_2O$. The clay is allowed to sit overnight in the 3rd or 4th wash.

2. The excess salt is washed out with a solution of 10^{-3} molar $BaCl_2$. This may take 2 or 3 washings depending on the size of the centrifuge tubes used. The concentration of the centrifuged supernatant may be quickly checked with a conductivity meter.

3. Wash the clay once with methanol or ethanol to hasten air drying.

4. Allow to air dry and grind down until it passes a 100 mesh sieve.

5. X-ray the clay powder just as it is (i.e., in equilibrium with the atmosphere.

185.

The above procedure does not attempt to remove all of the excess $BaCl_2$ in the pore water. Enough $BaCl_2$ is left in solution to prevent any exchange of Ba^{++} by H^+ or H_3O^+ during washing. The error involved is very small, amounting to no more than 2 per cent in a clay having a cation exchange capacity value as low at 10 m.eq./100 g.

B. Preparation of Standards

Four barium standards were prepared by mixing barium carbonate with the clay to be analyzed (i.e., M21, Batch 2). The clay in its natural state contained no barium. A carbonate was used as it has about the same matrix adsorbing effect as a clay mineral. (Prof. Hower, personal communication).

The barium $K\alpha$ x-ray emission peaks for the four standards are shown in Fig. A-1. The known barium content was expressed in m.eq./100 g. of mix. The heights of the peaks were plotted against the barium contents (cation exchange capacity) to obtain a curve of standards as shown in Fig. A-2. The points fall on a straight line passing through the origin. The instrument settings are indicated in Fig. A-2 and are listed below.

To determine the cation exchange capacity of a clay, all one has to do is make it homoionic in barium, using the procedure previously outlined, and obtain a barium $K\alpha$ emission peak on it. The cation exchange capacity is then read off Fig. A-2 using the peak height obtained on the unknown clays.

C. X-Ray Spectrometer Instrument Settings

Norelco X-Ray Spectrometer - 50 kv., 15 ma.

Baseline Variable: 85 volts used

Window = 7 volts

Scale Factor = 64

Rate of Scan, $1/4°$ 2θ/min.

Counter Voltage = 650

Crystal = LiF

Barium Kα, peak at 10.04$°$ 2θ (Average of Kα_1 & Kα_2)

It is advisable to run through a set of standards prior to every run, as the baseline voltage required for a background plateau was found to vary considerably.

V. TOTAL POTASSIUM DETERMINATIONS

Total potassium was determined using the same x-ray spectrometer that was used for the cation exchange capacity determinations.

Potassium with its low atomic number (19) has a low intensity of x-ray emission. For this reason, the machine must be evacuated and a sensitive flow counter employed.

Two clay samples having known potassium contents (previously determined chemically) were used to prepare a standard curve. In Fig. A-3, a straight line is drawn from the origin through the two points. In this figure the Kα peak heights are plotted against per cent potassium determined chemically. Because most of the potassium contents are in the region of these two points, it is considered that the curve is satisfactory. The per cent potassium in an unknown is determined by comparing the height of its Kα peak with the standard curve.

The following spectrometer instrument settings were used:

Norelco X-Ray Spectrometer

40 kv., 40 ma.

Baseline Variable; 58 volts used

Window = 6 volts

Proportional Counter, P10 gas, Flow Rate = 0.1 ft.^{3}/hour

Gain = 10

Counter voltage = 1650 volts

Crystal EDDT

Rate of scan = $1/2^{\circ}$ 2θ/min.

Scale Factor = 8

Time Constant = 2

Potassium Kα peak at 50.30 2θ.   (Average of Kα_1 & Kα_2 peaks)

VI   GLYCOL RETENTIONS

The retention of ethylene glycol by clays is a useful indicator of soil properties and possibly surface area. The method used was that of Dyal and Hendricks (1952) as modified by Martin, 1955. The method will not be discussed further in this report.

VII.   EXTRACTION OF ALUMINUM AND IRON

A clay sample of M21, Batch 3 was analysed for easily extractable aluminum and iron. The initial method involved the exchange of aluminum and iron with sodium by washing the sample in 1N NaCl, which had been brought to pH 3 with HCl. Four 24 hour washes were performed, the four solution extracts being saved for chemical analysis. The aluminum and iron analyses were run by a laboratory technician under the supervision of Dr. Martin. The methods used were modifications of Peach and English (1944).

This extraction procedure did not remove any of the interlayer aluminum and iron so the sodium citrate extraction of Tamura (1958) was employed. This method involves boiling a clay sample in 1N sodium citrate (pH = 7.3). The solution is charged every hour by centrifuging and decanting. Only one soil sample was actually extracted. The sample was treated for 48 hours, the solution being charged 8 times during this time. The mixture was left at room temperature overnight. All extracts were clear, but had a distinct yellow-brown color.

The aluminum and iron contents in the extracting solution were determined spectrographically using the same equipment as for the barium and potassium analyses. A strip of filter paper was immersed once in the extract and hung up to dry. This strip was then x-rayed. The concentrations of aluminum and iron were determined by comparing with standard solutions. Filter paper strips were immersed in these solutions, air dried and x-rayed exactly like the unknowns. Reasonably good working curves were obtained for both the aluminum and iron despite the very low concentrations involved. For example, the aluminum Kα peaks were picked up above background on filter strips dipped in aluminum solutions as weak as 10^{-5} Normal.

The instrument procedure was quite similar to that for the potassium analyses and will not be described further.

BARIUM Kα X-RAY EMISSION PEAKS

BARIUM STANDARDS FOR C.E.C. DETERMINATIONS

Standard I:
Ba^{++} = 91.5 meg./100gm
Height = 6.70 inches

Materials:
BaCO_3 for source of Ba^{++}
Matrix: M21, Batch 2

Standard 2:
Ba^{++} = 45.6 meg./100gm
Height = 3.40 inches

Standard 3:
Ba^{++} = 22.8 meg./100gm
Height = 1.62 inches

Standard 4:
Ba^{++} = 11.3 meg /100gm
Height = 0.86 inches

11.5° 2θ   11.5° 2θ   11.5° 2θ   11.5° 2θ

FIGURE A-1

BARIUM STANDARDS CURVE
PEAK HEIGHT vs CATION EXCHANGE CAPACITY

Materials: BaCO₃ in a clay matrix of M21, Batch 2

X-RAY SPECTROMETER INSTRUMENT SETTINGS

Baseline = 85 volts   50 KV
Window = 7 volts   15 ma
Gain = 60   Rate of scan:
Scale factor = 64   ¼° 2θ/min.
Time constant = 2
PHA in   Counter voltage = 650
                        Crystal : LiF
                        Peak at 10.04° 2θ

PEAK HEIGHT IN INCHES

CATION EXCHANGE CAPACITY (meg/100g)

FIGURE A-2

SPECTROMETER INSTRUMENT SETTINGS

Crystal EDDT	40 Kv
Baseline = 58 volts	40 MA
Window = 6 volts	Rate of scan:
Gain = 10	$\frac{1}{2}°$ 2θ /min.
Scale factor = 8	
Time constant = 2	Counter voltage = 1650

PHA in

Proportion counter

P 10 gas, Flow rate 0.1 FT^3/ hr

Potassium Kα peak at 50.3° 2θ

Y-axis: PEAK HEIGHT (INCHES)

X-axis: PERCENT POTASSIUM

FIGURE A-3   POTASSIUM STANDARDS CURVE
(PERCENT POTASSIUM vs Kα PEAK HEIGHT)

APPENDIX B

DETAILS OF MINERALOGY - M21, BATCHES 1 and 2

These two batches of clay came from the same bulk sample and have almost the same composition. However, Batch 2 sat in water for about one year after Batch 1 was prepared. During this time, some changes in the distribution of the soil aluminum probably occurred. Complete mineralogical data was obtained only for Batch 2. In Table B-1, the mineralogical data are summarized.

I. COMPOSITION

Batches 1 and 2 have the following approximate composition:

Grain size ~ 90% smaller than 2 microns

Illite ~ 60%

Vermiculite or degraded illite ~ 15%

Chlorite ~ 5%

Quartz ~ 20%

The percentage of illite was determined by assuming a 6.0 per cent K_2O content for pure illite. After potassium fixation and washing with $BaCl_2$, the illite content had increased to about 70 per cent at the expense of the vermiculite. The percentage of quartz has been taken as the difference, after assuming the presence of about 5 per cent chlorite.

II. X-RAY ANALYSES

X-ray film patterns were obtained to study the effects of potassium fixation and mineral collapse. A pattern was obtained on every sample after consolidation to study the effects of KCl and $NaCl$ leaching. The films which were not too dark were run through a

light intensity meter.

The inverse of the light intensity readings on the x-ray film of clays from consolidation tests 10 and 11 are shown in Fig. B-1. The clay samples were air dried, glycerol saturated, and pressure oriented before x-raying. It is immediately obvious that the clay in consolidation test 10 has retained all of its vermiculite throughout the testing. It is also obvious that the KCℓ leaching in consolidation test 11 has collapsed nearly all of the vermiculite. The small residual peak left after fixation has shifted towards the illite peak.

According to the peak height ratios, the 7$\overset{o}{A}$ peak has also diminished in size. This decrease, however, is not as pronounced as for the 14$\overset{o}{A}$ peak. This suggests that there may be a little kaolinite or iron chlorite in the sample. A heat treatment of M21, Batch 3 indicated the presence of iron chlorite so Batch 2 probably contains some also.

Two x-ray diffraction traces for consolidation tests 10 and 11 are shown in Fig. B-2. The specimens were oriented by centrifugation on to porous ceramic plates and x-rayed in an air-dry condition. These traces also indicate that K fixation has caused nearly complete collapse of the vermiculite. The shift of the tiny residual peak towards a smaller d value, and the shoulder on the 10$\overset{o}{A}$ illite peak suggest an interlayered illite-vermiculite type of structure.

On the basis of these two figures (B-1 and B-2) we may conclude that the KCℓ leaching produced a complete collapse of the vermiculite to illite in consolidation tests 11 and 19.

Light intensity curves for the clays from consolidation tests 17 and 18 are presented in Fig. B-3. Both samples were KCl treated to collapse the vermiculite before deposition in 9% NaCl. Tests 17 and 18 were leached with NaCl and KCl solutions respectively, before consolidation. As before, the vermiculite peak has vanished in the KCl leached sample. In the NaCl leached sample, however, the potassium was not tightly fixed, and the washing with 2N NaCl before deposition followed by NaCl leaching removed some of it.

III. CATION EXCHANGE CAPACITY DETERMINATIONS

Cation exchange capacities, determined by the x-ray spectrographic technique described previously, were obtained for the untreated clay and on samples from consolidation tests 10, 11, 17 and 18. Although the changes are not large , they are all consistent and quite significant. Cation exchange capacity values of 18 and 19 m.eq./100 g. were obtained on two samples of clay which had never been subjected to potassium solutions. Values of 13, 14, 15 and 16 m.eq./100 g. were obtained on KCl treated samples. In all cases, the KCl treatment was accompanied by potassium fixation and a small decrease in exchange capacity.

Potassium analyses were run on barium saturated clay samples from tests 10 and 11 (see Table B-1). The total potassium content increased from 3.0 per cent K^+ to 3.4%K^+ in the KCl leached clay from test 11. It is of interest to note that this increase in fixed potassium should result in a decrease in exchange capacity of about 10 m.eq./100 g. of soil. The measured decrease for this sample was only 3 m.eq./100 g. It is possible that fixed aluminum adsorbed on

the clay was removed during the time of the consolidation test and replaced by potassium. This reaction would not produce any change in exchange capacity while it would increase the potassium content. Displacement of fixed aluminum by neutral salts has been discussed by Paver and Marshall, 1934, and Coleman, Weed and McCracken, 1959. Coleman, et al displaced large amounts of aluminum by leaching with 1 N KCl, so the above hypothesis seems reasonable.

IV. DIFFERENTIAL THERMAL ANALYSES

Differential thermal analyses were run on powdered samples from several of the consolidation tests. In Fig. B-4, curves for the clay from tests 10, 11, 17 and 18 are presented. The clay from each of these tests was washed once with methanol, air dried, passed through a 60 mesh sieve, and placed in an atmosphere of approximately 50 per cent relative humidity. The partially hydrated clay was then heated.

All of the curves are essentially the same; the KCl leached clays showing little difference from the NaCl leached clays. The only significant difference in the curves appears in the adsorbed water peak. The clays with KCl in the pore fluid have a peak temperature of about 155°C whereas the clays with NaCl have a peak temperature at about 185°C. This difference in peak temperature may be related to the greater ionic potential of Na^+; the ionic potentials for Na^+ and K^+ being 1.0 and 0.75, respectively. The Na^+ adsorbs water more firmly than the K^+, hence the higher the temperature of reaction.

V. GLYCOL RETENTIONS

As shown in Table B-1, the values of glycol retention show no significant change from test to test despite potassium fixation. The average value for tests 10, 11, 17 and 18 is 34 mg./g. of clay. Two lower values were obtained on clay which had not been subjected to NaCl or KCl solutions during a consolidation test. It is possible that these values (28 and 31) are lower because the clay has more adsorbed aluminum in it. As mentioned before, some adsorbed aluminum may have been removed by the neutral salt solutions during the consolidation tests.

TABLE B-I: M21, BATCH 2,   MINERALOGICAL DATA   (90% smaller than 2 microns)

Sample No.	Sample Description	* C.E.C. (m.eq./100g.)	* (%) K	Glycol ** Retention (mg./g.)	D.T.A. No.	D.T.A. Ion	D.T.A. R.H.%	X-ray No.	X-ray Ion	Type
10	Test clay - no NaCl pretreatments.	18	-	28	3727	Ca	50	1508	Ca	GPO film
44	Test clay - treated with 0.5N KCl	14	-	31	3728	K	50	1513	K	"
38	Clay from Consol. 10 (0.154N NaCl)	19	3.0	35	3723	Na	50	1520	Na	"
39	Clay from Consol. 11 (0.154N KCl)	16	3.4	34	3724	K	50	1519	K	"
40	Clay from Consol. 17 (collapsed, 0.154N NaCl)	15	-	34	3725	Na	50	1717	Na	"
41	Clay from Consol. 18 (collapsed, 0.154N KCl)	13	-	33	3726	K	50	1718	K	"

*   Obtained by x-ray spectrographic methods.

** Glycol retentions run on Ba clays unless otherwise indicated.

LIGHT INTENSITY TRACES OF X-RAY FILM PATTERNS
(M2I, BATCH 2)

Vermiculite peak

Consol IO

NaCl only
Expanded form
Film 1520

Peak Height Ratios

7Å/10Å = 7.1/10
14/10 = 63/10
14/7 = 8.9/10

Residual peak after collapsing. Note its shift towards the lower spacings

Consol II

KCl leached
Collapsed form
Film 1519

Peak Height Ratios

7Å/10Å = 5.4/10
14/10 = 2/10
14/7 = 3.7/10

Note:
Do not compare relative intensities of one curve with the other. Can compare peak height ratios.

~10Å

~7Å

FIGURE B-1

X-RAY DIFFRACTION PATTERNS
M21, BATCH 2

(SHOWING COLLAPSE PRODUCED BY KCl LEACHING)

Consol No. 11

Consol No. 10

10.28 Å

10.163 Å

14.49 Å

7.31 Å

14.73 Å

7.25 Å

FIGURE B-2

LIGHT INTENSITY TRACES OF X-RAY FILM PATTERNS
(M2I, BATCH 2)

Reconstituted
vermiculite
peak

Consol 17
   Collapsed, sedimented NaCl
   Leached NaCl
   Film #1717

Peak Height Ratios
   7Å / 10Å = 7.9/10
   14/10 = 5.0/10
   14/7 = 6.4/10

Residual peak
after collapse
shifted somewhat

Consol 18
   Collapsed, sedimented NaCl
   Leached KCl
   Film #1718

Peak Height Ratios
   7Å/10Å = 5.2/10
   14/10 = 2.2/10
   14/7 = 4.3/10

Note:
   Do not compare
   curves directly.
   Compare peak
   height ratios.

~10Å

~7Å

FIGURE B-3

FIGURE B-4   DIFFERENTIAL THERMAL ANALYSES
M21, BATCH 2

APPENDIX C

DETAILS OF MINERALOGY - M21, BATCH 3

This batch of clay was prepared in an attempt to obtain a
very active clay which showed marked potassium fixation properties.
Batches 1 and 2 contained about 15 per cent of collapsible vermiculite.
It was hoped that a batch of clay containing more than 50 per cent
collapsible clay could be produced. Two trial runs were made on
soil M21 to make sure that such a clay could be produced by fraction-
ation. The results of these runs are briefly presented below. The
details are presented in Appendix E.

I. HYPOTHESIS

Many recent papers have discussed the effects of potassium
fixation. More recently, several papers have been written concerning
the mechanism and rate of potassium release from fine grained mica-
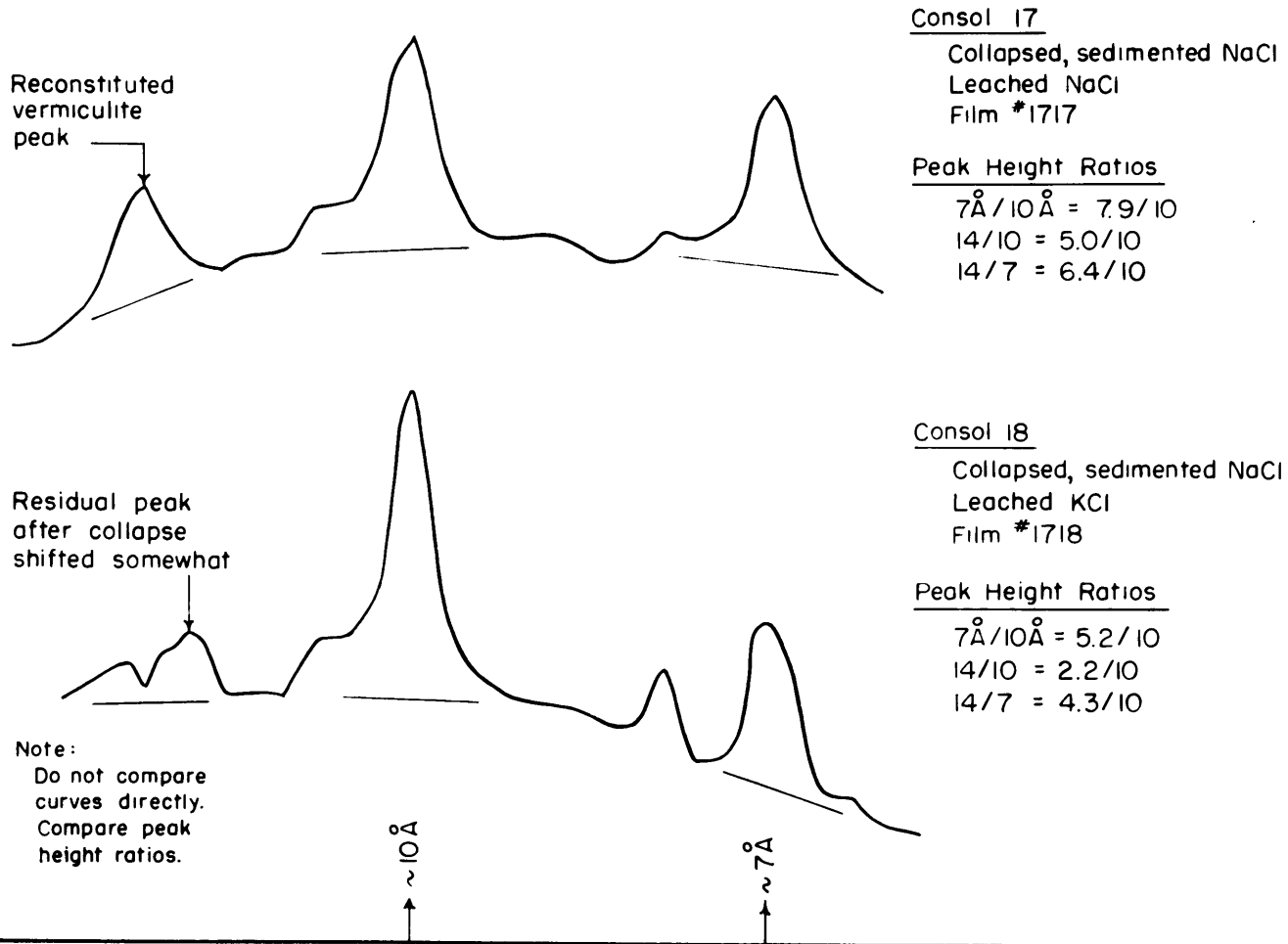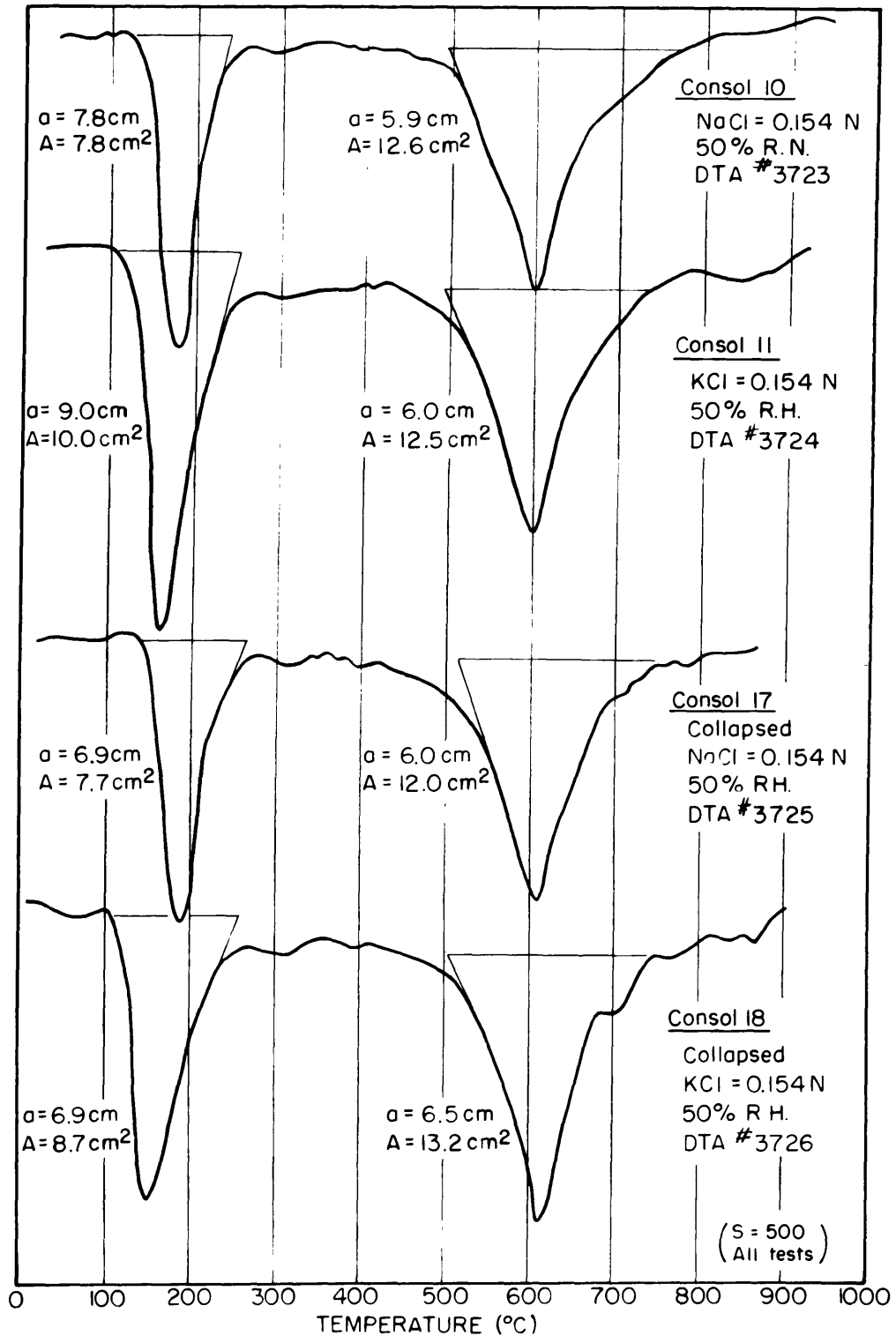like clays. The experiments indicate that potassium is released
more easily from the fine fraction than the coarse fraction of a
clay soil. (Mortland, 1958; Reed and Scott, 1960)

Because soil M21 consists of degraded illites, it was
thought that the fine fraction would be very deficient in potassium
and show marked fixation characteristics.

Several fine clay fractions were obtained from soil M21 to
study their fixation properties before a large batch of clay was
prepared for engineering testing. Unfortunately, the important role
of mobile aluminum and iron in acid soils was not realized. Consid-
erable difficulties arose because the release of interlayer potassium
was accompanied by the fixation of aluminum and iron in the soil profile.

II. RESULTS OF TRIAL RUNS

A sample of M21, Batch 2 was fractionated to obtain the less than one micron clay. The cation exchange capacity of this clay increased to 27 m.eq./100g. from a value of 18 m.eq./100 g. The water peaks on the differential thermal curves also showed a pronounced increase in size. X-ray film data on this clay gave a positive indication of a swelling clay with a basal spacing around 18$\overset{o}{A}$. It was concluded from this that the cation exchange capacity and expandable clay content could be increased by fractionation.

A trial run was initiated on a new bulk sample of clay taken from the upper 16 inches on the soil profile previously described. Three size fractions were obtained:

Smaller than 1 micron

Smaller than 0.5 microns

Smaller than 0.35 microns

The 1 micron fraction from which the smaller sizes were derived sat around for about 2 months in strong neutral salt solutions before further fractionation. The wash was changed 2 or 3 times in this 2 month period. The $<$0.35 micron clay had a cation exchange capacity of 110 m.eq./100 g. After a 1N KCl treatment this decreased to 55 m.eq./100 g., and the preliminary K analyses indicated an undetermined increase in total potassium.

On the basis of these tests and some favorable x-ray patterns a large quantity of M21, Batch 3 was prepared. This batch of clay was prepared over a period of about 1 week and

was not allowed to sit in a strong neutral salt solution. This difference in preparation caused significant differences in properties between Batch 3 and the pilot run clay. Apparently, large amounts of fixed aluminum were removed in the pilot run giving the clay its pronounced potassium fixation properties. M21, Batch 3 exhibited no potassium fixation properties, although reversible layer lattice contractions were produced in clays homoionic in potassium.

III. COMPOSITION

Table C-1 contains a list of the tests performed on this batch of clay and some of the test results. Batch 3 has approximately the following composition:

Grain size - smaller than 0.4 microns

Illite ~ 60%

Vermiculite ~ 15%

Chlorite ~ 20%

Quartz ~ 5%.

The illite content was determined assuming 6.0% K_2O for pure illite. The amount of vermiculite was estimated to be 15% on the basis of the decrease in glycol retention when the clay was potassium saturated. Pure vermiculite was assumed to have a glycol retention of 150 mg/g of clay. The sodium citrate extraction of Batch 3 increased the exchange capacity by 15 m.eq./100 g. If we assume that vermiculite was formed from chlorite by this treatment as indicated by the x-ray analyses, we get 10 per cent increase in the vermiculite content. Pure vermiculite was assumed to have a C.E.C. of 150 m.eq./100 g. Assuming that there was 10 per cent iron chlorite in the sample (estimated from the x-ray peak intensities

after heat treatment) we obtain a 20 per cent chlorite content for the untreated clay. All percentages are quite approximate.

IV. X-RAY ANALYSES

A great deal of x-ray diffraction work was performed on this batch of clay in order to determine its composition and potassium fixation properties. Much of the x-ray work on Batch 3 was described in Part One as part of the soil profile study. To keep this Appendix as complete as possible, some of this work is repeated here.

A. Typical Patterns

Powder patterns of air dry clay, homoionic in sodium and potassium, are shown in Fig. 1-2. The most obvious feature of these curves is the very low intensity of the (00ℓ) reflections compared with the $(hk0)$ reflections. This possibly is due to random interlayering which can reduce the size of the (00ℓ) reflections. The 10Å illite peak is slightly better defined in the potassium clay. The presence of a broad 3.50Å peak and the absence of a 3.66 Å peak suggests a 2M rather than 1M polymorphic or crystal form. The slope of the 2.57 Å peak downward towards the 2.59 Å spacing is also indicative of a 2M structure. (The 2.59 Å peak is stronger than the 2.57 Å peak in 1M mica.)

The patterns of centrifuge oriented, glycol saturated clay, homoionic in sodium and potassium are shown in Fig. 1-3 and 1-4. The trace in Fig. 1-3 indicates that illite and a vermiculite-like mineral (10.15 Å and 14.26 Å) are very abundant constituents. A tiny amount of 18 Å montmorillonite-like material is also present.

Fig. 1-4 shows that a marked reduction in the vermiculitic phase has been produced by the presence of interlayer potassium. The high order reflections are close to being at integral values of the (00l) peaks. The two peaks at 4.29 $\overset{o}{A}$ and 4.11 $\overset{o}{A}$ are difficult to explain. It is possible that they represent some high order reflection of a regularly interlayered mineral phase. The potassium treatment (Fig. 1-4) had little effect on these two peaks, whereas it caused a large reduction in the high order vermiculite peaks. This suggests that illite,and chlorite may be the interlayer constituents. Lambe and Martin, (1955) describe similar strong, high order reflections at different d values and ascribe them to regularly interstratified illite-chlorite mixtures.

The very weak 3.55 $\overset{o}{A}$ peak after KCl treatment (Fig. 1-4) indicates that if kaolinite is present, it is a very minor constituent.

B. Heat Treatment

A sample of clay was heat treated and x-rayed at successively higher temperatures to test for the stability of the fixed aluminum hydroxide complex, and to see if any chlorite was present. The 100° and 200°C treatments were for 1/2 hour each. The 350° and 500°C treatments involved heating the specimen in an oven as the oven temperature rose, and removing it when the required temperature was reached. The hot samples were put in a dessicator containing silica gel and carried to the diffractometer. X-ray time was about 15 minutes so that sufficient time was available for the re-expansion of any expanding mineral.

X-ray patterns are shown in Fig. 1-8. Air drying seems

to have caused a great deal of collapse in a randomly interlayered phase producing a high background between 14$\overset{o}{A}$ and 10$\overset{o}{A}$. The 100°, 200° and 350° treatments caused the 14$\overset{o}{A}$ peak to decrease in size until it is completely gone at 350°C. This collapse is probably caused by the loss of hydronium water, H_3O^+, (Brown and Norrish, 1952) and hydroxyls from the fixed aluminum hydroxide complex. The individually fixed aluminohexahydronium cations (Jackson, 1960) would probably lose their water before those which are fixed as a semicontinuous gibbsite sheet. The aluminum also probably prevents the re-expansion by water adsorption during x-raying. Tamura, 1956, reports progressive water losses and structural collapse with incremental heat treatments on a similar soil.

The 500°C treatment resulted in the sudden development of a double peak at 13.8$\overset{o}{A}$ and 12.3$\overset{o}{A}$. The 7.1$\overset{o}{A}$ (002) peak nearly vanished. The shift of the (001) peak to a lower d value and an increase in its intensity relative to the 7$\overset{o}{A}$ (002) peak are characteristics of iron chlorite (Martin, 1955).

C. Potassium Treatments

X-ray patterns, run on the barium clays prepared for the cation exchange capacity determinations, are shown in Fig. C-1. Each vertical row of traces was obtained from one sample. The first trace was obtained from the water saturated sample immediately after centrifuge preparation. The second was run on the same sample after air drying and the third after glycol saturation. The barium clays were prepared by the method outlined for the cation exchange capacity determinations. The potassium treatments

involved washing the clays in IN KCℓ solutions. A 24 hour treated clay was washed 5 times and allowed to sit overnight in the 3rd or 4th wash. A 14 day treatment involved 7 or 8 washes. All of the samples were washed free of excess salt before air drying and bottling. The air dry samples were prepared for x-ray by the method previously described.

At first glance, the curves do not appear to show much change as a result of potassium treatment. Air drying has produced a noticeable increase in background between the 14, 10 and 7Å peaks and a slight decrease in background above the 14Å in all of the barium clays. This change was reversed to a large extent by glycol saturation. The potassium clays showed no change with air drying and glycol treatment.

The traces can be compared only in terms of peak height ratios. In Table C-II, the 14Å:10Å peak height ratios for Fig. C-I are presented. The ratios are largest for the clay which has never been KCℓ treated and smallest for the clay which is homoionic in potassium. The barium clays previously treated with KCℓ gave intermediate ratios. It appears as though most of the potassium is exchangeable resulting in re-expansion of the collapsed structure during BaCℓ_2 washing.

It is interesting to note that the 14 day KCℓ treatment gave higher ratios and hence less collapse than the one day treatment. The cation exchange capacity was increased rather than decreased by this long treatment. These irregularities were apparently caused by the release of interlayer aluminum and are discussed in detail in Part One.

In Fig. C-2, similar traces for the clay homoionic in sodium and potassium are plotted. The $14\overset{o}{A}:10\overset{o}{A}$ peak height ratios are presented in Table C-III. The results are the same as before except that the sodium clay exhibits much stronger $14\overset{o}{A}$ peaks than the barium clay.

V. CATION EXCHANGE CAPACITY DETERMINATIONS

The cation exchange capacities are given in Table C-I. Samples 64 and 66 have values of 35 and 37 m.eq./100 g. respectively, showing that the long treatment may actually have increased the exchange capacity. Coleman, et al, 1959, removed considerable Al by KCl leaching and this probably happened here. Sample 65, with its 24 KCl treatment, has a value of 27 showing a reduction of about 8 m.eq./100 g. This roughly corresponds to the increase in potassium in the sample. The glycol retention does not show a corresponding drop with the potassium fixation.

A cation exchange capacity of 35 m.eq./100 g. compared with 18 m.eq./100 g. for Batch 2, indicates that much more swelling clay exists in Batch 3.

VI. DIFFERENTIAL THERMAL ANALYSES

Six differential thermal curves are shown in Fig. C-3. The curves are all remarkably similar despite the different treatments and exchange ions. As mentioned in Part One, the clay appears to contain some amorphous iron which crystallizes giving a small exothermic hump between 350 and $400^{o}C$. A more distinctive water peak might have been obtained if the clay had been Mg or Ca saturated. According to Barshad (1948), vermiculites containing

these cations have two water peaks. Barshad's hydroxyl peaks occur at 790° C followed by a sharp exothermic reaction at 800° C. Neither of these peaks occur here. The hydroxyl peak at 600 to 620° C is characteristic of illite and iron chlorite, both of which are present.

VII. GLYCOL RETENTIONS

Six glycol retention values for this clay are given in Table C-I. All are essentially the same (averaging 61 mg./g.) except Sample 62, which is homoionic in K and has a lower value of 43 mg./g. Some collapse has occurred in this clay causing the lower value. The potassium is not fixed, however, as shown by Samples 63, 65 and 66 in which the potassium has been easily washed out by $BaCl_2$ solutions resulting in a return to the original glycol retention. The per cent vermiculite was estimated from the reduction in glycol retention after KCl saturation.

VIII. ALUMINUM AND IRON EXTRACTIONS

The aluminum and iron extractions have been discussed in detail in Part One where they form an integral part of the soil profile discussion. They will not be mentioned further here.

TABLE C-I: M21, BATCH 3,   MINERALOGICAL DATA   (Smaller than 0.4 microns)

Sample No.	Sample Description	* C.E.C. (m.eq./100g.)	* K$^+$ (%)	Glycol ** Retention (mg./g.)	D.T.A.			X-ray Diffraction	
					No.	Ion	R.H.%	Ion	Type
61	Homo Na, 0.154N NaCl	-	3.1	59$_{Na}$	3741	Na	50	Na	Wet Air dry G.P.O.
62	Homo K, 0.154N KCl	-	-	43$_K$	3742	K	50	K	"
63	Homo Na, 0.154N NaCl, (24 hr. KCl treatment)	-	3.2	58$_{Na}$	3743	Na	50	Na	"
61A	Homo Na, no excess salt	-	-	-	-	-	-	Na	"
62A	Homo K, no excess salt	-	-	-	-	-	-	K	"
63A	Homo Na, no excess salt, (24 hr. KCl treatment)	-	-	-	-	-	-	Na	"
64	Homo Ba, no excess salt	35	3.1	64	3744	Ba	50	Ba	"
65	Homo Ba, no excess salt (24 hr. KCl treatment)	27	3.6	61	3745	Ba	50	Ba	"
66	Homo Ba, no excess salt (14 day KCl treatment)	37	3.15	62	3746	Ba	50	Ba	"
67	Homo K, no excess salt (14 day KCl treatment)	-	-	-	-	-	-	K	"

* Obtained by x-ray spectrographic methods
** Glycol retentions run on Ba clay unless otherwise indicated.

TABLE C-II: RATIO 14Å:10Å PEAK HEIGHTS

Sample No.	64	65	66	67
Treatment	Homo Ba, Expanded form	Homo Ba, 24 hr. KCl treatment	Homo Ba, 14 day KCl treatment	Homo K, 14 day KCl treatment
Wet	.42	.35	.37	.30
Air Dry	.55	.38	.37	.30
Glycol	.47	.40	.43	.34

Centrifuge oriented specimens (see Fig. C-1)

TABLE C-III: RATIO 14Å:10Å PEAK HEIGHTS

Sample No.	61A	62A	63A
Treatment	Homo Na, Expanded form.	Homo K, 24 hr. KCl treatment	Homo Na, 24 hr. KCl treatment
Wet	.57	.31	.59
Air dry	.43	.32	-
Glycol	.46	.34	.44

Centrifuge oriented specimens (see Fig. C-2)
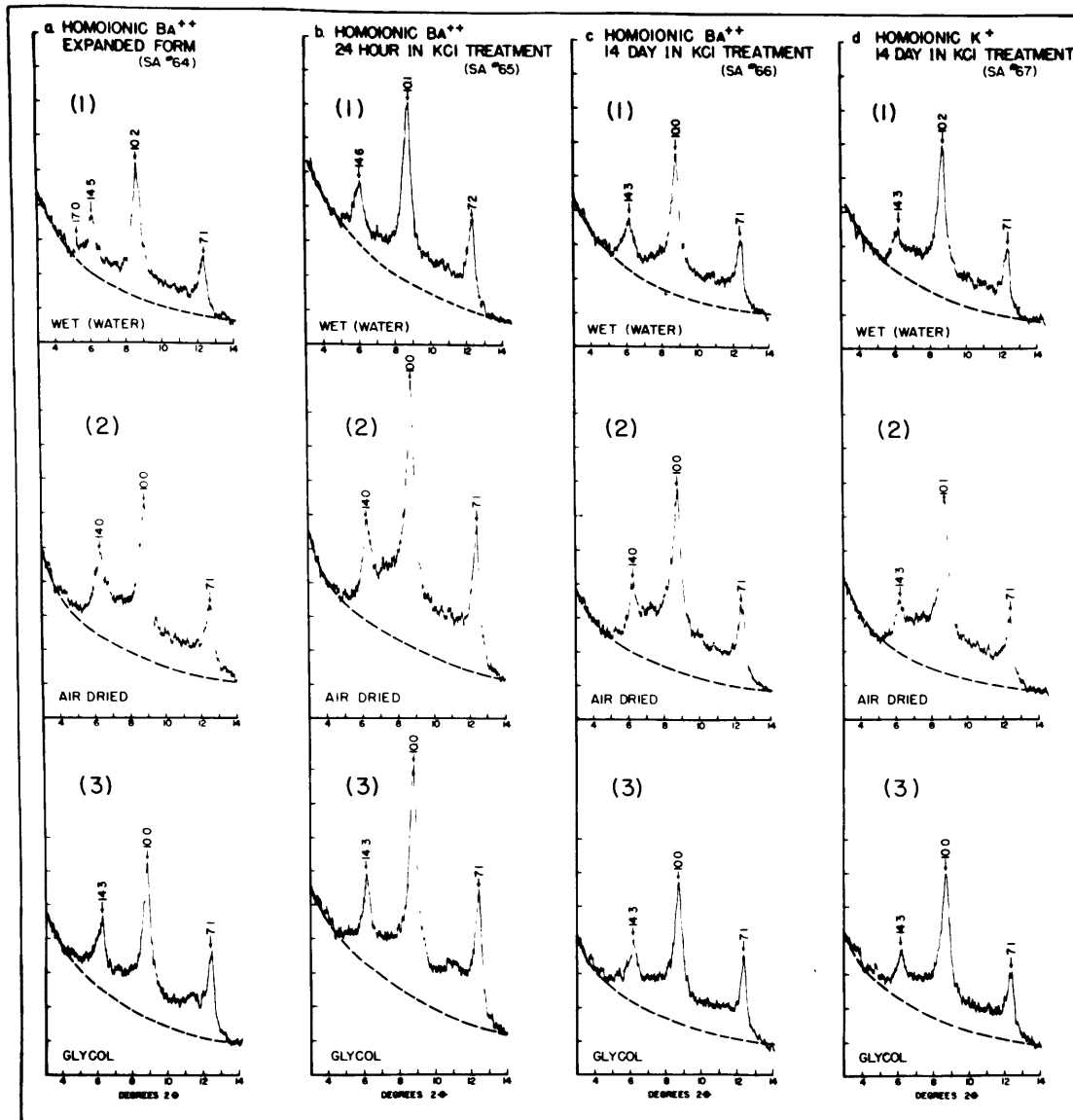
a. HOMOIONIC Ba++
EXPANDED FORM
(SA #64)

(1)

170
145
102
71

WET (WATER)

4 6 8 10 12 14

(2)

140
00
71

AIR DRIED

4 6 8 10 12 14

(3)

143
100
71

GLYCOL

4 6 8 10 12 14
DEGREES 2θ

b. HOMOIONIC Ba++
24 HOUR IN KCl TREATMENT
(SA #65)

(1)

101
146
72

WET (WATER)

4 6 8 10 12 14

(2)

001
140
71

AIR DRIED

4 6 8 10 12 14

(3)

001
143
71

GLYCOL

4 6 8 10 12 14
DEGREES 2θ

c. HOMOIONIC Ba++
14 DAY IN KCl TREATMENT
(SA #66)

(1)

100
143
71

WET (WATER)

4 6 8 10 12 14

(2)

001
140
71

AIR DRIED

4 6 8 10 12 14

(3)

001
143
71

GLYCOL

4 6 8 10 12 14
DEGREES 2θ

d. HOMOIONIC K+
14 DAY IN KCl TREATMENT
(SA #67)

(1)

102
143
71

WET (WATER)

4 6 8 10 12 14

(2)

101
143
71

AIR DRIED

4 6 8 10 12 14

(3)

100
143
71

GLYCOL

4 6 8 10 12 14
DEGREES 2θ

X-RAY DIFFRACTION TRACES

CENTRIFUGE ORIENTED SPECIMENS
M21, BATCH 3 USED FOR ENGINEERING TESTS

SOIL DESCRIPTION

EXCESS SALT WASHED OUT

EQUIVALENT GRAIN SIZE < 0 4 MICRONS

FINE FRACTION FROM THE "A" & "B" HORIZONS OF A
WEATHERED TILL CONSISTING OF ILLITE, VERMICULITE,
SWELLING CLAY, RANDOMLY INTERLAYERED MINERALS,
AND CHLORITE

LABORATORY SOIL M21

NOTE
THE d SPACINGS IN ANGSTROMS ARE
INDICATED ABOVE THE DIFFRACTION
PEAKS

INSTRUMENT DATA
COPPER RADIATION, 40 KV,
15 MA, SCALE FACTOR = 8,
TIME CONSTANT = 4
SCANNING RATE = 1°/MIN
PHILLIPS DIFFRACTOMETER

FIGURE C-1

213.

a HOMOIONIC Na⁺
EXPANDED FORM
(SA #61A)

(1)

WET (WATER)

DEGREES 2θ

(2)

AIR DRIED

(3)

GLYCOL

DEGREES 2θ

b HOMOIONIC K⁺
SEMI-COLLAPSED STATE
(SA #62A)

(1)

WET (WATER)

(2)

AIR DRIED

(3)

GLYCOL

DEGREES 2θ

c HOMOIONIC Na⁺
RE EXPANDED FORM
(SA #F3)

(1)

WET (WATER)

(3)

GLYCOL

DEGREES 2θ

X-RAY DIFFRACTION TRACES

CENTRIFUGE ORIENTED SPECIMENS
M21, BATCH 3 USED FOR ENGINEERING TESTS

SOIL DESCRIPTION

EXCESS SALT WASHED OUT

EQUIVALENT GRAIN SIZE < 0.4 MICRONS

FINE FRACTION FROM THE "A" & "B" HORIZONS OF A
WEATHERED TILL CONSISTING OF ILLITE, VERMICULITE,
SWELLING CLAY, RANDOMLY INTERLAYERED MINERALS,
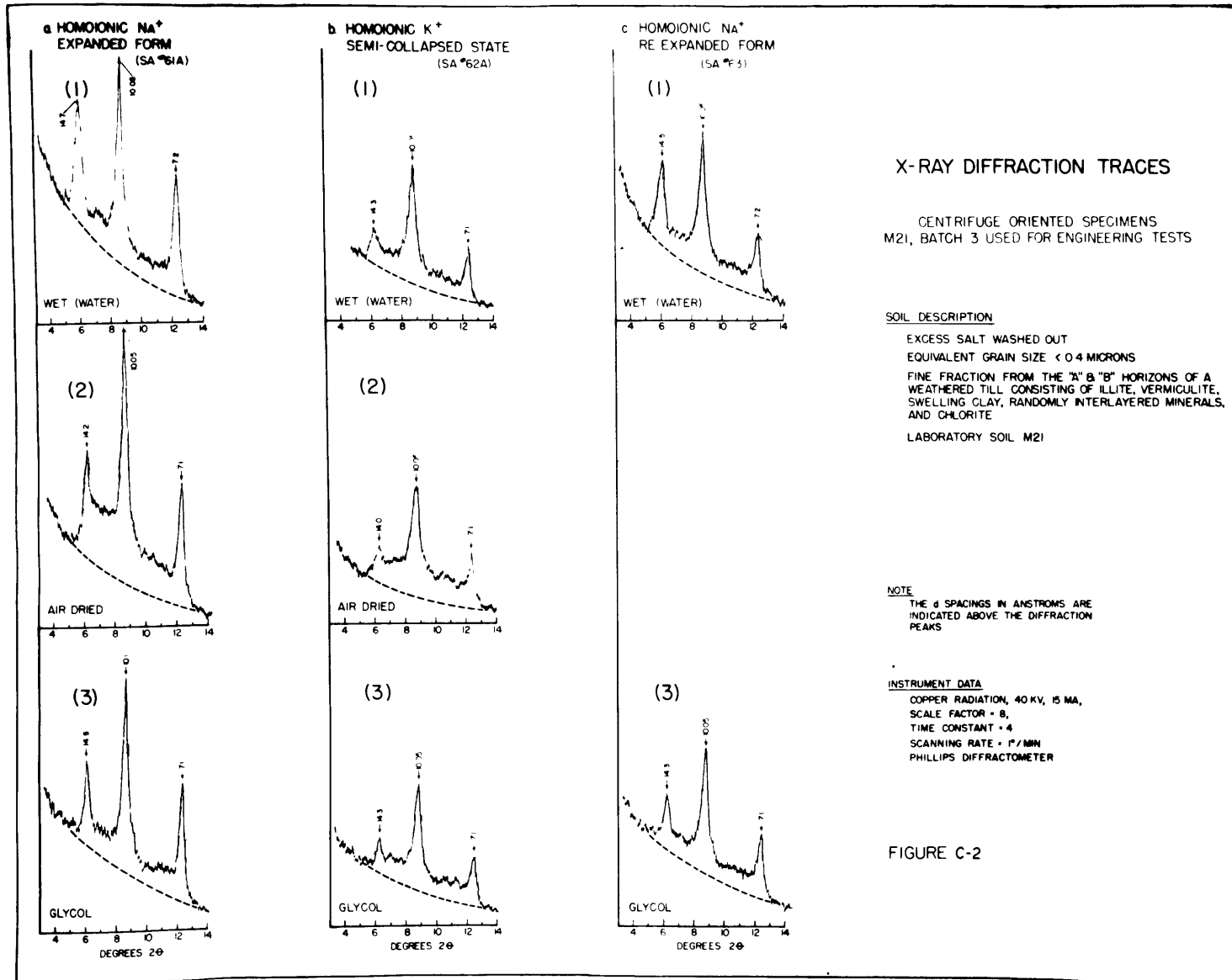AND CHLORITE

LABORATORY SOIL M21

NOTE
THE d SPACINGS IN ANSTROMS ARE
INDICATED ABOVE THE DIFFRACTION
PEAKS

INSTRUMENT DATA
COPPER RADIATION, 40 KV, 15 MA,
SCALE FACTOR · 8,
TIME CONSTANT · 4
SCANNING RATE · 1°/MIN
PHILLIPS DIFFRACTOMETER

FIGURE C-2

DIFFERENTIAL THERMAL ANALYSES

M2I, BATCH 3, USED FOR ENGINEERING TESTS

SOIL DESCRIPTION
EQUIVALENT GRAIN SIZE < 0.4 MICRONS,
FINE FRACTION OF WEATHERED TILL CONSISTING OF
ILLITE, VERMICULITE, AND SWELLING CLAY AND CHLORITE
SAMPLES IN EQUILIBRIUM WITH RH ≈ 50% BEFORE HEATING
LABORATORY SOIL M2I
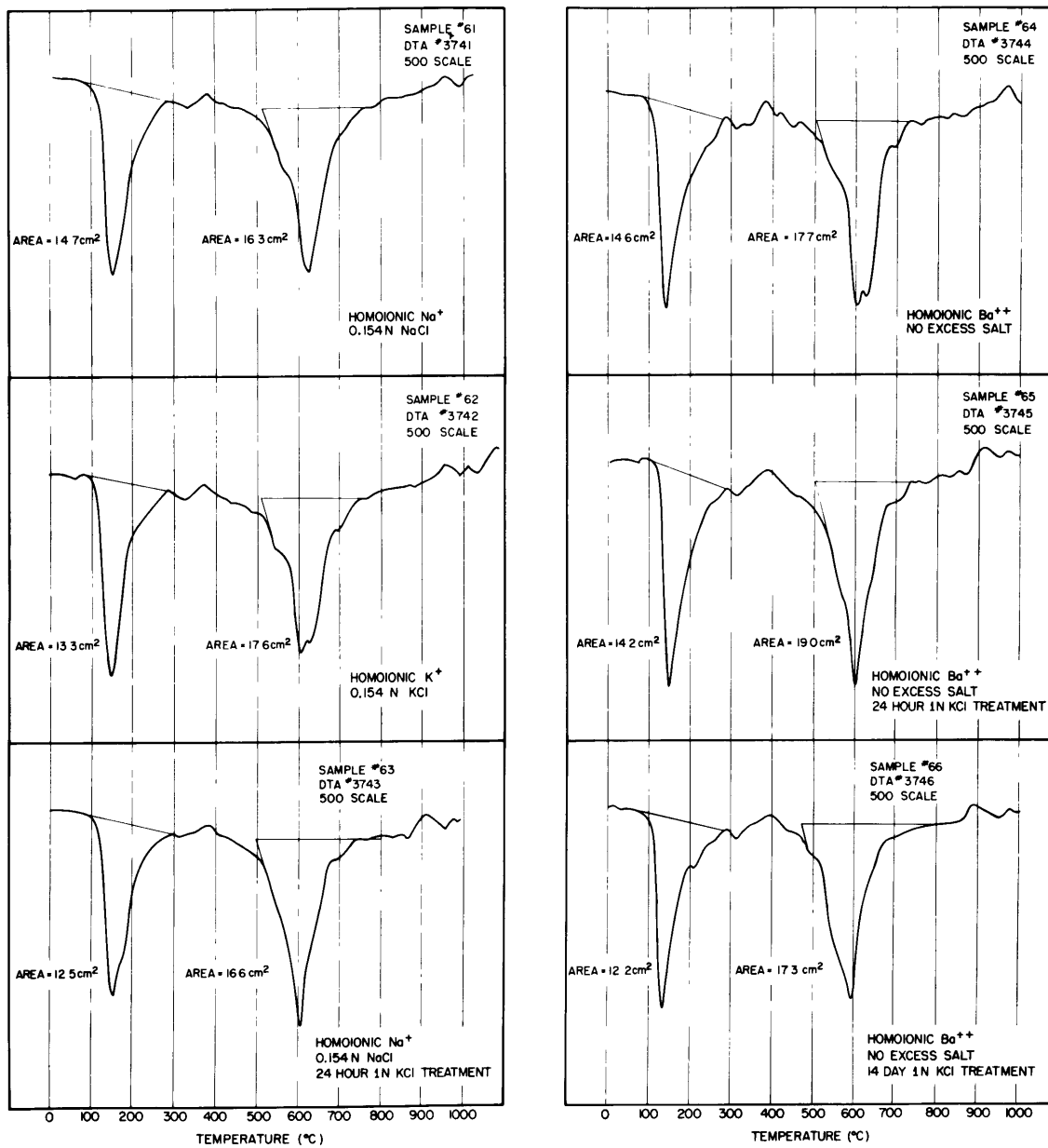

FIGURE C-3

APPENDIX D

DETAILS OF MINERALOGY - M21, BATCH 4

This batch of clay was prepared from a bulk sample of till taken from the upper six inches ("A" horizon) of the soil profile previously described. It was hoped that this material would be very deficient in potassium and quite active. Using a supercentrifuge, the less than 0.17 micron fraction was obtained. (For procedure, see Appendix A.)

I. CATION EXCHANGE CAPACITY, TOTAL POTASSIUM, GLYCOL RETENTION

Table D-I contains a summary of the tests performed. Sample 106 Ba represents the clay fraction used for engineering testing. A cation exchange capacity value of only 28 m.eq./100 g. was obtained on Batch 4 compared with a value of 35 for Batch 3, despite a lower potassium content in Batch 4. This decrease in cation exchange capacity is due to an increase in interlayer aluminum or a higher degree of chloritization in the upper part of the soil profile. The higher glycol retention of Batch 4 (71 mg./g.) is probably due to an increase in surface area as a result of fractionation.

The soil used to prepare Batch 4 was fractionated into a variety of grain sizes to see if the degree of potassium release varied from size to size. The table shows that the cation exchange capacity increases with decreasing grain size from 5 to 32 m.eq./100 g. The total potassium increases as the amount of clay increases in Samples 103 to 105 (20μ to $.17\mu$). For sizes smaller than 0.17 microns the K content decreases slightly. The glycol retentions increase; like the cation exchange capacity values from 9 to 85 mg./g.

A 24 hour KCℓ treatment on Batch 4 (Sample 108) produced no change in either cation exchange or total K. The 14 day KCℓ treatment (Sample 110) actually caused a small decrease in K and an increase in cation exchange capacity from 28 to 36 m.eq./100 g. The increase in cation exchange capacity is attributed to the slow removal of adsorbed aluminum by the potassium which itself was exchangeable by barium.

II. X-RAY ANALYSES

X-ray diffraction traces of oriented specimens from several of the size fractions are shown in Fig. I-9. Samples 104 and 105 show very pronounced 14, 10 and 7Å peaks with very little background between the peaks in the air dry state. With decreasing grain size and potassium content (Samples 106 and 107) the clay becomes randomly interlayered with pronounced swelling properties in water and glycol. The peaks intensify upon air drying with considerable background between 14 and 10 Å peaks. It appears as though the removal of potassium by leaching, accompanied by an undetermined amount of aluminum fixation, has produced a randomly interlayered swelling clay in the fine fractions and vermiculite or chlorite in the coarser clay. The strength of the 7 Å peak compared to the 14 Å peaks suggests that abundant iron chlorite is present.

KCℓ treatments were performed only on Sample 106 which is the engineering test clay. A series of x-ray analyses were run on the treated clay to see if any collapse occurred. All KCℓ treated clays which were subsequently washed showed no collapse. The clays homoionic in potassium showed a little collapse but much less than Batch 3.

III. DIFFERENTIAL THERMAL ANALYSES

Thermograms obtained on the various size fractions and on the KCℓ treated samples are shown in Fig. D-I. Both the water and hydroxyl peaks show a fairly regular increase in size with decreasing grain size. The thermograms of Samples 105 and 106 are quite similar to M21, Batch 3.

Samples 108 and 110 were prepared by treating Sample 106 (Batch 4, test clay) with 1 N KCℓ for 24 hours and 24 days respectively. Both were then made homoionic in barium. The KCℓ treatment appears to have produced a very pronounced hump in the curve around $800^{\circ}C$ followed by a sharp dip. This type of curve is somewhat characteristic of some chlorites, but why it should occur only after KCℓ treatment is not known.

The relationship of this batch of clay to the soil profile is discussed in Part One.

TABLE D-I: M21, BATCH 4, MINERALOGICAL DATA (whole soil)

Sample No.	Sample Description	* C.E.C. (m.eq./100g.)	* K⁺ (%)	**Glycol Retention (mg./g.)	D.T.A. No.	D.T.A. Ion	D.T.A. R.H.%	X-ray Diffraction Ion	X-ray Diffraction Type
100	Untreated (-100 mesh)	-	-	-	3760	H &Al	50	-	-
102$_{Ba}$	Homo Ba, (50-20μ)	5	-	4	-	-	-	Ba	Wet Air dry
103$_{Ba}$	Homo Ba, (20-5μ)	5	1.9	9	-	-	-	Ba	"
104$_{Ba}$	Homo Ba, (5-2μ)	14	2.9	22	3761	Ba	50	Ba	Wet Air dry Glycol
105$_{Ba}$	Homo Ba, (2-0.17μ)	20	3.1	51	-	-	-	Ba	"
106$_{Ba}$	Batch 4, Test clay, Homo Ba (<0.17μ)	28	2.7	71	3764	Ba	50	Ba	"
107$_{Ba}$	Homo Ba (<0.11μ)	32	2.5	85	-	-	-	Ba	"
108	Sa.#106, 24 hr. KCl treatment, Homo Ba.	28	2.8	69	3765	Ba	-	Ba	"
109	Sa.#106, 24 hr. KCl treated, Homo K.	-	-	-	-	-	-	K	"
110	Sa.#106, 14 day KCl treated, Homo Ba.	36	2.6	73	3766	Ba	50	Ba	"
111	Sa.#106, 14 day KCl treated, Homo K.	-	-	-	-	-	-	K	"

* Obtained by x-ray spectrographic methods.

** Glycol retentions run on Ba clays unless otherwise indicated.

DIFFERENTIAL THERMAL ANALYSES

VARIOUS SIZE FRACTIONS OF WEATHERED TILL
USED TO PREPARE M21, BATCH 4
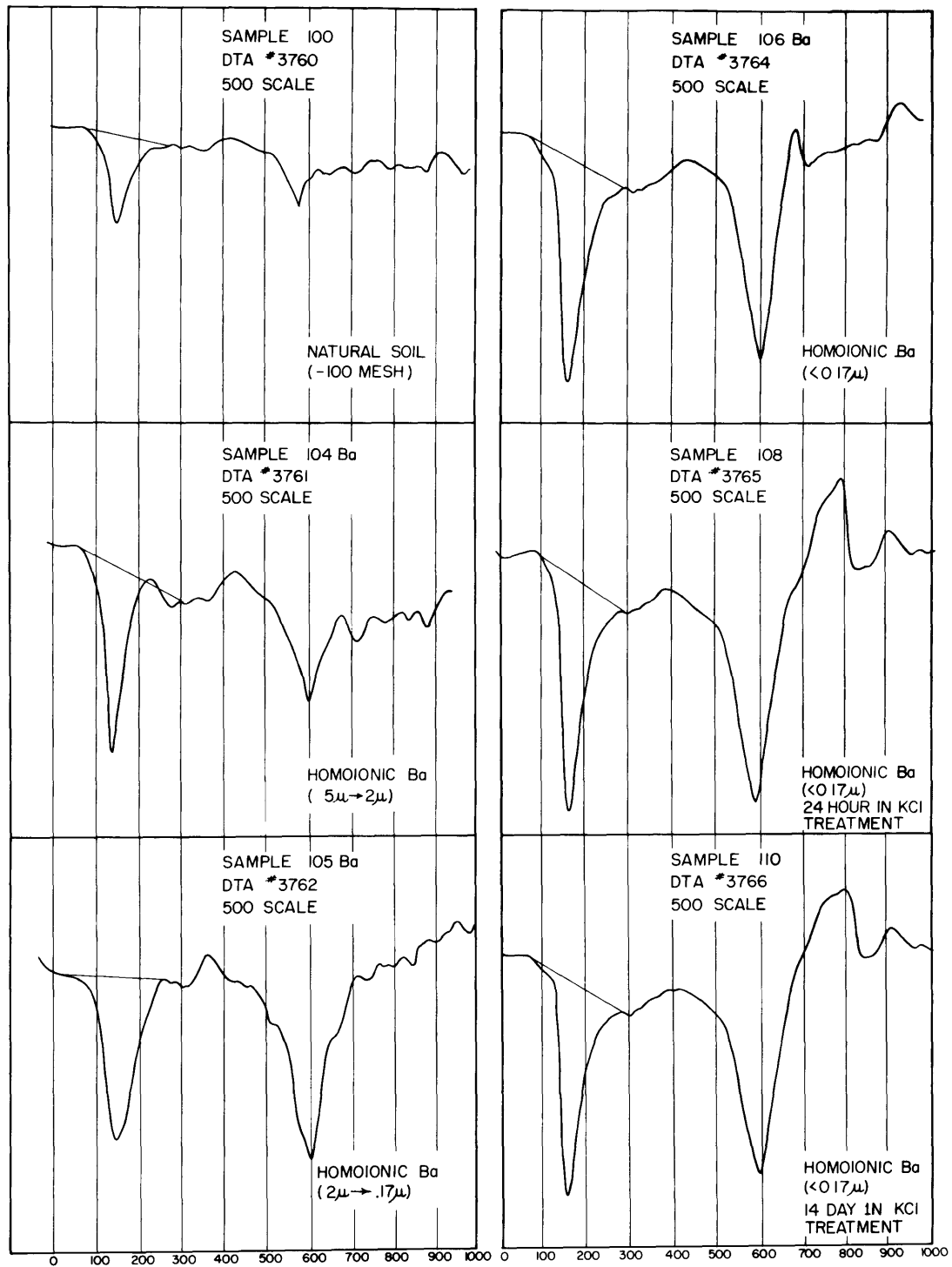
(SAMPLES IN EQUILIBRIUM WITH RH ≈ 50% BEFORE HEATING)

SAMPLE 100
DTA #3760
500 SCALE

NATURAL SOIL
(-100 MESH)

SAMPLE 106 Ba
DTA #3764
500 SCALE

HOMOIONIC Ba
(<0 17μ)

SAMPLE 104 Ba
DTA #3761
500 SCALE

HOMOIONIC Ba
(5μ→2μ)

SAMPLE 108
DTA #3765
500 SCALE

HOMOIONIC Ba
(<0 17μ)
24 HOUR IN KCl
TREATMENT

SAMPLE 105 Ba
DTA #3762
500 SCALE

HOMOIONIC Ba
(2μ→.17μ)

SAMPLE 110
DTA #3766
500 SCALE

HOMOIONIC Ba
(<0 17μ)
14 DAY 1N KCl
TREATMENT

0 100 200 300 400 500 600 700 800 900 1000 0 100 200 300 400 500 600 700 800 900 1000

FIGURE D-1

APPENDIX E

RESULTS OF PILOT RUNS ON CLAY

In Appendix C, the preliminary tests on M21, Batches 2 and 3 were briefly mentioned. These pilot runs were carried out in an effort to prepare a very active clay with pronounced K fixation properties. The pilot run on Batch 3 indicated that this could be done quite satisfactorily by fractionation. However, when the large batch of clay was prepared for engineering testing, it bore little resemblance to the pilot run clay and would not fix potassium. It is believed that differences in the method and time of preparation and some errors in the pilot run are responsible for the differences in properties.

I. PRELIMINARY TESTS ON M21, BATCH 2

A small sample of M21, Batch 2 was fractionated to obtain the less than 1 micron size. The clay was dispersed and separated by washing and centrifuging 6 or 7 times with demineralized water containing a little NaOH. X-ray, differential thermal analyses, cation exchange capacities, and glycol retentions were run on the two fractions.

1. 90% smaller than 2 microns

2. Smaller than 1 micron

The results are tabulated in Table E-I and summarized as follows:

1. The cation exchange capacity rose from 18 to 27 meq./100 g. The barium $K\alpha$ peaks are shown in Fig. E-I.

2. The size of both the water and hydroxyl peaks in the differential thermal curves were

markedly larger for the finer fraction. The

differential thermal curves are shown in Fig. E-2.

3. The glycol retention increased from 35 to 58

mg./g. Much of this increase is due to an increase

in swelling clay content.

4. The x-ray films on oriented glycerol solvated

samples showed a marked change. The "d" values

were not accurately measured, but the washing

and fractionation produced a very expandable

clay having a basal spacing around $18\overset{o}{A}$. The

coarser clay fraction showed a maximum basal

spacing of $14\overset{o}{A}$.

It was concluded from this work that the swelling clay

content, and hence the cation exchange capacity, could be greatly

increased by fractionation. It was, therefore, decided to obtain a

new batch of clay and run a more thorough investigation on the

various size fractions. The mineralogical work on this new batch

(Batch 3) is discussed next.

II. PILOT RUN ON M21, BATCH 3

This pilot run was made on the same soil that was later

fractionated and used for engineering testing. The fines were first

separated from the till by sieving and then washing and centrifuging.

The method was a long manual one in which the shaking was done by

hand, and the material centrifuged in an International centrifuge

having a maximum allowable speed of 2000 r.p.m. Three equivalent

size fractions were obtained:

1. Smaller than 1 micron

2. Smaller than 0.5 microns.

3. Smaller than 0.35 microns.

X-ray, differential thermal analyses, glycol retentions, and cation exchange capacities were obtained on each size fraction after they were made homoionic in barium. In addition, the <0.35 micron fraction was treated with 1 Normal KCℓ to collapse it. The KCℓ treatment involved washing the clay 5 times in 1 Normal KCℓ; the clay sitting overnight in the 4th wash. The clay was then made homionic in barium without allowing the clay to dry out.

The initial results of the mineralogical work are given in Table E-II. This work was later checked in some detail when some of it was found to be in error.

A. Cation Exchange Capacity and Total Potassium

In Table E-II, the K content appears to decrease with decreasing grain size. KCℓ treatment of Sample 48 increased the K content to 2.83% from 2.34%. A pronounced decrease in cation exchange capacity accompanied this increase in potassium. It is believed, however, that the value of 110 m.eq./100 g. for Sample 48 is far too high.

B. Glycol Retention

The glycol retentions change very little from one size to another with the KCℓ treatment. This might be taken as an indication of no permanent layer lattice contraction as a result of potassium fixation.

C. Differential Thermal Analyses

Differential thermal curves are shown in Fig. E-3 for the three size fractions. All clays were homoionic in barium and in equilibrium with an atmosphere at 50 per cent relative humidity. It can be seen that the fine clay has a larger water peak than the two coarser fractions. Using a persistent plateau at approximately $770^{o}C$ to measure peak height, we can see that the coarse clay has the largest hydroxyl peak. The temperature for all peaks is about $620^{o}C.$

The thermograms initially run on KCℓ treated clay gave very misleading results. A shift of the hydroxyl peak from $620^{o}C$ to $710^{o}C$ as a result of KCℓ treatment was traced to instrument error. When the machine was repaired, the peak shifted back to its proper position at $620^{o}C.$ This error, like the rest, was not discovered until a large quantity of Batch 3 had been prepared for engineering testing.

D. X-Ray Analyses

When Batch 3 did not behave as expected, a series of x-ray analyses were run on the pilot run clay to find out why. Diffraction traces are shown in Fig. E-4 for the three size fractions of the clay. When wet, all show quite weak peaks which sharpen up greatly upon air drying. This intensification appears to be related to the contraction of an interlayered swelling clay. A great deal of background exists between the 14, 10 and $7\overset{o}{A}$ peaks just as in Batch 3. Glycol solvation partially re-expands the clay resulting in a pronounced shoulder on the high angle side of the $14\overset{o}{A}$ peaks.

X-ray diffraction traces of KCl treated clays are not presented here as they were quite similar to those of M21, Batch 3 discussed in Part One. One important difference was that the vermiculite nearly completely collapsed in the clays homoionic in potassium. As before, however, much of this potassium did not seem to fix because the 14Å clay was reconstituted by washing with either NaCl or BaCl_2 solutions.

Table E-III contains the 14Å:10Å peak height ratios. If we compare Sample 53 with Sample 66 in Table C-II, we see that the 14Å:10Å ratios are much lower in the former indicating greater collapse of the pilot run clay. The initial barium clays have about the same ratios as shown by a comparison of Samples 48 and 64. The greater collapse of the pilot run clay is probably due to the removal of interlayer aluminum by the long term salt treatment before fractionation.

TABLE E-I: PILOT RUN, M21, BATCH 2,   MINERALOGICAL DATA

Sample No.	Equiv. Size (μ)	Sample Description	* C.E.C. (m.eq./100g.)	*K (%)	**Glycol Retention (mg./g.)	D.T.A. No.	D.T.A. Ion	D.T.A. R.H.%	X-ray film No.	X-ray film Ion	X-ray film Type
10	90% <2μ	Untreated, as used in engineering tests.	18	-	35	3727	Ca	50	1508 1520	Ca Na	GPO GPO
33	<1μ	As above but fract-ionated.	27	-	58	3729	Ca	50	1609 1632	Ca Na	GPO GPO

*   Obtained by x-ray spectrographic methods.

** Glycol retentions run on Ba clays unless otherwise indicated.

TABLE E-II: PILOT RUN, M21,   BATCH 3,   MINERALOGICAL DATA

Sample No.	Equiv. Size (μ)	Sample Description	* C.E.C. (m.eq./100g.)	* K (%)	**Glycol Retention (mg./g.)	D.T.A. No.	Ion	R.H.%	X-ray Diffraction Ion	Type
45	<1	Homo Ba, Coarse fraction.	28	3.06	57	3731	Ba	50	Ba	Wet Air dry Glycol
47	<0.5	Homo Ba, Intermediate fraction.	43	3.00	61	3730	Ba	50	Ba	"
48	<0.35	Homo Ba, Fine fraction.	110?	2.34	59	3732	Ba	50	Ba	"
51	<0.35	Homo Ba, #48 with 24 hr. KCl treatment.	55	2.83	64	3734	Ba	50	Ba	"
53	"	Homo K, #48 with 14 day KCl treatment.	-	-	-	-	-	-	K	"
54	"	Homo K, #48 with 20 day KCl treatment.	-	-	-	-	-	-	K	"
55	"	Homo Na, #48 with 27 day KCl treatment.	-	-	-	-	-	-	Na	"

*   Obtained by x-ray spectrographic methods.
** Glycol retentions run on Ba clays unless otherwise indicated.

TABLE E-III: RATIO 14$\overset{\circ}{A}$:10$\overset{\circ}{A}$ PEAK HEIGHTS   (Pilot run, Batch 3)

Sample No.	45	47	48	51	53	54	55
Treatment	Homo Ba, Expanded ($<$1μ)	Homo Ba, Expanded ($<$0.5μ)	Homo Ba, Expanded ($<$0.35μ)	Homo Ba, 24 hr. KCl ($<$0.35μ)	Homo K, 14 day KCl ($<$0.35μ)	Homo K, 20 day KCl ($<$0.35μ)	Homo Na, 27 day KCl ($<$0.35μ)
Wet	.34	.53	.40	.45	.22	.26	.50
Air dry	.43	.46	.36	.43	.17	.19	.32
Glycol	.47	.50	.43	.45	.17	.28	.38

Centrifuge oriented specimens (see Fig. E-4)

BARIUM Kα PEAKS

M21, BATCH 2

CEC DETERMINATIONS, TWO SIZE FRACTIONS

amplitude = 1.31 inches

CEC = 18 meg/100 gm

11.5° 2θ

Equivalent Size: 90% <2μ

amplitude = 2.00 inches

CEC = 27 meg/100 gm

11.5° 2θ

Equivalent Size: 100% <1μ
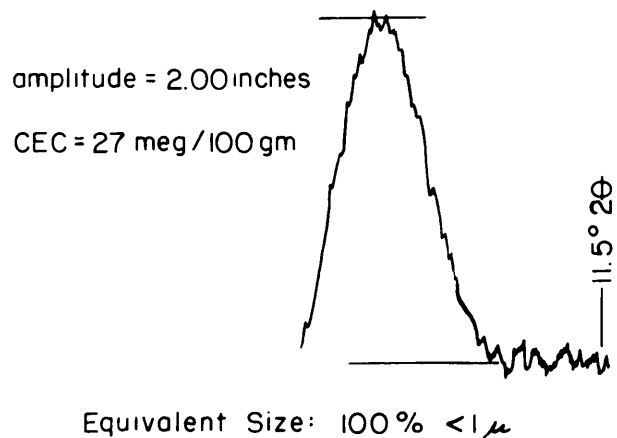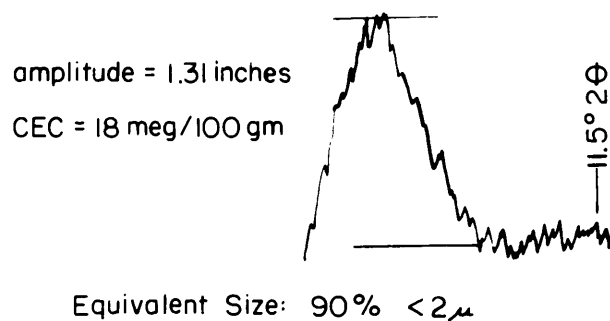
Note:
Notice the increase in cation
exchange capacity as a result
of fractionation

FIGURE E-1

DIFFERENTIAL THERMAL ANALYSES
M21, BATCH 2
SHOWING EFFECT OF FRACTIONATION

a = 7.8 cm
A = 10.0 cm^2

a = 6.2 cm
A = 13.0 cm^2

M21, Batch 2
90% <2μ
50% RH
CEC = 18 meg/100 gm

a = 10.0 cm
A = 12.5 cm^2

a = 8.1 cm
A = 17.8 cm^2

As above
Fractionated
<1μ
50% R.H.
CEC = 27 meg/100 gm

TEMPERATURE (°C)

FIGURE E-2

231.
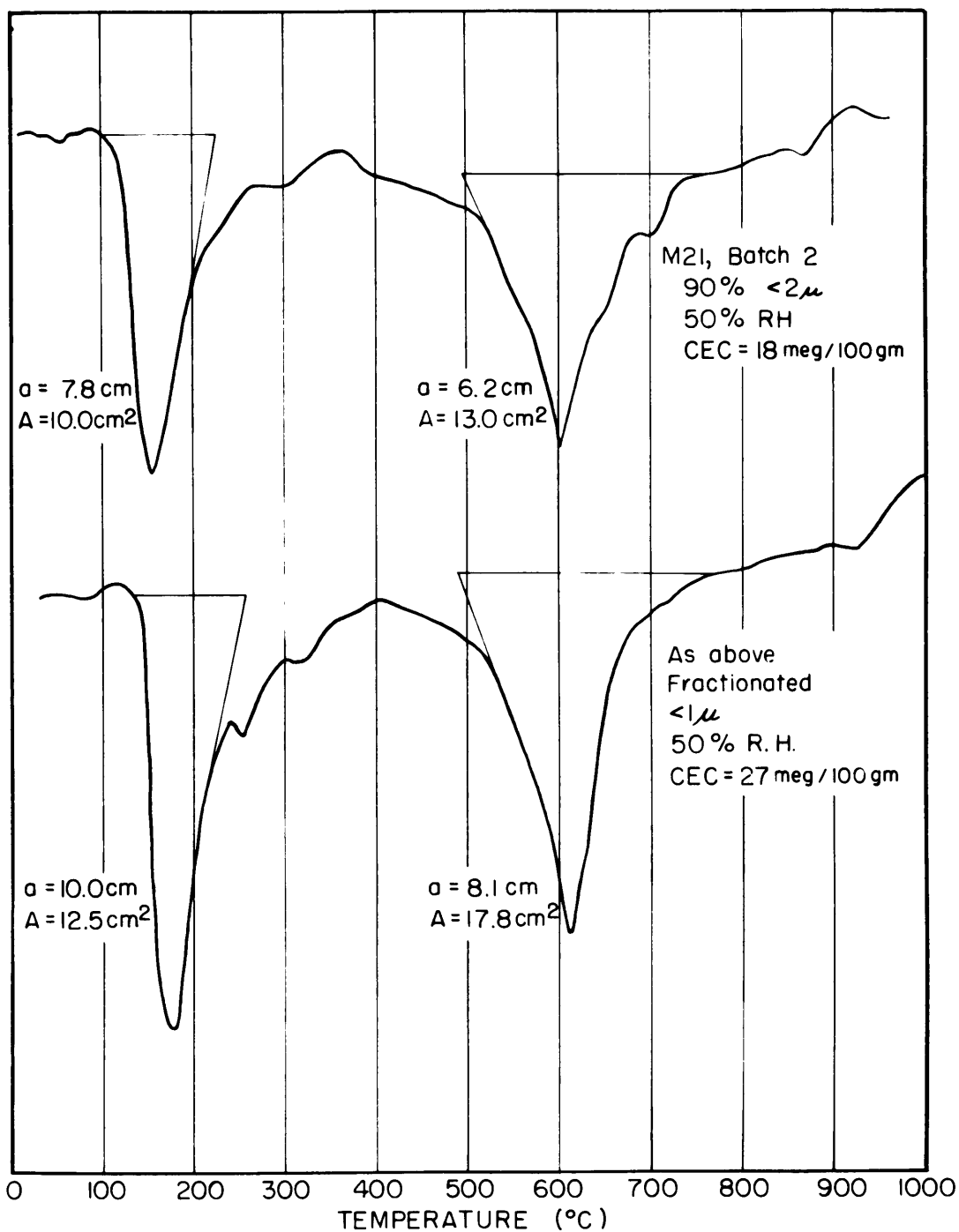
DIFFERENTIAL THERMAL ANALYSES
M21, BATCH 3
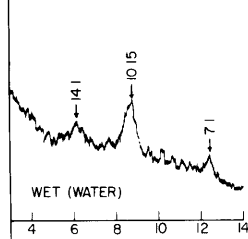### THREE CLAY SIZE FRACTIONS
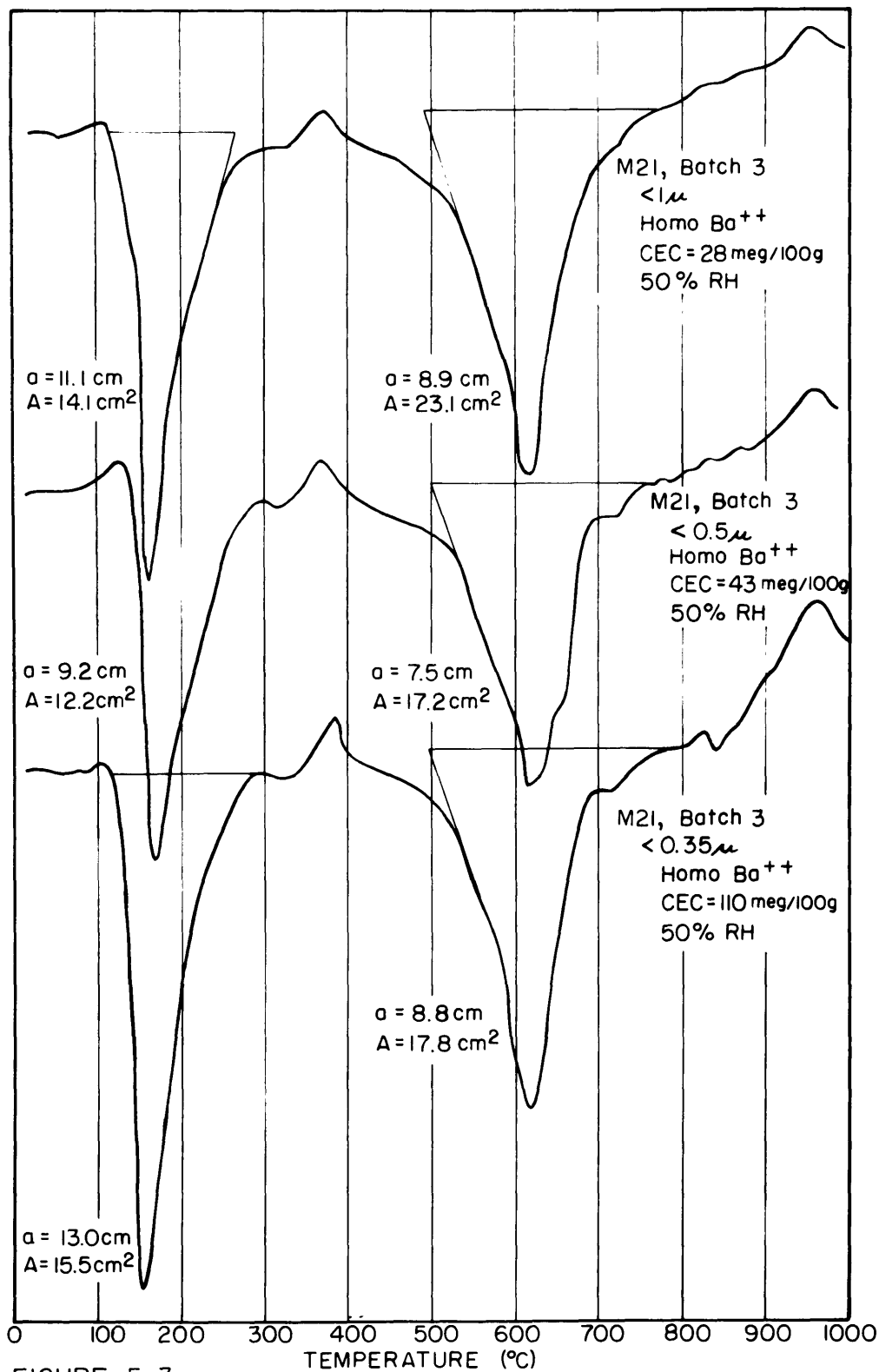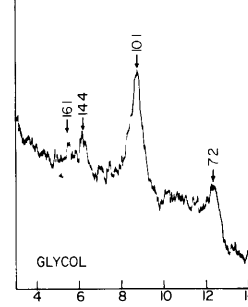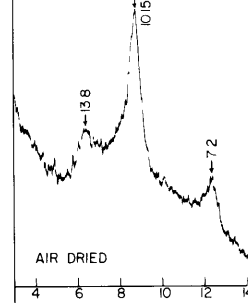

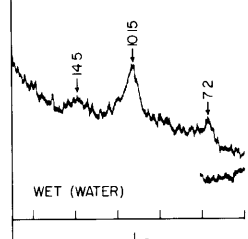FIGURE E-3

a HOMOIONIC Ba
   < I MICRON
      (SA #45)
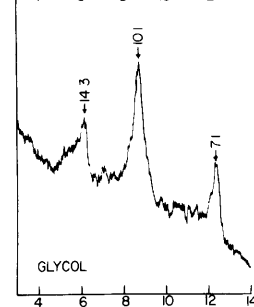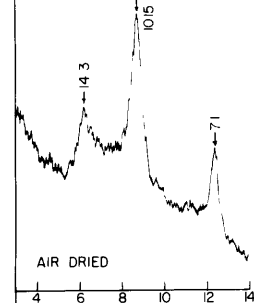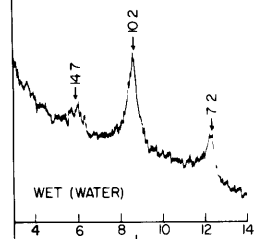
b HOMOIONIC Ba
   < 0 5 MICRONS
      (SA #47)
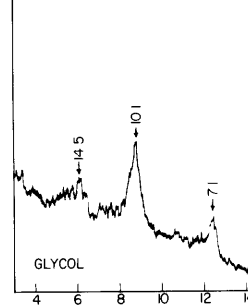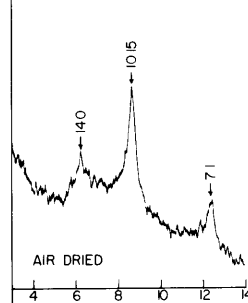
c HOMOIONIC Ba
   < 0 35 MICRONS
      (SA #48)

X-RAY DIFFRACTION TRACES

CENTRIFUGE ORIENTED SPECIMENS

PILOT RUN, M2I, BATCH 3

SOIL DESCRIPTION

EXCESS SALT WASHED OUT

ALL SAMPLES HOMOIONIC Ba

THREE CLAY SIZE FRACTIONS FROM "A" & "B"
HORIZONS OF WEATHERED TILL

NOTE

THE d VALUES IN ANGSTROMS ARE INDICATED
ABOVE THE DIFFRACTION PEAKS

INSTRUMENT DATA

PHILLIPS DIFFRACTOMETER
COPPER RADIATION
40 KV, 15 MA
SCALE FACTOR = 8
TIME CONSTANT = 4
SCANNING RATE < I° 2θ/ MIN

FIGURE E-4

APPENDIX F

COMPOSITE PLOTS OF DATA

Water and glycol consist of polar molecules which adsorb and orient around charged cations and clay particles. The retention of glycol should be directly related to the retention of water. A measure of the water retention of a clay is the size of the water peak on thermograms of the clay. For this reason, nearly all of the D. T. A. samples were brought into equilibrium with an environment at 50 per cent relative humidity.

The amount of glycol and water adsorbed are, in part, a function of the charge deficiency of the clay minerals and hence of the exchange capacity. In this Appendix, composite plots are presented showing the relationships between the cation exchange capacity, glycol retention and the size of the water peaks for all of the samples tested. The data are tabulated in Table F-1.

In Fig. F-1, the water peak area is plotted against glycol retention. Although there is some scatter, there is a well established zone of points trending along a straight line.

Glycol retention is plotted against the cation exchange capacity in Fig. F-2. Once again we get a well defined trend with increasing scatter at the higher values.

Plots of water peak height and water peak area versus cation exchange capacity are shown in Fig. F-3 and F-4, respectively. Although both figures show a definite trend, it is apparent that the size of the water peak is rather insensitive

to large changes in exchange capacity. The most useful situation
would be for the water peak to be very sensitive to small changes
in exchange capacity. Some of the scatter may be caused by the
adsorbed aluminum. This aluminum is known to be partially hydrated
by water which comes off gradually from 100°C to 350°C. This affects
the shape of the water peaks and probably their size also.

The tops of the water peaks were established by drawing
straight lines from the 300°point on the thermograms to the base-
line on the left side of the water peak. According to Martin
(unpublished data) this gives the best correlation with the other
soil properties.

TABLE F-I: RELATION OF WATER PEAK AREAS AND HEIGHTS TO GLYCOL
RETENTION AND CATION EXCHANGE CAPACITY.
(M21, Batches 2, 3, and 4)

Soil Description	D.T.A. No.	Sample No.	Area (cm^2)	Height (cm)	C.E.C. m.eq./100g.)	Glycol Retention (mg./g.)
M21, Batch 2:						
Consol. 10, <2μ	3723Na	38	**7.8**	7.8	19	35
" 11, "	3724K	39	10.0	9.0	16	34
" 17, "	3725Na	40	7.7	6.9	15	34
" 18, "	3726K	41	8.7	6.9	13	33
Untreated, "	3727Ca	10	11.6	7.6	18	28
" , <1μ	3729Ca	33	13.8	9.9	27	58
M21, Batch 3:						
<1μ	3731Ba	45	14.8	11.3	28	57
<0.5μ	3730Ba	47	13.2	9.8	43	61
<0.35μ	3732Ba	48	16.2	13.3	110?	59
<0.35μ	3734Ba	51	14.3	9.5	55?	64
Test clay, <.4μ	3741Na	61	14.7	9.5	-	59Na
" "	3742K	62	13.3	10.0	-	43K
" ♥	3743Na	63	12.5	9.0	-	58Na
" "	3744Ba	64	14.6	10.6	35	64
" "	3745Ba	65	14.2	11.2	27	61
" "	3746Ba	66	12.2	9.8	37	62
M21, Batch 4:						
5-2μ	3761Ba	104Ba	10.3	9.5	14	22
2-0.17μ	3762Ba	105Ba	14.5	11.3	20	51
<0.17μ	3764Ba	106Ba	16.5	8.2	28	71
<0.17μ	3765Ba	108	16.0	11.9	28	69
<0.17μ	3766Ba	110	13.7	10.9	36	73

Glycol retentions run on Ba clay unless otherwise indicated.
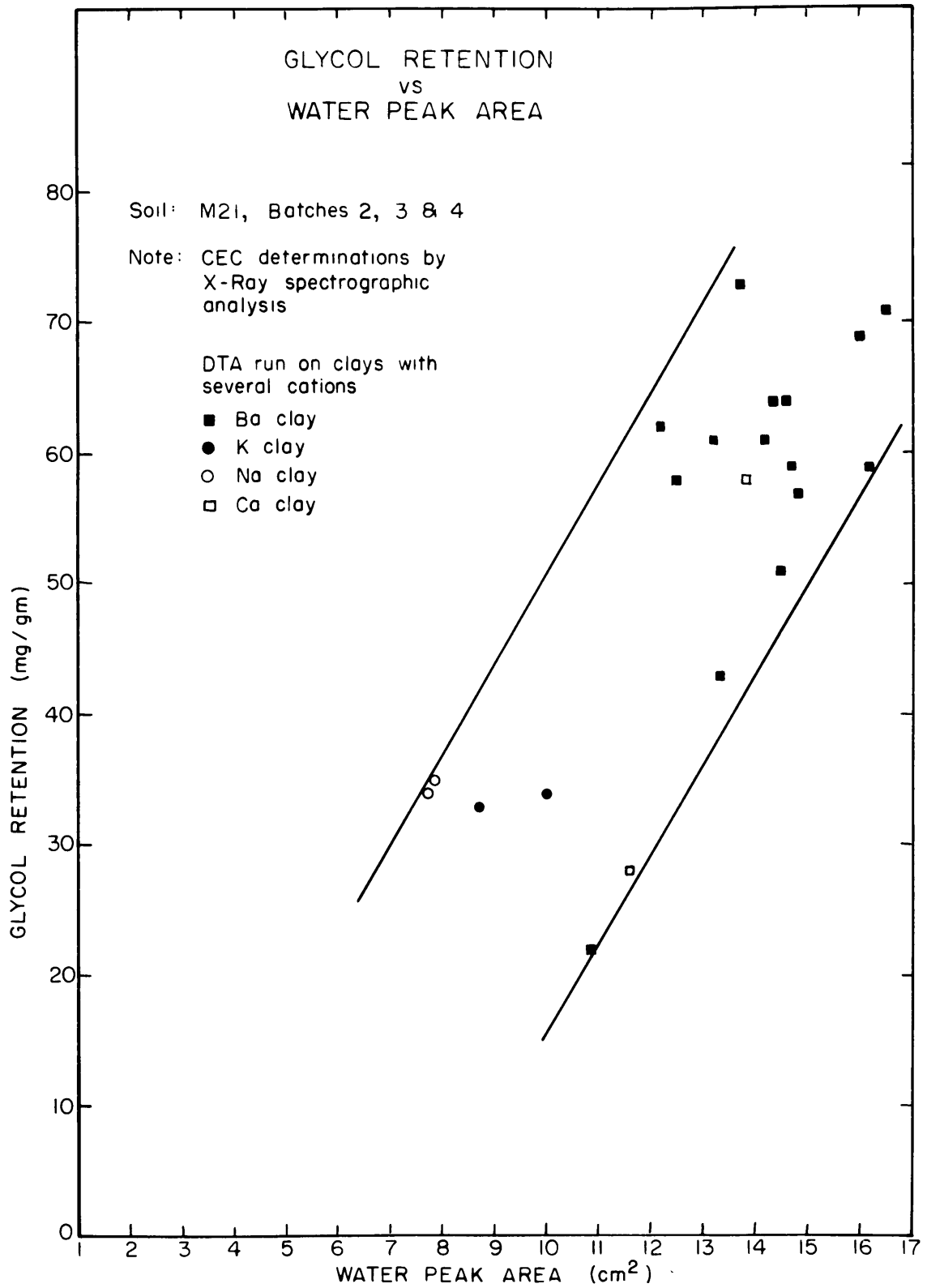
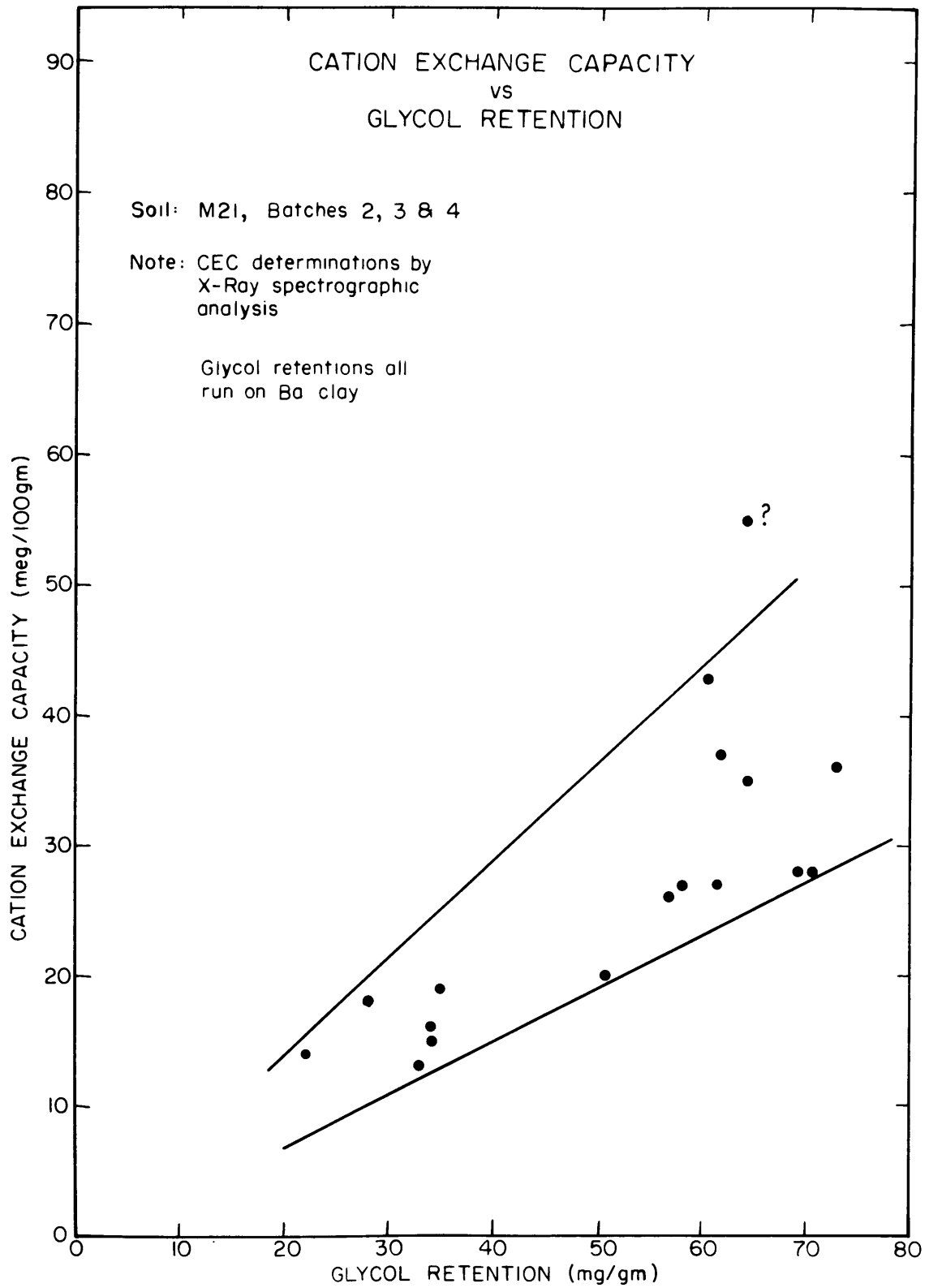D.T.A. numbers also show saturation cation.
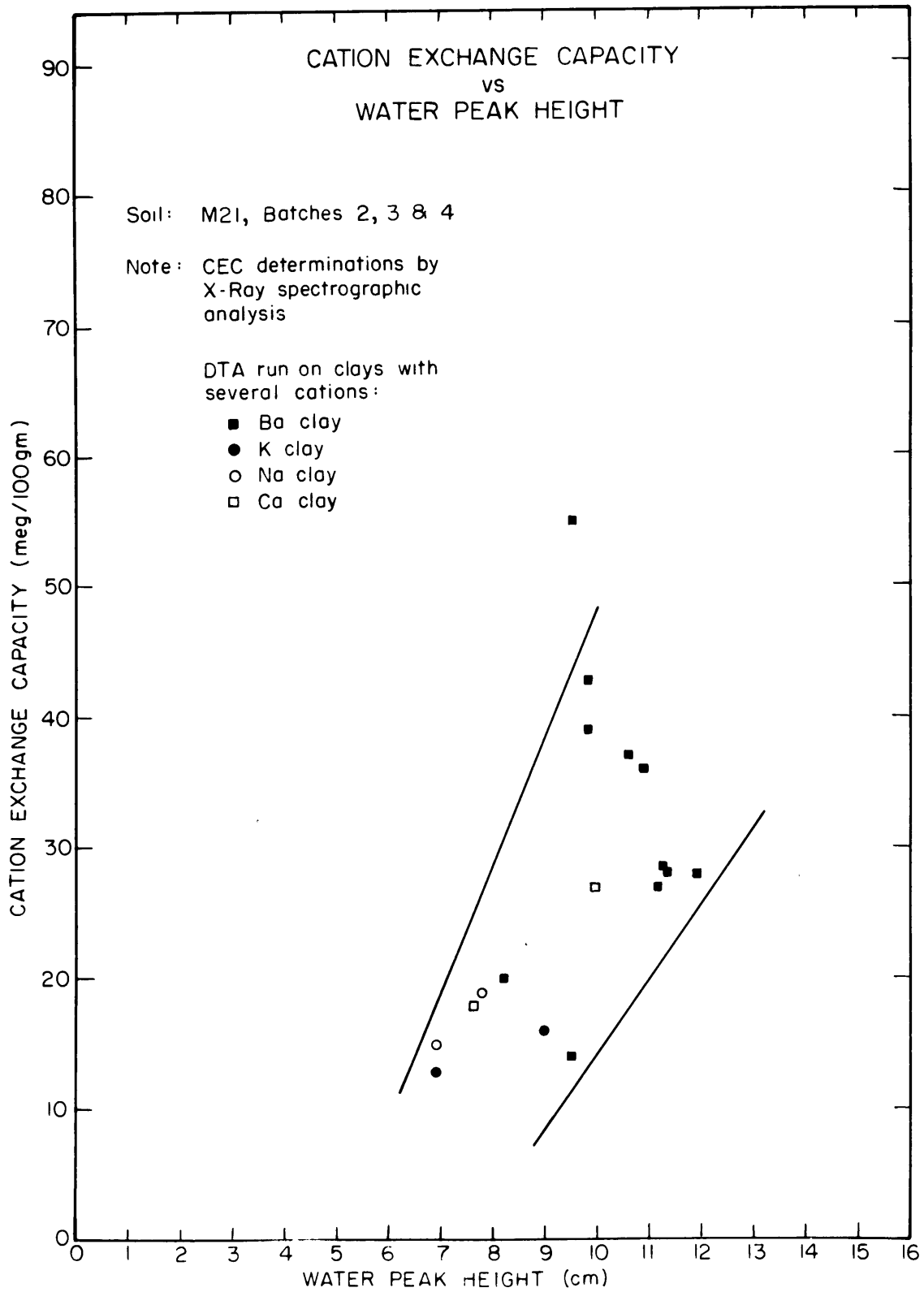
FIGURE F-1

FIGURE F-2

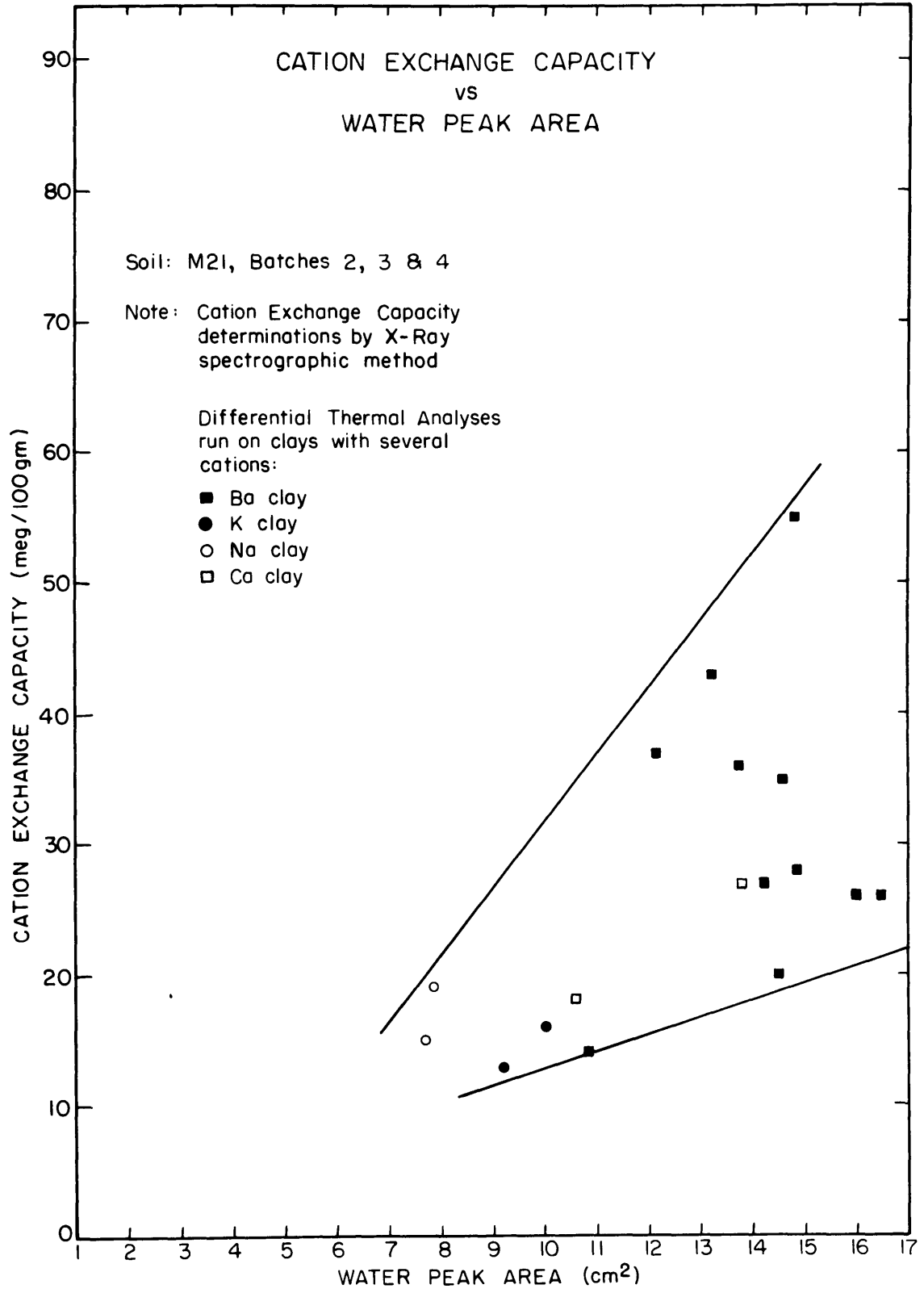CATION EXCHANGE CAPACITY
vs
WATER PEAK HEIGHT

Soil: M2I, Batches 2, 3 & 4

Note: CEC determinations by
X-Ray spectrographic
analysis

DTA run on clays with
several cations:
■ Ba clay
● K clay
o Na clay
□ Ca clay

FIGURE F-3

CATION EXCHANGE CAPACITY
vs
WATER PEAK AREA

Soil: M21, Batches 2, 3 & 4

Note: Cation Exchange Capacity
determinations by X-Ray
spectrographic method

Differential Thermal Analyses
run on clays with several
cations:
■ Ba clay
● K clay
○ Na clay
□ Ca clay

FIGURE F-4