



A proposed model for soil crusts
by Dante Maliwat Ferry

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
© Copyright by Dante Maliwat Ferry (1972)

Abstract:

Investigations regarding the causes of the fairly common but virtually unexplained phenomenon of soil crusting were made. Attention was focused on the clay fraction of the soil. The behavior of clay particles in crusting and aggregation was shown in a molecular level. Variations in the conventional methods of physical and chemical testing of soils in the laboratory were employed to arrive at the conclusions.

Soil crusting was considered to be a step in the reversion of the weathering of mica to the various clay minerals; soil aggregation was considered a necessity in the formation of soils with good structure and a must in bringing back badly-crusted soils to their original productiveness.

New methods of preparing H⁺-saturated clays are proposed. The methods involved the use of a mixed-bed ion-exchange resin.

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature Dante Mahiwaat Ferry

Date 9 August 1972

A PROPOSED MODEL FOR SOIL CRUSTS

by

DANTE MALIWAT FERRY

A thesis submitted to the Graduate Faculty in
partial fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

Approved:

E. W. Anacker

Head, Major Department

Ralph A. Olson

Chairman, Examining Committee

K. Goering

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1972

ACKNOWLEDGMENTS

Sincere gratitude goes to Mr. and Mrs. Robert H. Howe for recommending Montana State University for higher studies. Utmost thanks is given to Dr. Ralph Olsen, my adviser, for proposing the subject matter of my research, and for the many hours of invaluable help he has given me. Professors and co-graduate students will always be remembered for their suggestions and companionship.

The artistic inclinations of Mr. Jim Chacko made possible the beautiful graphs. Heartfelt thanks is given to Mr. Gerry Nelson, who helped in obtaining good photomicrographs.

Pylon soil samples and enlightening ideas were charitably given by Dr. Gerald Nielsen of the Plant and Soils Department.

Last but not least, the life of a poor graduate student was eased with financial aid in the form of a graduate tuition assistantship (March-June 1970), a graduate teaching assistantship (September 1970-June 1971, September 1971-August 1972) and a graduate research assistantship (July-August 1971) from beloved alma mater.

TABLE OF CONTENTS

Chapter		Page
I	INTRODUCTION	1
	HYPOTHESIS REGARDING MODEL OF SOIL CRUSTS	3
II	SAMPLE PREPARATION	11
	Fractionation	11
	Materials and Methods	11
	Discussion	13
	Cation Saturation	14
	Materials and Methods	14
	Discussion	16
III	TURBIDIMETRY	20
	Materials and Methods	20
	Results and Discussion	23
IV	MODULUS OF RUPTURE	36
	Materials and Methods	36
	Shrinkage	40
	Results and Discussion	41
	Shrinkage	64
V	BULK DENSITY	67
	Materials and Methods	67
	Results and Discussion	68
VI	THIN SECTIONING	71

TABLE OF CONTENTS - continued.

Chapter		Page
	Materials and Methods	71
	Results and Discussion	71
VII	WATER AND OXYGEN PERMEABILITY	76
	Water Permeability	76
	Materials and Methods	76
	Results and Discussion	76
	Oxygen Permeability	78
	Materials and Methods	78
	Results and Discussion	81
VIII	SOIL AGGREGATION	85
IX	CONCLUSION	91
	Role of Water	92
	The Rock-Clay Cycle	93
	Curbing Soil Crusting	95
X	H ⁺ -SATURATED CLAYS	96
	Procedure	96
	Observations	97
	Conclusion	99
	REFERENCES	101
	APPENDICES	111
A	Pylon Soils	111

TABLE OF CONTENTS - continued.

APPENDICES		Page
B	Original Data	116
C	Plates	143
D	Photomicrographs of Thin Sections	146

LIST OF TABLES

Table		Page
I	Size Limits of Soil Separates from Two Schemes of Analysis	4
II	Amounts of Salts Added to the Soil	15
III.1	Amounts of Added Cation Present in 30 ml of 0.001% Clay Suspension	23
III.2	pHs of the Chlorides Used in Turbidimetry	24
IV	Unhydrated Sizes of Saturating Cations	48
VIII	Possible Aggregate Bonding Mechanisms	86
X.1	pHs of Suspensions Treated with MB-3 Resin	98
X.2	Concentrations of Na^+ , Mg^{++} and Ca^{++} Remaining in the Clay Suspensions before and after Equilibration with and Passage through MB-3 Resin	99

LIST OF FIGURES

Figures		Page
I.1	A Rock-Clay Cycle	5
I.2	Structures of Montmorillonite and Muscovite	6
I.3	A Scheme of the Transformations in the Crystal Lattices of Minerals Occurring in Weathering and Crusting	8
I.4	A Scheme on the Formation of Friable Crusts and Hard, Cemented Crusts	10
III.1	Block Diagram of the Turbidimetry Set-up	21
III.2	The Turbidimetry Set-up in Full View	21
III.3	The Relationships between Light Scattering and Concentration of Added Electrolyte in Pylon Clay	26
III.4	The Relationships between Light Scattering and Concentration of Added Electrolyte in Bentonite	27
III.5	Schematic Representation of Ion and Potential Distribution in the Double Layer according to the Theories of Helmholtz, Guoy and Stern	28
III.6	Dispersion and Flocculation Caused by Monovalent and Divalent Cations Respectively	31
III.7	Flocculation Caused by Trivalent Cations	31
IV.1	Modulus of Rupture Set-up before the Briquette Is Broken	39
IV.2	The Briquette-breaking Assembly with a Broken Briquette	39
IV.3	Position of the Tube Delivering the Jet of Water after the Briquette Has Been Broken	40

LIST OF FIGURES - continued.

Figure		Page
IV.4	Binding Force Relationships among Different Size Particles in Pylon Soil	44
IV.5	Schematic Diagram of How Particles in Different Soil Fractions Could Come Close Together and Form Crusts	46
IV.6	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Radius of Cation Relationships	49
IV.7	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Valence of Cation Relationships	49
IV.8	Various Cations and the Oxygen Hexagon	53
IV.9	Stacking in Cation-Saturated Soil Crusts	56
IV.10	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Concentration of Added Electrolyte Relationships	59
IV.11	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Concentration of Added Phosphate Relationships	59
IV.12	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and pH Relationships	60
IV.13	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Diameter of Sand Particles Relationships	63
IV.14	Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Al_2O_3 Content Relationships	63
IV.15	A Comparison between Modulus of Rupture, Shear and Tensile Strengths	66
V.1	Bulk Density Relationships in Different Size Soil Particles	69

LIST OF FIGURES - continued.

Figure		Page
V.2	Bulk Density Relationships in Cation-Saturated Soils	69
V.3	Parallel Stacking in Monovalent Cation-Saturated Clay Systems and in Polyvalent Cation-Saturated Clay Systems	70
VI	An Apparent Line of Weakness in a Soil Aggregated by the Presence of Ferric Ions	74
VII.1	Water Permeability and Size of Particles Relationships	77
VII.2	Water Permeability and Valence of Saturating Cation Relationships	77
VII.3	Oxygen Permeability Apparatus	79
VII.4	Partial Pressure of O_2 versus Time Relationships in Silt Crust	82
VII.5	Oxygen Permeability versus Average Diameter of Soil Particles Relationships	83
VII.6	Oxygen Permeability versus Valence of Saturating Cation Relationships	83
VIII	Scheme of Aggregation	90
IX	The Transformation of a Mg-Montmorillonite to Muscovite in the Reverse Weathering Process	94

ABSTRACT

Investigations regarding the causes of the fairly common but virtually unexplained phenomenon of soil crusting were made. Attention was focused on the clay fraction of the soil. The behavior of clay particles in crusting and aggregation was shown in a molecular level. Variations in the conventional methods of physical and chemical testing of soils in the laboratory were employed to arrive at the conclusions.

Soil crusting was considered to be a step in the reversion of the weathering of mica to the various clay minerals; soil aggregation was considered a necessity in the formation of soils with good structure and a must in bringing back badly-crusted soils to their original productivity.

New methods of preparing H^+ -saturated clays are proposed. The methods involved the use of a mixed-bed ion-exchange resin.

-xii-

sa aking mga magulang, sa kanilang matiyagang paghihintay

Chapter I

INTRODUCTION

The successful growth of crops depends upon favorable soil conditions. In many areas of the world, especially areas which have been extensively cultivated, soils have a tendency to develop hard and impene- trable surface crusts. These hardened topsoils inhibit seedling emergence and root penetration. Clark (1970) and Moe, et al (1971) described crusting as a major problem in the Blaine, Cascade, Choteau, Fergus, Hill, Liberty, Pondera, Teton and Toole counties of northcentral Montana. Crusts in one- to ten-acre inclusions in otherwise productive fields have been estimated to occupy as much as 150,000 acres of farmland in the "golden triangle". They are therefore regularly cultivated, fertilized and planted to crops even though production of grain is inadequate on these inclusions to pay for expenses.

Similar problems exist in other regions of the world. In England, for example, Pilpel (1971) ascribed a condition in some farm areas of the Midlands and East Anglia to poor granulation and inability of the soil to form and maintain a proper crumb structure.

Problems associated with soil crusting include the preparation of favorable seedbeds in the cloddy surface, soil loss and water run-off due to impermeability to water, poor aeration and difficulties in the manipulation of the soil by farm machinery (Moe, et al, 1971; Pilpel, 1971).

Many factors are believed to contribute to the formation of soil crusts. Internal factors include the inherent characteristics of the soil, which depend upon its origin and formation. Location, mineralogical composition and the nature of ions present influence soil behavior. External factors include effects of the atmosphere and the treatment given to those soils by man. Climate, weather disturbances and drying are atmospheric factors, while puddling (mechanical manipulation of the soil while still wet), monoculture (failure to use crop rotation), "over-cultivation" and excessive use of synthetic fertilizers (and inadequate use of natural fertilizers) are among those caused by man.

Conversely, many treatments which decrease crusting have been known for ages; the arts of maintaining soil friability have been practised for thousands of years. In tropical regions, for example, growth of native trees and shrubs is allowed to occur on a regular basis as a means of restoring the good qualities of the soil. The laborious return of plant and animal residues to the soil is a common practice in the Orient for the same purpose of ameliorating the soil. The underlying causes of soil crusting, on the other hand, are not well understood at all.

In this thesis, a tentative model for the soil crusting phenomenon is proposed. An attempt is made to show how the model can be used to explain many of the observations previously made pertaining to crusting. The validity of the model is tested by laboratory experiments.

HYPOTHESIS REGARDING MODEL OF SOIL CRUSTS

When rocks and minerals comprising the bulk of the earth's surface are exposed to the physical and chemical processes of weathering (freezing and thawing, heating and cooling, dissolution and recrystallization, hydrolysis, etc.), the larger rocks and minerals are slowly transformed into smaller fragments. Erosive effects of wind and water transport these small fragments from one place to another on the earth's surface providing raw materials for the soils of the earth. The action of the factors of soil formation (topography, climate, vegetation, etc.) forms a soil with characteristic properties; these properties depend upon the particular factors of formation imposed upon the soil over a period of possibly thousands of years. In this formative period, the original minerals are changed via a sequence of degradative and synthetic processes to the so-called clay minerals comprising the bulk of the earth's soils.

The solid phase of the soil is composed of fractions which are categorized according to particle size. The larger fractions, viz., gravel and sand, apparently do not play a significant role in crust formation, except in the sense of preventing soil crusting; the smaller size fractions, viz., silt and clay, play very important roles in crust formation. The clay fraction, being colloidal in nature, is considered the more active of these, so attention will be focused on this fraction.

The organic fraction, a relatively small amount of which is present in soils, plays a significant role in preventing soil crusting.

These particles are not related to clay minerals in composition, and will be considered later in the thesis.

Table I - Size Limits of Soil Separates
from Two Schemes of Analysis*

U.S. Department of Agriculture Scheme		International Scheme	
Name of Separate	Diameter range (mm)	Fraction	Diameter range (mm)
Very coarse sand ¹	2.0-1.0		
Coarse sand	1.0-0.5	I	2.0-0.2
Medium sand	0.50-0.25	II	0.20-0.02
Fine sand	0.25-0.10	III	0.020-0.002
Very fine sand	0.10-0.05	IV	Below 0.002
Silt	0.050-0.002		
Clay	Below 0.002		

¹ Prior to 1947, this separate was called fine gravel. Now, fine gravel is used for coarse fragments from 2mm to $\frac{1}{2}$ inch in diameter.

On a geological time scale, one might visualize one of a series of related events (Fig. I.1). The processes occurring in crust formation

* Soil Survey Staff, Soil Survey Manual, U.S.D.A. Handbook No. 18 (Washington: U.S. Government Printing Office, 1951), p. 207.

and degradation might be viewed on a smaller and less grandiose, but more rapid, scale than the one described. An attempt to understand what might be happening on a molecular level will be shown.

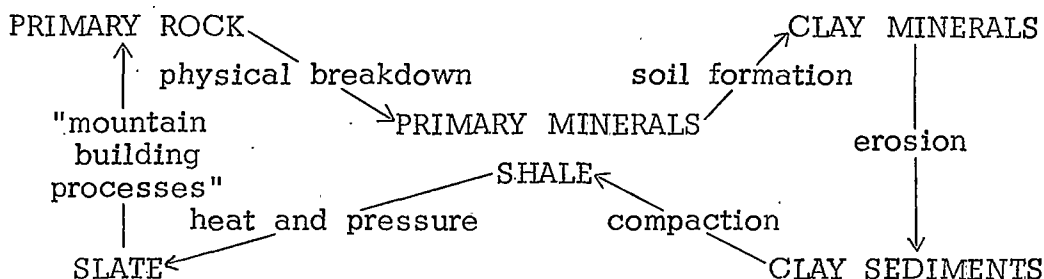


Figure I.1 - A Rock-Clay Cycle.

The structure of an ideal clay mineral would consist of an inner aluminum octahedral sheet bordered by two outer silica tetrahedral sheets (Fig. I.2). This arrangement brings about a three-layer plate-like system, giving rise to the 2:1 types of clay minerals. In nature, clay minerals always divert from this ideal structure. Aluminum substitutes for silicon in the tetrahedral configuration and/or magnesium, iron, chromium, zinc and nickel, etc. for aluminum in the octahedral configuration (Marshall, 1935; Hendricks, 1942). These isomorphous substitutions cause electrical imbalance in the crystal lattice, which is compensated partly by the presence of alkali and alkaline-earth cations (K^+ , Mg^{++} and Ca^{++} being the most abundant) in exchangeable form. Electrostatic forces sometimes retain these cation-bridges between adjacent plates, as in muscovite (Fig. I.2).

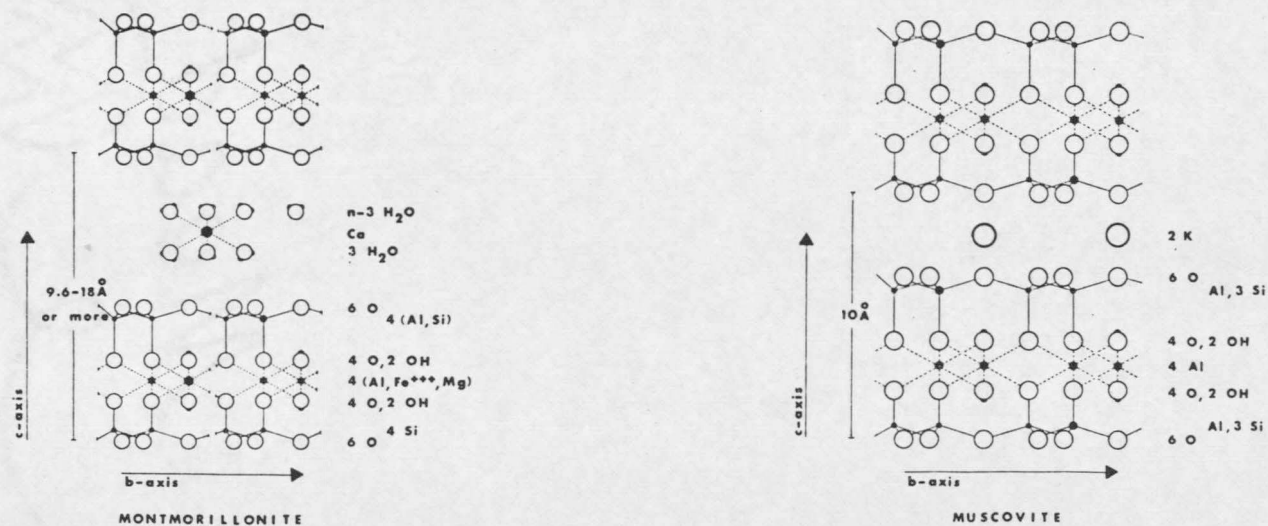


Figure I.2 - Structures of Montmorillonite and Muscovite.
(Reference: Bear's Chemistry of the Soil)

Two common primary minerals, muscovite and biotite (collectively known as the micas), have structures which are very similar to montmorillonite and illite (2:1 clay minerals). Their flakes are commonly large enough to be readily seen in rocks and in detrital material derived from rocks. The transformation of a muscovite particle into a montmorillonite particle is a relatively simple process involving hydration and/or hydrolysis of the alkali cations and their loss from binding positions between the plates. Adjacent plates can then be readily fragmented and dispersed throughout the aqueous medium and function as independent entities. It is pertinent to note that the process is reversible: a high concentration of soluble K^+ added to a clay system can cause montmorillonite to revert to muscovite (Jackson, et al, 1952). A systematized diagram of the said transformations, with other clay minerals acting as intermediates, may be seen in Fig. I.3.

A central feature of the hypothesis proposed in this investigation pertains to a comparable reversible transformation between montmorillonite particles in suspension and the crust which results upon drying. The independent particles of clay, of course, do not combine to form a single crystal, but some of the characteristics of the crust which forms will be shown to be roughly comparable to those of a crystal. The formation of a crust composed of montmorillonite clay particles is therefore visualized as a step towards the reversion of weathering, i.e., from clay minerals back to primary minerals. Subsequently, if this hypothesis is

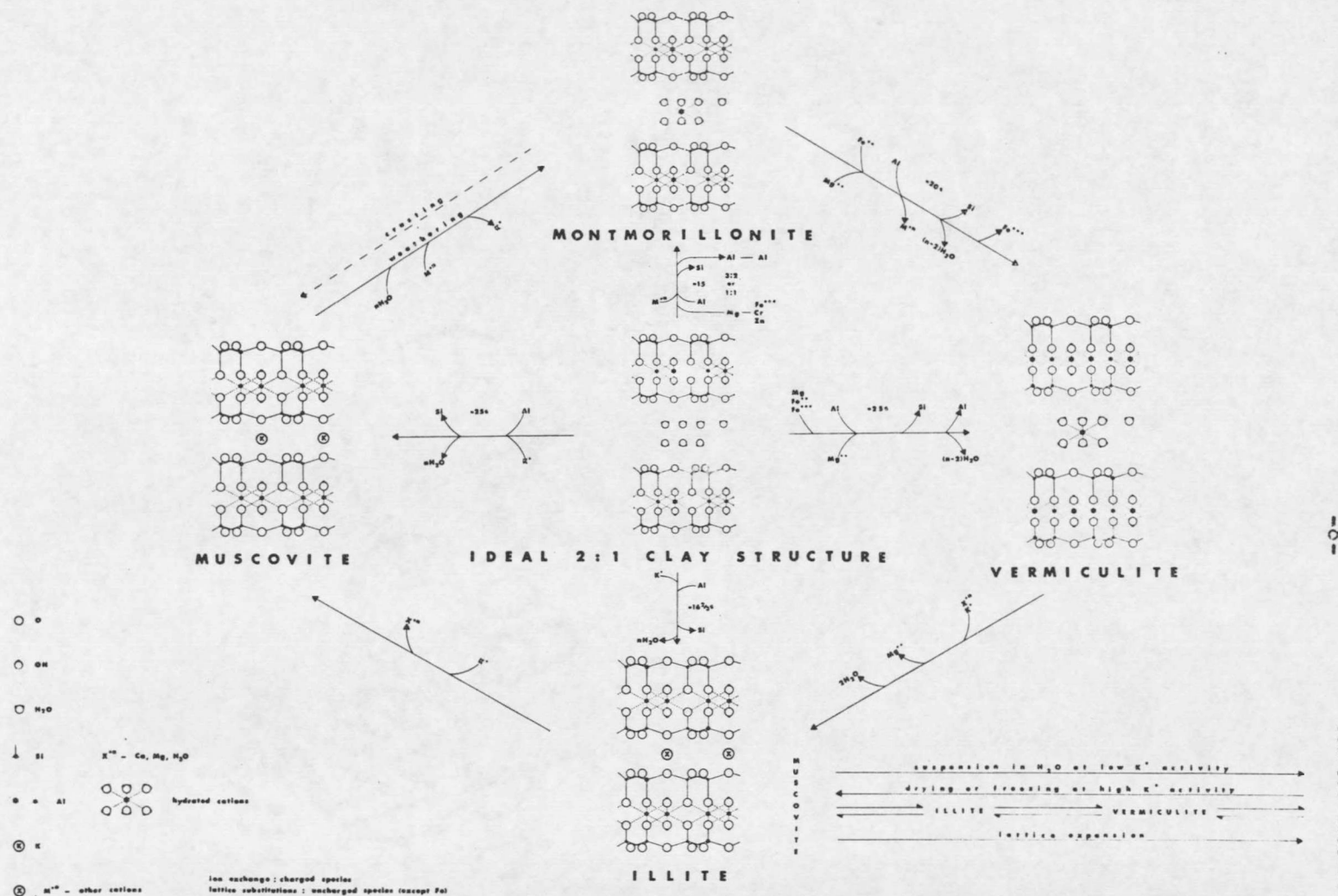


Figure I.3 - A Scheme of the Transformations in the Crystal Lattices of Minerals Occurring in Weathering and Crusting.

reasonably correct, one immediately wonders why all clayey soils do not form crusts upon drying, i.e., why some retain good structure and are friable even when dry. Here is where the more favorable counterpart of soil crusting, soil aggregation, enters into the picture. Many substances (e.g., polyvalent cations, organic matter, polymers, etc.) form aggregates in a variety of ways (electrostatic interactions, adhesion, adsorption, physical entanglement, etc.) from the more active clay fraction (Harris, et al, 1966). If silt and fine sand are entrapped in these clay aggregates, the aggregates increase in size. Should the clay surface-aggregating substance binding forces be of greater magnitude than the aggregate-aggregate cohesive forces, planes of weaknesses are apt to appear along the aggregate surfaces. Dry soils with stable aggregation of particles are therefore easily friable and would easily crumble, yet retain a good structure.

Fig. I.4 outlines the above hypothesis and other relevant considerations.

Much of the experimentation undertaken in this investigation was designed in an attempt to test the validity of the preceding hypothesis regarding the crusting phenomenon. The focal point of the experiments is Fig. I.4. A literature review wherein the usefulness of the hypothesis in explaining many of the observations pertaining to crusting and non-crusting (i.e., aggregation), is included in every Results and Discussions section.

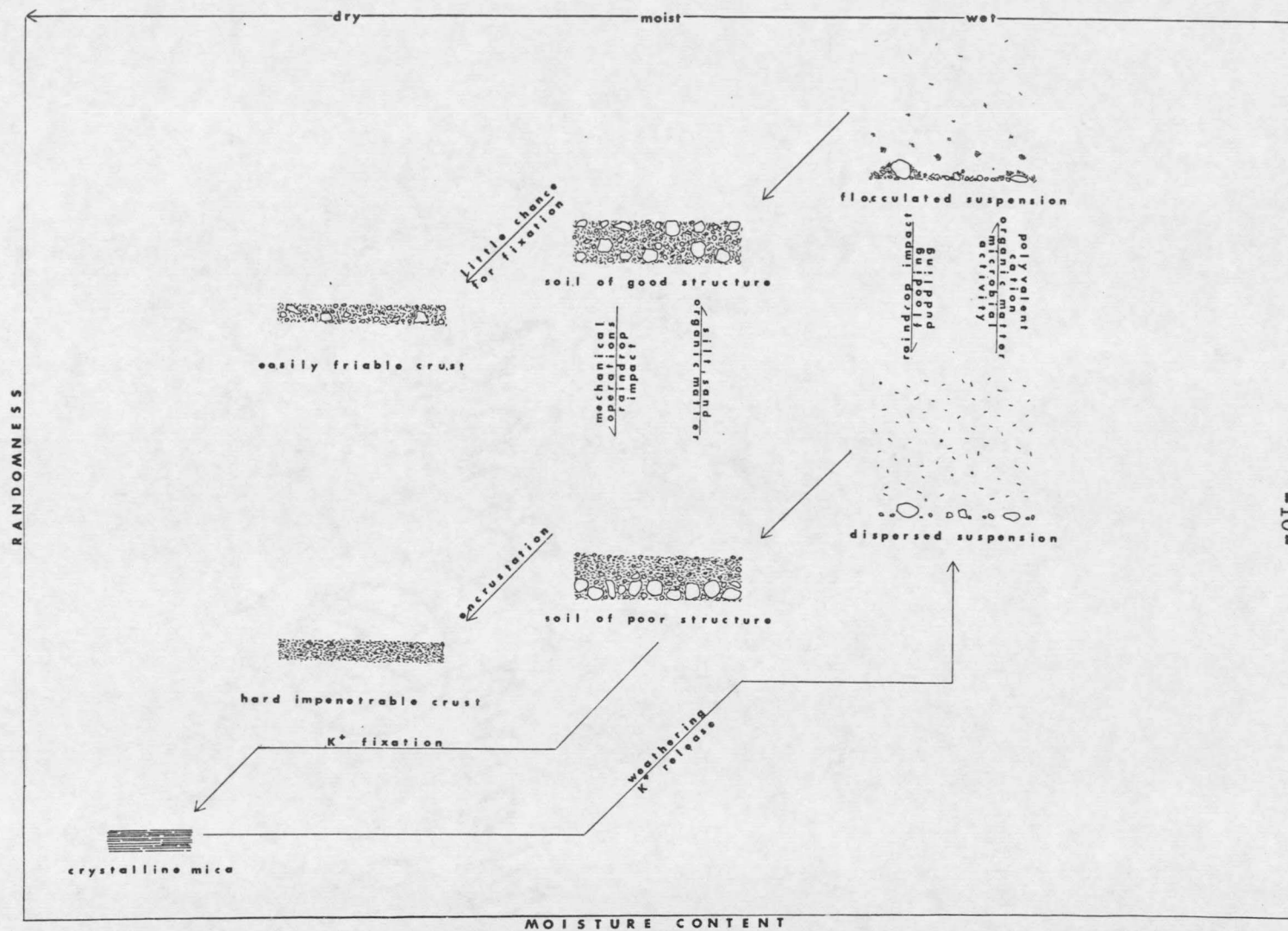


Figure I.4 - A Scheme on the Formation of Friable Crusts and Hard, Cemented Crusts.

Chapter II

SAMPLE PREPARATION

Fractionation

Materials and Methods. The method is a modification of the procedure found in Methods of Soil Analysis, Part I¹. Portions of Pylon² topsoil were passed through a 2-mm square-hole sieve. In four 9-liter bottles, 7% suspensions of this soil in water were prepared. The suspensions were homogenized for about three minutes using an electric mixer and were allowed to stand in a section of the laboratory with the least temperature fluctuations.

Stoke's Law defines v , the rate of settling of small, spherical particles (in cm/sec) as:

$$v = \frac{2r^2 g (\rho_s - \rho_l)}{9\eta}$$

where r = radius of particles (in cm); g = acceleration of gravity (in cm/sec²); ρ_s = density of particles (in g/cm³); ρ_l = density of liquid medium (in g/cm³) and η = viscosity of water at a particular temperature (in g/cm-sec or poise). In terms of particle diameter, the above equa-

¹P.R. Day, "Particle Fractionation and Particle-Size Analysis", in C.A. Black (ed.), Methods of Soil Analysis, Part I, Agronomy No. 9 (Madison: American Society of Agronomists, Inc., 1965), pp. 545-567.

²For a detailed description of Pylon soils, refer to Appendix A.

tion is transformed into:

$$v = \frac{X^2 g(\rho_s - \rho_l)}{18\eta}$$

where X = diameter of particles (in cm).

Also,

$$v = \frac{h}{t}$$

where t = time (in sec) required for particles 2 μ and below in diameter to settle through a preselected depth, h (in cm). t was found by equating

$$\frac{X^2 g(\rho_s - \rho_l)}{18\eta} = \frac{h}{t}$$

The values 2×10^{-4} cm (= 2 μ , the upper limit of the clay size fraction), 980 cm/sec², 2.6 g/cm³(3), 1 g/cm³, 8.57×10^{-3} poise⁽⁴⁾ and 30 cm (= 80 % of the total height of the bottles) were given for X, g, ρ_s , ρ_l , η and h respectively. A value of 73,800 sec (= 20 hours and 30 minutes) was obtained for t, after which, a marked glass tubing was carefully lowered into the suspensions and maintained at about 3 cm below the 30-cm mark. This allowed a distance of about 9 cm from the bottom of the bottles to the tip of the glass tubing. The suspended clay fraction (<2 μ) was withdrawn by siphoning.

³ An arbitrary figure which satisfies the two definitions of the clay fraction: particles having an effective diameter of 2 μ and a settling velocity of 10 cm in 8 hours at 20°C (International Society of Soil Science, 1929).

⁴ Corresponds to a temperature of about 27°C.

Suspension and sedimentation of the soil were done repeatedly until most of the clay in all four bottles had been fractionated. A clay paste was obtained by introducing the clay suspension to a Sharples Supercentrifuge with a bowl radius of 3 cm and a maximum speed of 23,000 rpm. The rate of feeding was maintained at 200-300 ml/min. The clay paste was resuspended in the smallest amount of water and was stored in that state.

A jet of water was directed to the silt and sand fractions left in the bottles. After vigorous shaking, they were transferred to a large beaker where additional water kept the fractions in suspension. After sufficient mixing, the suspension was allowed to pass through a 44- μ square-hole sieve. Sand particles retained on the screen were air-dried. The suspended silt fraction was introduced into a Sharples Supercentrifuge at a rate of 300 ml/min. The silt paste was air-dried, pulverized by grinding, and passed through a 1-mm square-hole sieve.

Discussion. Groups of soil particles under 2 mm in diameter are the only ones called "soil separates"; coarser fragments commonly found interspersed are classified as mineral particles, but are not included under soil separates. In separating the clay fraction from the silt and sand fractions, the principle of sedimentation is involved. The soil as coming from the fields had been passed through a 2-mm sieve to eliminate coarse material prior to suspension in water. Dispersion and suitable agitation detaches a single particle from the others, and effectively, this particle is suspended.

In the derivation of equations for sedimentation, spherical particles were considered. Soil particles are mostly anisometric, but for all practical purposes, they are either assumed to be spherical or special mention of the particular method used in sedimentation is made. Suspensions are kept in a room with the least temperature fluctuations since particle movement is dependent on turbulence.

Separation of silt from sand involves wet sieving. The upper limit for the size of a particle to be classified under the silt fraction category is $50\ \mu$ ($= 5 \times 10^{-2}$ mm). Using a $44\text{-}\mu$ sieve would not only prevent the passage of $50\ \mu$ particles which are longer than wide, but also correct for any mechanical defects the sieve might have.

It was more convenient for the clay fraction to be kept suspended in water than dried, because of the difficulties encountered in resuspension. Great care was practised in pulverizing the dried fractions. Rupture of crystal lattices might have occurred, but there was no better way of bringing them back to their original powdery states.

Cation Saturation

Materials and Methods. A proposed new method of preparing H^+ -saturated clays is treated separately in Chapter X.

To 250-g portions of the soil, measured amounts of chlorides of seven cations were added (Table II). The mixtures were allowed to stand until decantation was feasible. They were washed free of Cl^- by decantation and centrifugation, a Servall Superspeed Centrifuge, type SS-1 being

used⁵. Washing was continued until the soils were free of Cl^- as determined with the AgNO_3 test.

The cation-saturated soils were dried, pulverized and passed through a 1-mm square-hole sieve.

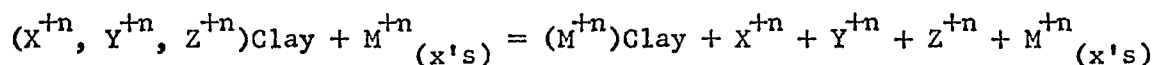
Table II - Amounts of Salts Added to the Soil⁶

salt	formula weight	g/meq	g/500 meq (250 g soil)
LiCl	42.4	0.0424	21.2
NaCl	58.45	0.05845	29.225
KCl	74.55	0.07455	37.275
MgCl ₂			
.6H ₂ O	203.3	0.10165	50.825
CaCl ₂	110.99	0.055495	27.7475
AlCl ₃			
.6H ₂ O	241.44	0.08048	40.24
FeCl ₃			
.6H ₂ O	270.3	0.0901	45.05

⁵ A Powerstat variable transformer maintained at the 80-volt level provided a high-enough speed for the centrifuge to settle the soils.

⁶ The cation-exchange capacity of the soil is 20 meq/100 g (refer to the chemical analysis of the topsoil, Appendix A). 250 g of soil have a cation-exchange capacity of 50 meq. Ten times this amount in salt concentration was added to make allowances for complete saturation of exchange sites.

Discussion. An initial objective was to prepare a homoionic soil with only the basic minerals and a selected cation present in the system. For this matter, the cation- and anion-exchange phenomena occurring in soils was depended upon. Ion exchange is a reversible process; addition of a salt of a cation, of an amount over and above the cation-exchange capacity of the soil, saturates the soil with the wanted cation and shifts the equilibrium to the right in the equation:



where X^{+n} , Y^{+n} and Z^{+n} are the original cations saturating the soil, and M^{+n} is the wanted cation. Washing-off of the supernatant containing the unwanted cations and excess added salt creates a homoionic soil.

Salts were used to saturate the soil because the other sources of cations, bases, have unwanted effects on the soil.

It is the clay and silt fractions and the organic matter that are almost entirely responsible for the exchange phenomena in the soil. They have the capacity to exchange ions due to their colloidal nature and net negative charge.

Isomorphous substitutions in clay mineral crystal lattices and the ionization of hydroxyl groups attached to the silicon of broken tetrahedrons impart the net negative charge on a clay particle (viz., Al^{+++} can substitute for Si^{+4} and $Si-OH + H_2O = SiO^- + H_3O^+$). In the former case, the charges reside at the basal planes and in the second case, at the corners or along the edges of the clay plates. These negative charges

are neutralized by the presence of an equivalent amount of positive charges, mainly from exchangeable cations. The most common of these ions occurring naturally are Ca^{++} , Mg^{++} , H^+ , K^+ , Na^+ and NH_4^+ , in roughly the same decreasing order of abundance. Therefore, the capacity of the soil to exchange cations is dependent on its clay and organic matter content and its mineral composition (Baver, 1956; Bear, 1964; Grim, 1968).

The cation-exchange capacity (CEC)⁷ of montmorillonite is placed at 80-150 meq/100 g⁸.

The soil is an ion-exchanger: in aqueous suspensions, the counterions are distributed along the soil particle surfaces within a certain space, forming a "diffuse layer". Counterions and diffusible free electrolytes are in constant motion and because of this, exchange of ions between the soil and the solution of free electrolytes is continuous. The rate of exchange is generally rapid and is dependent on the degree of swelling of the clay plates and on the size of the exchangeable cations present in the system (Baver, 1956; Bear, 1964; Grim, 1968; Koehnke, 1968). The clay in Pylon soils is montmorillonitic and is therefore considered to be freely expansible. With all other factors held constant, this characteristic of Pylon soils allows equilibrium to be reached in a matter of minutes.

⁷CEC is defined as the amount of cation species bound at a suitable pH, usually 7.

⁸R.E. Grim, Clay Mineralogy, 2nd ed. (New York: McGraw-Hill Book Co., 1968), p. 189, Table 7-1.

There is no universal order in the effectiveness of the replacement of cations by other cations, but for the alkali and the alkaline-earth series, the order has been found to be the same as that of the lyotropic series: $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$, and $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$ (Baver, 1965). However, in judging the relative replacing power of cations, the exchange material, its exchange capacity and the nature of ions present have to be taken into consideration.

Ion hydration has an important role in the adsorption of cations. The less hydrated and the nearer an ion fits the exchange sites, the more tightly it is held. If monovalent and divalent cations are present in a soil-water system, dilution would shift the equilibrium to the direction where adsorption of divalent cations increases while adsorption of monovalent cations decreases. If the solution concentration is increased, the reverse happens⁹. The degree of saturation by a cation M^{+n} , D_k , is governed by the mole fraction⁹.

The observed pH of the untreated soil was 6.75 and the relative effects of the cations to flocculation were as follows: $\text{Fe} = \text{Al} > \text{Ca} = \text{Mg} > (\text{K}) > \text{Na} = \text{Li}$. Potassium cannot be positioned exactly since the degree of flocculation due to its addition approached that of Ca and Mg, but this effect decreased more rapidly after subsequent washings. In washing, the very fine clay particles had to be sacrificed since they are in per-

⁹ L. Wiklander, "Cation and Anion Exchange Phenomena", in F.E. Bear (ed.), Chemistry of the Soil, 2nd ed., American Chemical Society Monograph Series No. 160 (New York: Reinhold Publishing Corp., 1964), pp. 163-205.

petual suspension and are easily eliminated by decantation. Each preparation was dried and pulverized; adverse effects of drying and grinding were considered negligible.

Chapter III

TURBIDIMETRY

Materials and Methods

Figs. III.1 and 2 show a block diagram and a photograph of the turbidimetry apparatus. It consists mainly of a sample compartment where a 35-ml rectangular optical-glass cuvette can be inserted, a G.E. AH4 mercury arc lamp, a 1P21 photomultiplier tube, a Rubicon galvanometer and a magnetic stirrer.

The set-up was kept in a dimly-lit room. To minimize the amount of stray light, the inner walls of the sample compartment were blackened and all corners and holes where stray light could enter were sealed.

The concentration of the clay suspension was adjusted to 10 g/l by dilution, using a Taylor hydrometer for soil colloids having a range of 2-60 g/l at 67°F (= 19.44°C). 0.1 N LiCl, NaCl, KCl, MgCl₂, CaCl₂, AlCl₃ and FeCl₃ solutions were prepared. FeCl₃ was prepared by dissolving iron powder in concentrated HCl. Excess HCl was subsequently boiled off. No color was imparted to the FeCl₃ solution.

0.1-ml portions of the 1% Pylon clay were transferred to 100-ml volumetric flasks. 0, 0.01, 0.05, 0.1, 0.2 and 0.5 ml of the electrolytes were delivered and distilled water was added to dilute the suspensions to the mark¹. The mixtures were aged for a day.

¹These made 0.001% suspensions, which were turbid enough to give readings within the galvanometer scales.

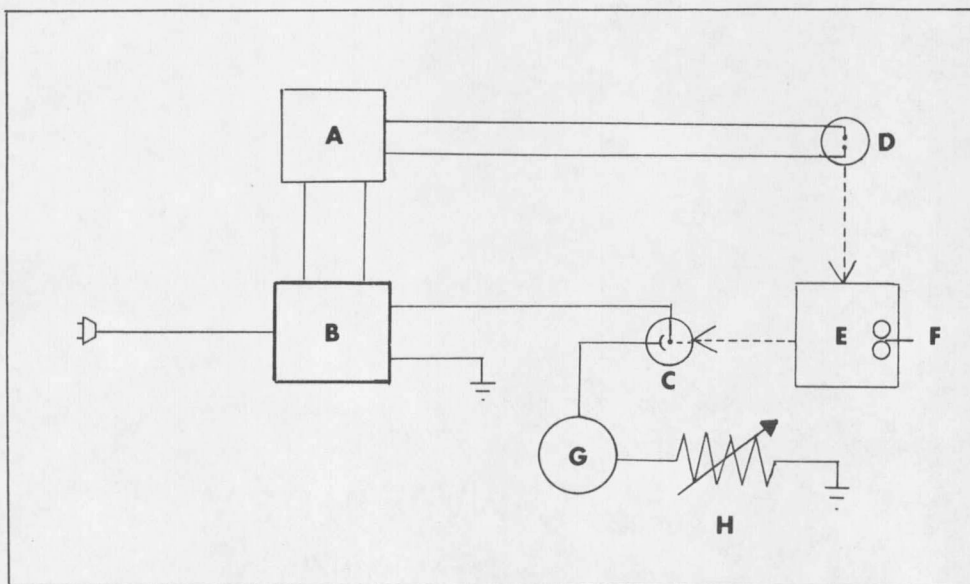


Figure III.1 - Block diagram of the turbidimetry set-up. A, voltage stabilizer; B, power supply; C, photomultiplier tube; D, mercury arc lamp; E, sample compartment; F, magnetic stirrer; G, galvanometer; H, variable resistor.

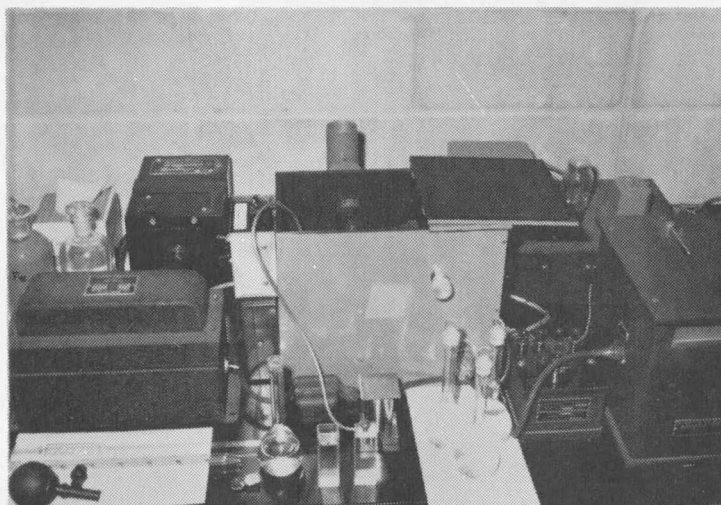


Figure III.2 - The turbidimetry set-up in full view.

30-ml aliquots of these suspensions were transferred to the cuvette. The mercury arc lamp and the photomultiplier tube were warmed up for about 10 minutes. A cuvette-full of clay suspension was introduced into the sample compartment at a time. To prevent settling due to flocculation, the cuvette was provided with a small magnetic bar which stirred the suspension at a constant rate. As the shield which intercepted the beam of light from the source to the phototube was slid out, the degree of light scattering was read from the galvanometer. Several readings were recorded since the galvanometer pointer oscillated. The average reading for a single cuvette-full of suspension was taken.

The pHs of the solutions were measured by means of a pH meter.

A standard clear plastic cuvette was read at proper intervals to correct for the diminution of light intensity common to many mercury arc lamps. Time plots, with clock time as the abscissa and galvanometer readings as the ordinate were constructed. From these graphs, the readings on the plastic cuvette at particular times were corrected, that is, what would have been the readings on the cuvette had the intensity of light diminished linearly with respect to time?

To obtain relative values, ratios of the galvanometer readings on the samples to the corrected galvanometer readings on the standard were computed:

$$\frac{\text{galvanometer reading for the clay}}{\text{corrected galvanometer reading for the standard}}.$$

The proportions

$$\frac{\text{galvanometer reading for the clay with added electrolyte}}{\text{corrected galvanometer reading for the standard}}$$

$$\frac{\text{galvanometer reading for the clay without added electrolyte}}{\text{corrected galvanometer reading for the standard}}$$

were plotted against concentration of added electrolyte.

The procedure was repeated using bentonite instead of Pylon clay.

Table III.1 shows the milliequivalents and concentrations of added electrolytes in each cuvette for both the Pylon and bentonite clay samples.

Table III.1 - Amounts of Added Cation Present
in 30 ml of 0.001% Clay Suspension

ml electrolyte	meq present	concentration of added electrolyte
0.01	1×10^{-3}	3.3×10^{-5} N
0.05	5×10^{-3}	1.66×10^{-4} N
0.10	1×10^{-2}	3.3×10^{-4} N
0.20	2×10^{-2}	6.67×10^{-4} N
0.50	5×10^{-2}	1.66×10^{-3} N

Results and Discussion

Turbidimetry or nephelometry is based on the observation of the Tyndall effect. The intensity of light scattered at right angles to the incident beam by a turbid medium is measured by means of a photosensitive tube. Larger particles scatter light more than do small particles, so if

samples of clay suspensions are subjected to such treatment, the degree of aggregation of clay particles in the presence of cations could be determined by the amount of light a suspension scatters.

Kolthoff, et al (1969) describes the usual methods in turbidimetry, one of which had been employed in this paper.

Fig. III.3 shows the relationships between the proportion

galvanometer reading for the clay with added electrolyte
corrected galvanometer reading for the standard

galvanometer reading for the clay without added electrolyte
corrected galvanometer reading for the standard

and the concentration of added electrolyte for each sample. The complete data in tabular form can be found in the Appendix.

The pHs of the Cl^- solutions used are listed under Table III.2.

Table III.2 - pHs of the Chlorides Used in Turbidimetry

cation	pH of a 0.1 N solution
Li^+	5.87
Na^+	6.00
K^+	6.03
Mg^{++}	6.08
Ca^{++}	6.74
Al^{+++}	3.58
Fe^{+++}	1.48

30 ml of the 0.001% clay suspensions contain 0.0003 g clay.

Fig. III.3 shows a distinctive pattern. The curves for clays with added Li^+ , Na^+ and K^+ imply the dispersing effects of those cations to a predominantly Mg^{++} - and Ca^{++} -saturated Pylon clay (refer to the chemical analysis of the topsoil, Appendix).

In explaining the above phenomenon, the concept of the diffuse double layer is found to be very appropriate. Four men are essentially responsible for the mathematical description of the double layer. In 1879, Helmholtz proposed an arrangement of particle surfaces and counterions equivalent to a simple parallel-plate capacitor. This model is inadequate because the thermal motion of the liquid molecules could scarcely permit such rigid array of charges at the interface (Moore, 1962). In 1910, Guoy, and later, Chapman, introduced the diffuse double layer theory. In this theory, the concentration of the counterions is highest in the immediate vicinity of the surfaces and decreases asymptotically to the outside solution of free electrolytes of uniform composition (Wiklander, 1964). In 1924, a modification of this theory was introduced by Stern. The inner part of the double layer in his model is similar to Helmholtz's condenser and the outer part, structurally similar to Guoy's treatment. These three concepts are represented in Fig. III.5.

Due to the greater osmotic activity of monovalent cations, a diffuse ion layer is created around clay particles. Interparticle repulsion, which increases as the distance between the particles decreases, results from the clay particles not being effectively neutralized. The

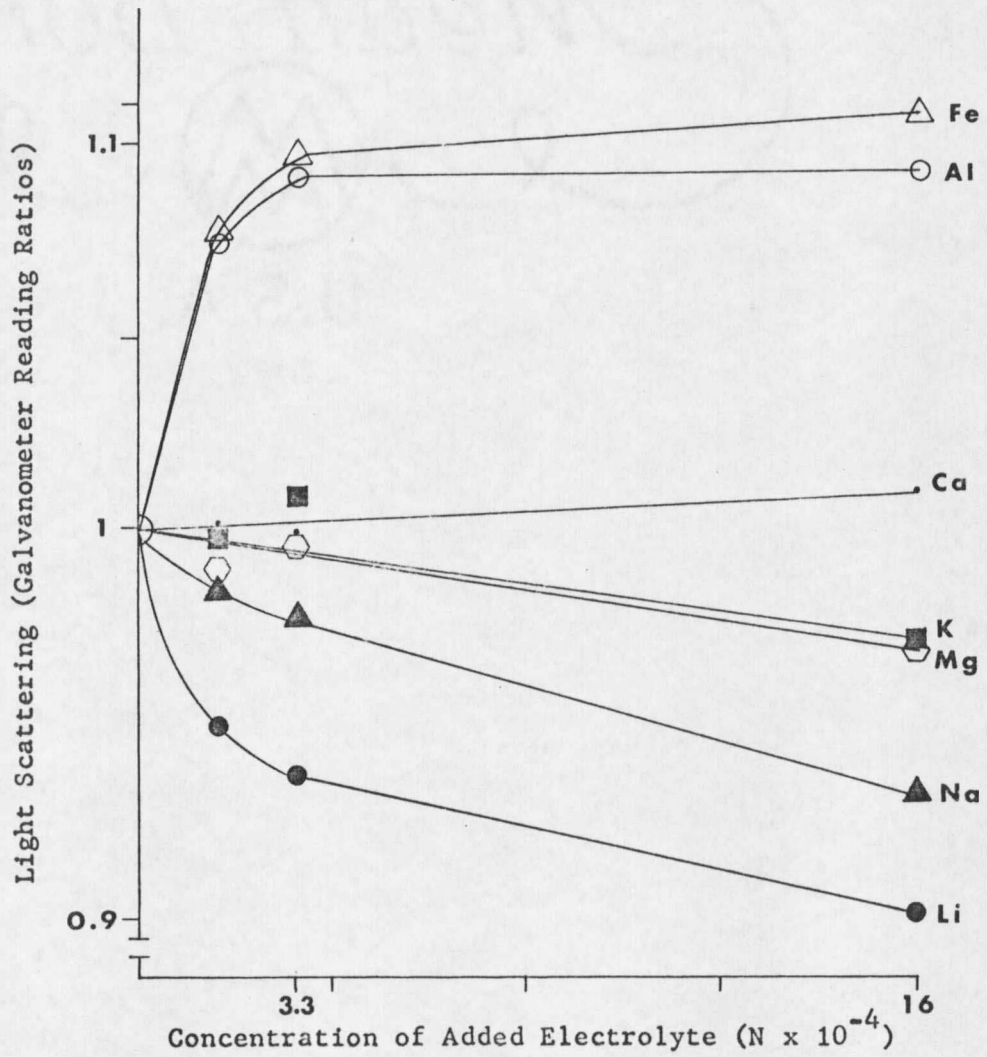


Figure III.3 - The Relationships between Light Scattering and Concentration of Added Electrolyte in Pylon Clay.

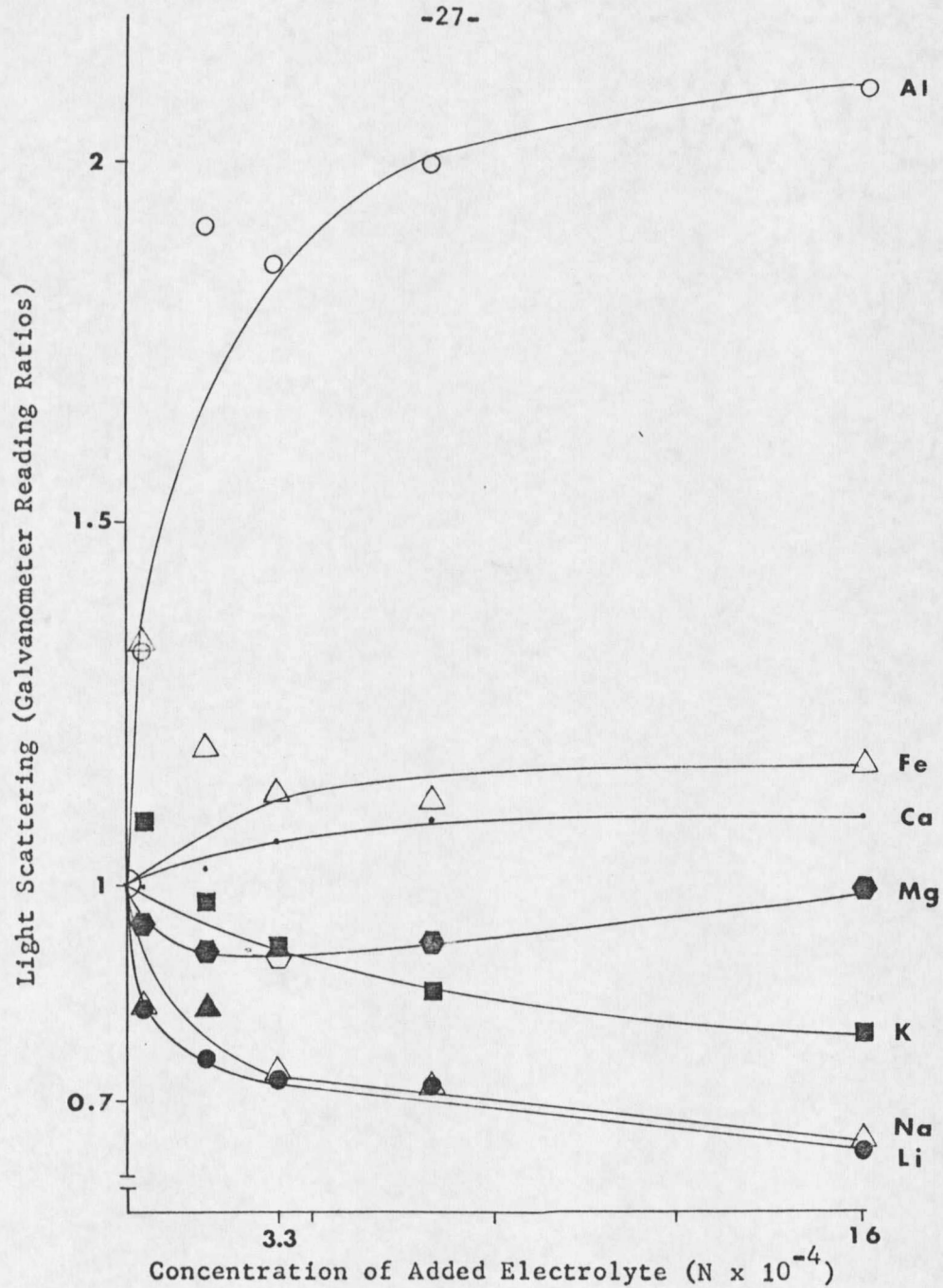


Figure III.4 - The Relationships between Light Scattering and Concentration of Added Electrolyte in Bentonite.

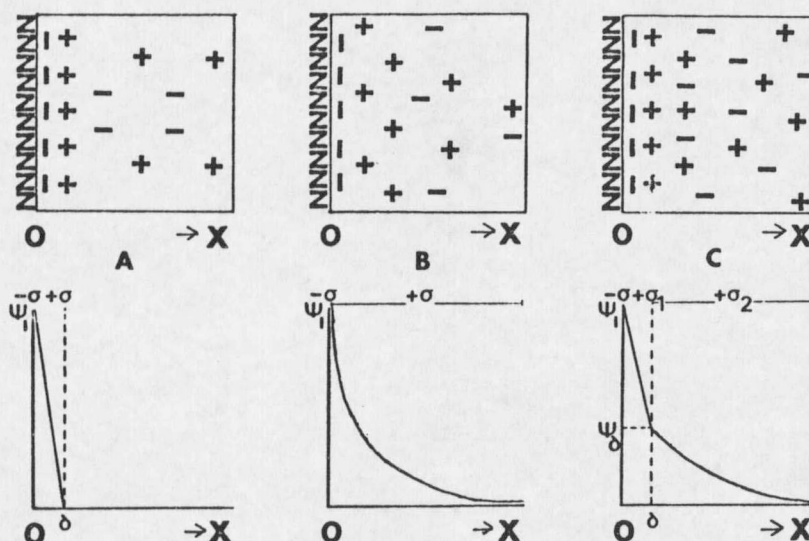


Figure III.5 - Schematic representation of ion and potential distribution in the double layer according to the theories of Helmholtz, Guoy and Stern. ψ_0 , total potential; ψ_δ , zeta potential; x , distance from particle surface; $-\sigma$, surface charge density; and δ , thickness of the Stern layer. (Reference: Bear's Chemistry of the Soil)

individual particles may stay dispersed for an indefinite period of time unless the concentration of the monovalent cations is increased. This effect will be seen later in modulus of rupture.

Within a group of cations in the periodic table, the thickness of the double layer decreases due to decreased ion hydration. The zeta potential, or the magnitude of charge on the surface of the clay particle is therefore decreasing in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, when such cations are present in a clay system. With increasing electrolyte concentration, the force of repulsion decreases. There is a tendency for more cations to surround the clay particles and neutralize the negative charges. The zeta potential reduces and the thickness of the double layer decreases.

The particles are allowed to come closer together and as a consequence, the floc size increases, causing more light to be scattered. This phenomenon would be apparent in the latter portion of the Li^{+-} , Na^{+-} and K^{+-} treated samples turbidimetry curves upon addition of more electrolyte.

The sodic nature of Mg^{++} is shown in the clay with added Mg^{++} curve. This behavior of clay systems when Mg^{++} is present will be further discussed in the Modulus of Rupture chapter. Decrease in light scattering (because of dispersion of particles) is caused by the displacement of Ca^{++} by Mg^{++} . Ca^{++} , a good flocculating agent, can be seen flocculating the clay particles at the very moment a few milliliters of CaCl_2 solution were added. Similarly, upon addition of more Mg^{++} , an upward swing in the latter portion of the Mg^{++} -treated sample turbidimetry curve would be apparent.

The higher valency of divalent cations causes these cations to stay nearer the negative sites they are neutralizing. A lower zeta potential and a narrower and more fixed double layer allow more particles to approach each other more closely. A higher degree of flocculation disperses more light. The effect of ion hydration within a group also holds for divalent cations.

As expected, clays with added Al^{+++} and Fe^{+++} were best flocculated. The first additions of electrolyte caused the greatest aggregation. An extension of the effects of monovalent and divalent cations to the double layer theory can explain the effects of trivalent cations to clay systems.

A parallelism exists between results obtained from turbidimetry studies made on Pylon clay to those obtained from identically-treated naturally-occurring bentonite (Fig. III.4). Bentonite, a montmorillonitic clay mineral, is predominantly saturated with Ca^{++} in its natural state. When saturated with Li^+ , Na^+ and K^+ , the particles were dispersed. The monovalent cations replaced Ca^{++} from the system. Mg^{++} dispersed bentonite particles after the first few additions of MgCl_2 , but started to reflocculate the particles after subsequent additions. This might be due to increased electrolyte concentration with respect to Mg^{++} . Ca^{++} , Al^{+++} and Fe^{+++} caused appreciable aggregation.

A working model for aggregation caused by cations is hereby presented:

A clay surface, due to isomorphous substitution, has a net negative charge. In montmorillonite, a charge of about -0.65 is present per unit cell² (Grim, 1968). Al-Si substitutions in the tetrahedral sheet are less than 15% but Mg-Al substitutions in the octahedral sheet may either be 1Mg/1Al or 3Mg/2Al; these types of substitutions may be present alone or in combination with each other. This does not mean that each unit cell is negatively-charged, but what it implies is that in a clay particle, isomorphous substitution occurs in some cells and does not occur in other cells.

²Unit cell: that configuration having a formula $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}$ in an unsubstituted clay crystal lattice.

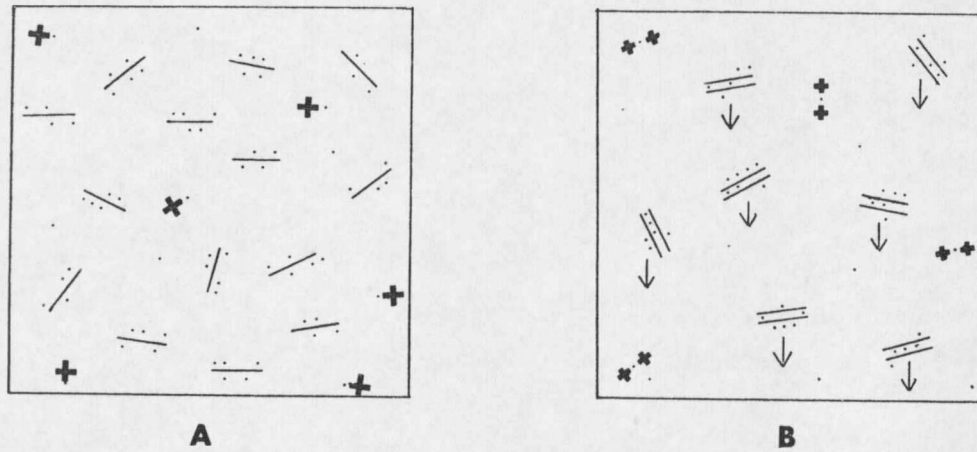


Figure III.6 - Dispersion and flocculation caused by monovalent and divalent cations respectively. Lines, clay plates; dots, cations. Arrows show that floccules tend to settle out.

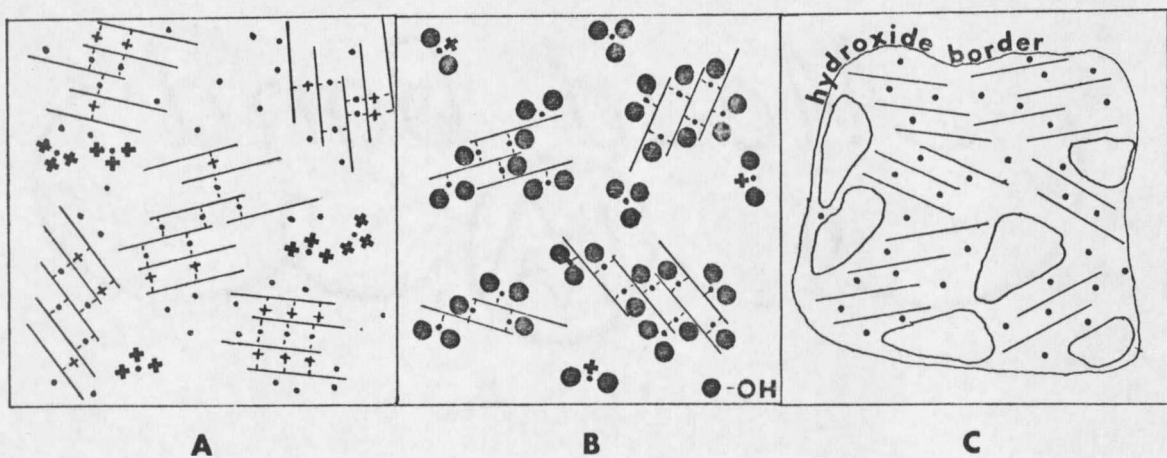
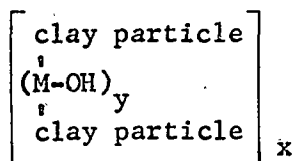


Figure III.7 - Flocculation caused by trivalent cations. A, when aggregates are imparted with a positive charge; B, when hydroxy hybrids are formed; C, when gels envelop the particles to form large aggregates.

As explained by applying the diffuse double layer theory, at electrolyte concentrations below the optimum that would cause complete saturation of exchange sites with the wanted cation, little or no aggregation is caused by monovalent cations.

Aggregation occurs when divalent cations are present in a system. This is because of the less diffuse nature of the double layer in divalent systems. Aggregates formed via these cation-bridge type linkages are stable even in water suspensions (Fig. III.6).

The above-mentioned phenomenon occurs at a greater extent when trivalent cations are present in a clay system. In Fig. III.7, three assumptions as to why aggregates are larger in such systems than in divalent systems are represented. Firstly, when a trivalent cation acts as a cation-bridge, only two of its possible three bonds might be used for positive-negative interactions. A positive charge could be imparted on an aggregate. If an unaggregated clay particle, which is negatively-charged, approached this charged aggregate, the former would be attached to the latter to form a larger aggregate. Secondly, an Al-hydroxy or a Fe-hydroxy and clay particle hybrid could exist in the form



where both x and y are integral numbers governing the size of the aggregates. Bower and Truog (1940) postulated that polyvalent iron introduced

into a clay system as FeCl_3 may be held in the exchange sites as positively-charged ferric dihydroxy ions. This is replacing one of the clay particles with an extra -OH group, and both species might actually be present in a system. Finally, if Al and Fe precipitate as hydroxides at the pH of the clay suspension (6.43), precipitates could form on clay-particle nuclei. More clay particles, or perhaps, silt and fine sand, could be occluded in these formations to allow growth of aggregates. It is also presumed that iron serves a dual purpose. The part which remains in solution functions as a flocculating agent and the remainder which could be precipitated as the hydroxide acts as a cementing agent (Lutz, 1936).

The possibility of light scattering being caused by the formation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ alone was remote. Precipitates were not seen by the naked eye. Moreover, Bower and Truog (1940) indicated that under certain conditions, clay can absorb as much as three times its exchange equivalent of Fe^{+++} . In this case, adsorption of trivalent cations on clay surfaces might have lowered the effective concentration of cations available for precipitation.

After stepwise dissolution of labile and poorly crystallized interlayer Al and Fe material and other amorphous Al coatings from soil samples, sufficient interlayered Al and Fe hydroxy material still binding the clay platelets prevented the expansion of clay crystal lattices with ethylene glycol treatment (Singleton and Harward, 1971). Further treatment caused deterioration of the clay in addition to stripping the hydroxy compounds

from between the layers. This indicates the stability and ease of formation of bonds between hydroxy compounds and clay surfaces in water, and in some polar solvents. However, a citrate-bicarbonate-sulfate treatment of soils removed Al and Fe presumed to control the stability of micro-aggregates (Deshpande, et al, 1968).

In addition to what have been discussed, differences in viscosity, specific heat capacity, water tension, optical density and weight conductance measurements of Na/Al-saturated Wyoming bentonite from values for Na-saturated Wyoming bentonite all indicate the good aggregating abilities of Al (and Fe). Such differences were caused by aggregation (Davey and Low, 1968).

The data obtained experimentally in this paper, together with the observations of investigators whose works have been discussed earlier, indicate that the presence of cations can alter the behavior of a soil system. The changes occurring in the physical properties of the soil clay reflect the idea that aggregation does cause an increase in size of aggregates. It would be seen more clearly in the remaining parts of the discussions that the size of soil separates influences the crusting or non-crusting tendencies of a soil. This concept of aggregation clearly supports the second half of the hypothesis presented, that is, why many soils retain a good structure in the moist and the dry state. Turbidity cannot fully explain the phenomenon of soil crusting because crusting occurs when a soil is dry, and turbidimetry studies rely on the

scattering of light by particles in a suspension. It is also suspected that the behavior of particles in a suspension is different from their behavior in the dry state.

Chapter IV

MODULUS OF RUPTURE

Materials and Methods

The procedure is a modification of the method described by Richards (1953).

The concentrated clay suspension was air-dried and pulverized. Air-dry clay, silt and sand were passed through a 1-mm square-hole sieve. Six rectangular brass molds having inner dimensions of $7 \times 3\frac{1}{2} \times 1$ cm were coated on the inside with petroleum jelly and were laid on glass-fiber filter papers on a wire screen drying platform. Six briquettes for each fraction were prepared by evenly distributing the fractions in the molds using a small plastic spoon. The excess was struck off using a straight stainless-steel spatula.

2000 ml of distilled water was poured into a soaking pan. The wire screen drying platform was lowered into the pan; water surrounded the molds completely, but did not overflow into them. After an hour, the screen was lifted from the soaking pan and water was drained off for 15 minutes. The screen with all six briquettes and molds was put in a drying oven at 50°C for 7 hours. The briquettes were carefully transferred to an anhydrous- CaCl_2 dessicator and were dried for another 12 hours. The weights, lengths and widths of the briquettes were carefully measured.

The modulus of rupture apparatus consists of a briquette-support and knife-edge assembly which makes use of two parallel bars 5 cm apart

for supporting the sample, and a third, overlying, centrally-located bar parallel to the other two to supply the breaking force. The bar above and one below are self-aligning, and all three bars are coated on edge with strips of soft rubber.

A beam balance was used to apply and measure the load to the briquette-breaking apparatus. The briquette-breaking apparatus was laid on the left pan of the balance and a sample was positioned on it. A container that would hold water sufficient to break the sample was put on the right pan of the balance¹. Weights were added to either pan to maintain the balance. A metal rod was securely clamped to two iron stands; the rod thus ran parallel to the bars and effectively constrained the upward motion of the upper bar.

Tygon tubing was attached to a cold-water faucet. The rate of water flow was adjusted to 2000 ml/min². The tubing was clamped to stop the flow of water with the tap still on, and suspended above the container in such a way that a jet of water just hit the walls of the container near the brim when the clamp was loosened. The clamp was released and water was allowed to flow and accumulate in the container. At the breaking point, the jet of water previously intercepted by the walls of the

¹Three containers, a 2000-ml beaker, a 4000-ml beaker and a 6000-ml Erlenmeyer flask were used. The first briquettes were sacrificed to determine which particular container was appropriate to hold the volume of water.

²This represents a force being applied at a rate of 1.96×10^6 dynes/min.

container is no longer intercepted, since the right pan has swung lower (Figs. IV.1-3).

The thickness of the broken briquettes at the cleavage plane was measured with calipers. The volume of water that accumulated and its weight were also measured.

The formula employed to compute for the modulus of rupture is:

$$S = \frac{3}{2} \frac{F L^2}{b d^2}$$

where S = modulus of rupture (in dynes/cm²; 10^6 dynes/cm² = 1 bar); F = breaking force (in dynes; weight of water in grams $\times$ 980); L = distance between supports (in cm); b = width of briquettes (in cm) and d = thickness of the briquettes at the breaking face (in cm). Weight effects on modulus of rupture were calculated by dividing the modulus of rupture by the weights of the briquettes. This gave a value of modulus of rupture/unit weight in bars/g.

The modulus of rupture of unwashed and washed soil was also determined. Washing the soil was done five times with the aid of a Servall Supercentrifuge, type SS-1.

The modulus of rupture of soils saturated with selected cations was determined similarly. In soaking the soils, solutions containing 30 meq of the cation in question in 2000 ml of water (made 0.015 N solutions) were used instead of distilled water.

Other modulus of rupture determinations included the effect of increasing electrolyte concentration in the soak solution using NaCl;

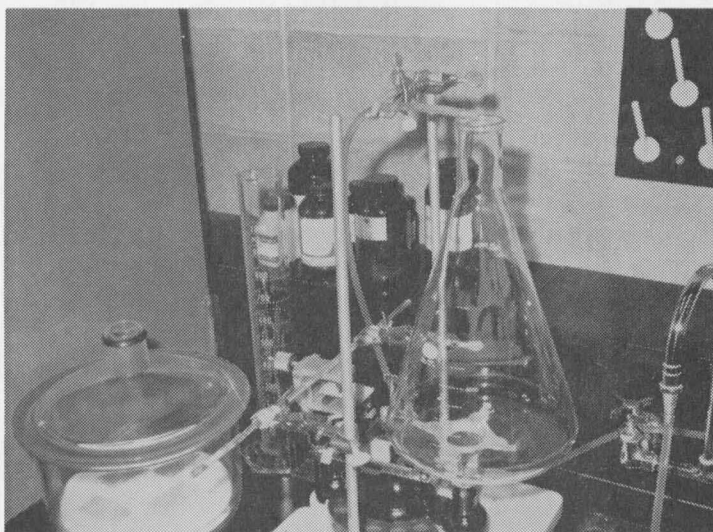


Figure IV.1 - Modulus of rupture set-up before the briquette is broken.

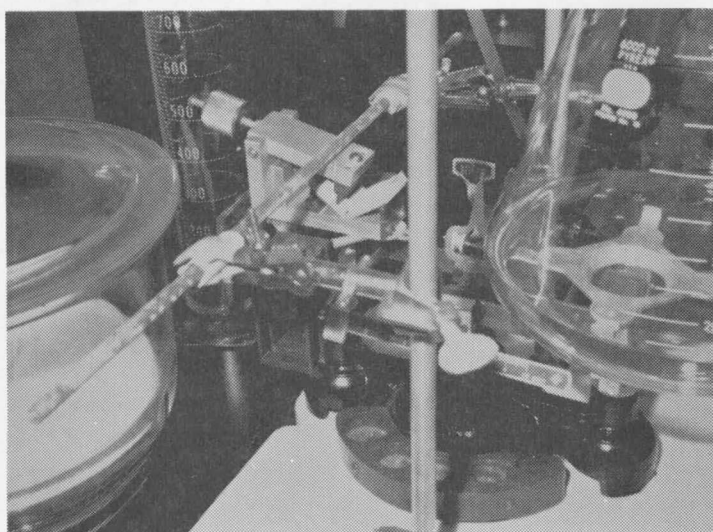


Figure IV.2 - The briquette-breaking assembly with a broken briquette.

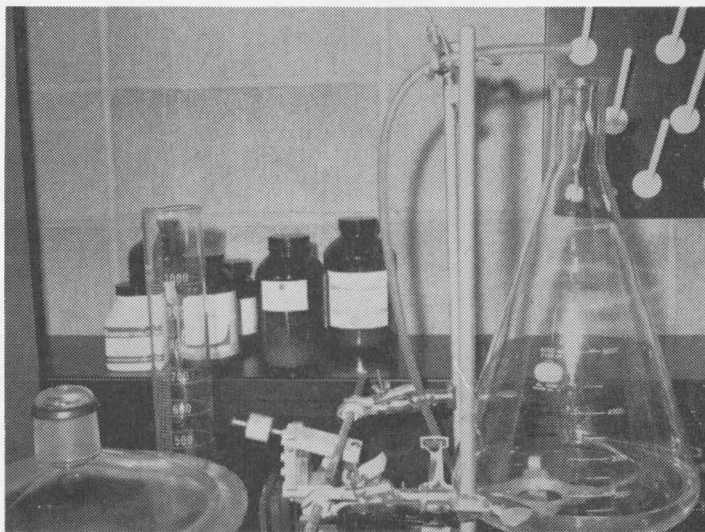


Figure IV.3 - Position of the tube delivering the jet of water after the briquette has been broken.

the effect of using sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ in the soak solution; the effect of varying pHs using HCl and NaOH in the soak solution and the effects of adding sand and Al_2O_3^3 .

Shrinkage. Shrinkage was calculated by the use of the formula

$$\%S = \frac{V_m - V_b}{V_m} \times 100$$

³Using Na^+ -saturated soils: for increasing electrolyte concentration, 2.5, 5, 10 and 20 ($\times 10^{-2}$ M) solutions of NaCl were used; for the phosphate, 8.2, 16.4, 32.8, 131.2, 262.4 and 524.8 ($\times 10^{-6}$ M) $(\text{NaPO}_3)_6$; for the pH study, 5 and 25 ($\times 10^{-3}$ M) HCl and NaOH. Using untreated soils: soils were made to contain 1%, 3% and 5% Al_2O_3 ; 4:1 soil:sand mixtures were made up, with sands of mesh numbers 60-120, 50-200 and 320-325.

where %S = percent shrinkage; V_m = volume of molds (in cm^3) and V_b = volume of briquettes (in cm^3).

Soil samples soaked in KCl solution were compressed under applied pressure. The modulus of rupture of these briquettes were determined in the usual manner. Prior to oven- and dessicator-drying, the moist briquettes, still in the molds, were laid on sheets of glass-fiber filter paper and were subjected to 50 psi (3.4 atm) gage pressure, in a press for three hours.

An estimation of the modulus of rupture of muscovite sheets was obtained. Well-crystallized muscovite was trimmed lengthwise and crosswise to yield a $7 \times 3\frac{1}{2}$ cm rectangular piece. Thin sheets were peeled off and laid on parallel supporting brass bars separated by a distance of 0.8 cm. The modulus of rupture was determined as usual.

Results and Discussion

Allison, R.V. (1923) devised one of the earliest methods in modulus of rupture determinations. His procedure involved the breaking of a supported soil sample by an applied load and measuring the weight of the load and the dimensions of the soil sample. The formula he used to compute for the breaking strength, R (in g/cm^2) is

$$R = \frac{3}{2} \frac{Wl}{Bd^2}$$

where W = load (in g); l = distance between the supporting fulcra (in cm); B = width of sample (in cm) and d = depth (in cm). Carnes (1936) modified the method by using the spring of a Jolly balance to suspend the breaking

load and determining the amount of take-up in the spring after the crust had been broken. Modulus of rupture (in g/cm^2) was calculated by the formula

$$R = \frac{3}{2} \frac{Pl_2}{bd^2}$$

where P = breaking weight (in g); b = width of sample (in cm) and d = thickness (in cm).

The procedure presently used by the U.S. Department of Agriculture Salinity Laboratory is essentially a modification by Richards (1953). Reeve (1965) had also described this procedure, which is used in this paper. The major changes made are:

1. The upper limit of the sizes of the aggregates was not 2 mm, but 1 mm. Moe, et al (1971) made studies on the effects of using finer-sized soil samples and found that the finer ones had greater modulus of rupture than the coarse ones. This does not hinder the determination of modulus of rupture of various cation-saturated soils because all samples were pulverized to the same degree of fineness and a legitimate basis of comparison was still present.

2. The use of glass-fiber filter paper instead of plain blotting paper prevented the soils from sticking to the paper upon drying.

3. Some soils were soaked for more than an hour (e.g., Li^+ - and Na^+ -saturated soils were soaked for two hours) if they wetted slowly.

4. A single weighing after thorough drying in a dessicator was done instead of weighing to constancy. This eliminated unnecessary dis-

turbances which might alter the magnitude of forces holding the particles together.

Extensive tables showing the results of the modulus of rupture determinations may be found in the Appendix.

Graphs of modulus of rupture, modulus of rupture per unit weight of sample and shrinkage averages of five determinations versus different parameters are shown on the following pages. Fig. IV.4 shows how washing the soil evidently increased the modulus of rupture. Water destroyed some aggregates and dissolved some of the aggregating agents. Repulverization through grinding also decreased the aggregate sizes. The modulus of rupture of soil fractions were such that washed soil > clay > silt >> sand. If observations are made from modulus of rupture per gram sample values, clay > washed soil > silt >> sand. The weight of the sample might have entered into the modulus of rupture values; a heavier sample containing more particles involved in bonding would have a higher modulus of rupture.

The high surface area of minute particles like clay and silt allow these particles to participate in more effective bonding. This is why crusts of clay and silt are stronger than those of sand. Clay and silt are mainly clay minerals, oxides and very fine organic matter, while sand is quartz. Most clay minerals exist as plate-like crystals with or without oxide coatings; sand particles are irregular in shape. The size and shape of particles greatly influence their behavior. It is well known

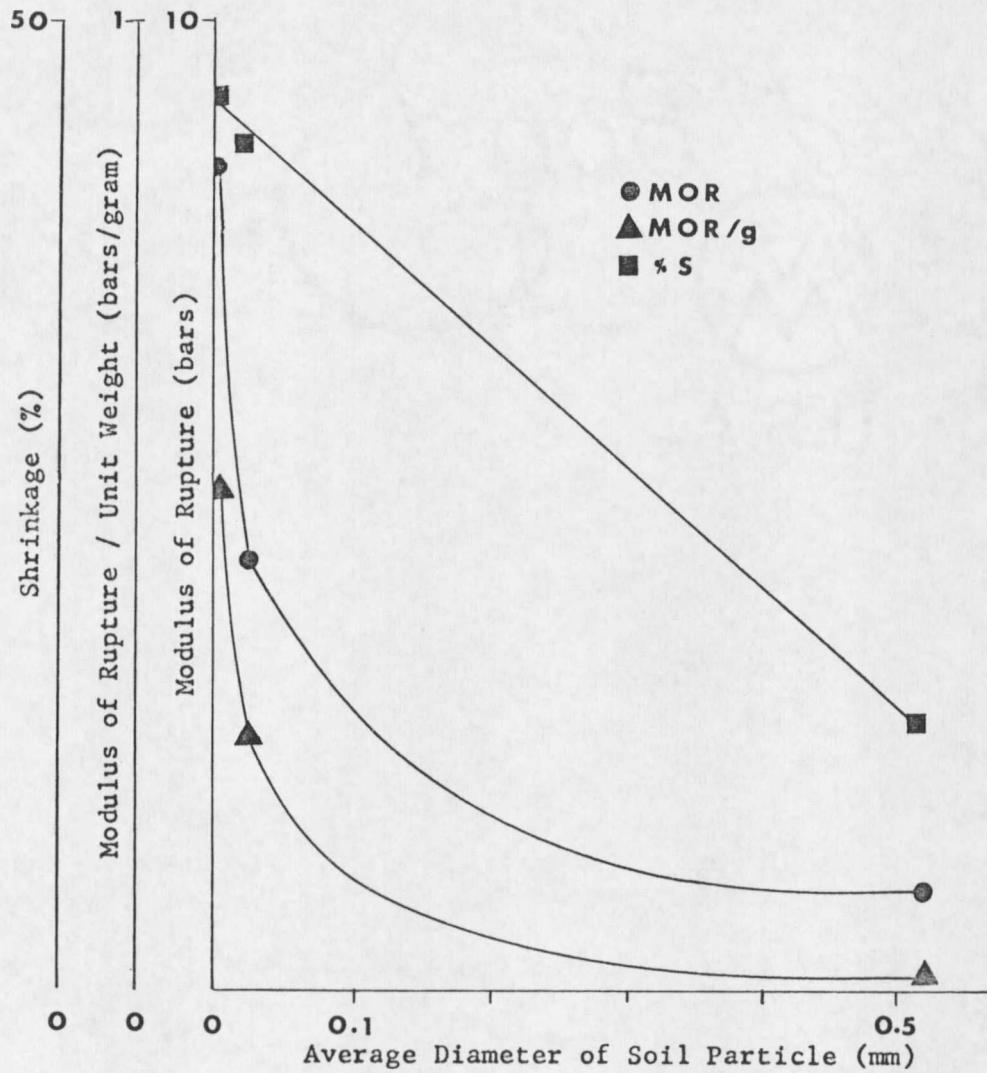


Figure IV.4 - Binding Force Relationships among Different Size Particles in Pylon Soil.

that small particles of a given weight have a greater surface area and more colloidal properties than large particles of the same weight. In comparing shapes, plate-like solids are usually more effectively brought closer together and held tighter than rough, irregular ones. More surface area is involved in plate-like systems.

Silt and clay seldom exist as individual particles in well-aggregated soils; they act as binding agents in the formation of wind-resistant clods (Chepil, 1955). Clodiness in certain soils was greatest with the soil fraction 0.005-0.010 mm in diameter and decreased as the particle size increased or decreased beyond this range. According to Chepil, mechanical separates greater than 0.10 mm in diameter were lower in crust strength than finer ones, and the bulk density of surface crusts was greater than that of the soil beneath. Crusts of mixtures with more clay-silt content than sand had greater strength than those with low clay-silt content (Gerard, 1965). Moe, et al (1971), working with the crusting Pylon soils of Montana, found that a higher silt content in soil contributed to a more solid crust, that is, cracks were absent. A higher clay content in the soil would allow more shrinkage, and consequently, more cracking. Seedlings would emerge to the surface through the cracks. If, however, crusts in clayey soils fail to crack, a worse situation than is encountered in silty soils, is expected.

Clays of the expanding lattice type are more apt to crust. This was found by Lemos and Lutz (1957) who related montmorillonite content to

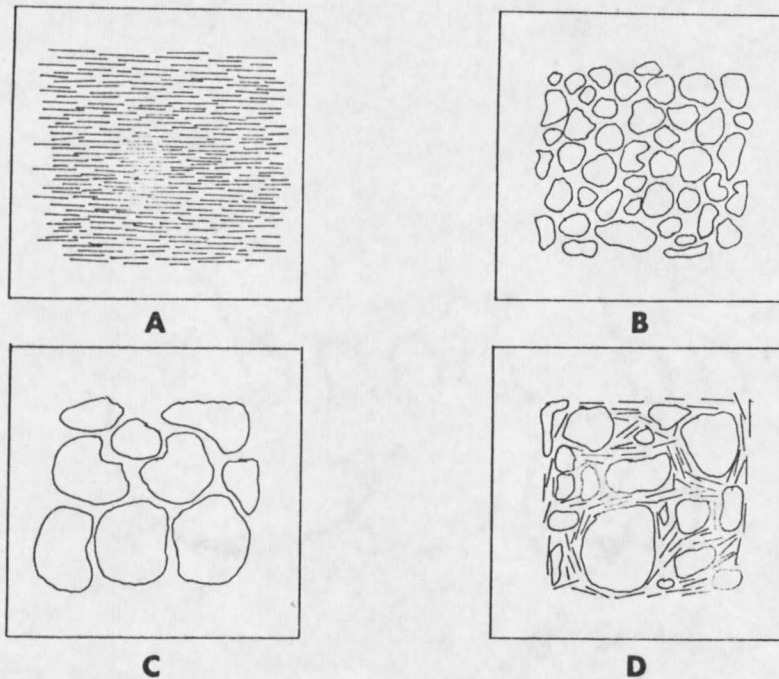


Figure IV.5 - Schematic diagram of how particles in different soil fractions could come close together and form crusts. A, in clay; B, in silt; C, in sand; and D, in soil. Surface contact among small, plate-like particles is more complete than contact among large, irregularly-shaped particles. The extent of contact among the particles in a heterogeneous mixture of clay, silt and sand is expected to be intermediary.

crusting. More montmorillonite was found to cause more crusting in a soil.

Differences in the modulus of rupture of various size soil particles uphold the hypothesis that the presence of aggregates in a soil system prevents the formation of hard crusts. It is also indicated that the consolidation of small size particles is of a more compact nature than the consolidation of large size particles. The former leads to a higher breaking strength. A visual representation of how clay, silt and sand parti-

cles might come close together and contribute to their respective modulus of rupture values as compared to naturally-occurring soil is shown in Fig. IV.5.

One reason for the differences in crust strength of soils saturated with different cations is the size of the saturating cation. Clay particles have flat surfaces; when the distance between the plates is small compared to their thickness, the mutual potential energy of attraction among particles is inversely proportional to the square of the distance between the plates⁴. If adsorbed cations are to stay between the plates, their sizes upon dehydration would surely influence the strength of this potential energy of attraction between the plates (Fig. IV.6).

The unhydrated sizes of the cations used in this study are given in Table IV.

Under a group of elements in the periodic table, ionic radius increases as atomic number increases. As ionic radius increases, the potential energy of attraction decreases. Along a period of elements in the periodic table, ionic radius decreases and as could be noticed, the modulus of rupture decreases. This apparent discrepancy will be discussed later.

Electrostatic attraction between the negative and the positive species of a clay system is assumed to depend on the radius of the posi-

⁴D.J. Alner (ed.), Aspects of Adhesion, Vol. II, Proceedings of the Conference Held at Northampton College of Advanced Technology, EC1, on 23 and 24 March 1964 (London: University of London Press, Ltd., 1966).

Table IV - Unhydrated Sizes of Saturating Cations⁵

ion	radius (Å)
Li ⁺	0.68
Na ⁺	0.98
K ⁺	1.33
Mg ⁺⁺	0.65
Ca ⁺⁺	0.94
Al ⁺⁺⁺	0.45
Fe ⁺⁺⁺	0.53

tive species and the distance between the center and the surface of the negative species. The observations from the modulus of rupture studies can be made to fit the generalized formula

$$F = k \frac{e_a \cdot e_c}{(r_a + r_c)^2}$$

where F = electrostatic or Coulombic attraction; k = a constant of attraction; e_a and e_c = charges on the anion and cation respectively and r_a and r_c = distances from the center of the clay particle to the surface of the clay particle and the radius of the cation respectively. As the radius of the cation increases, the force of attraction decreases.

⁵F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry - A Comprehensive Text (New York: John Wiley and Sons, 1962), p. 43, Table 2-3.

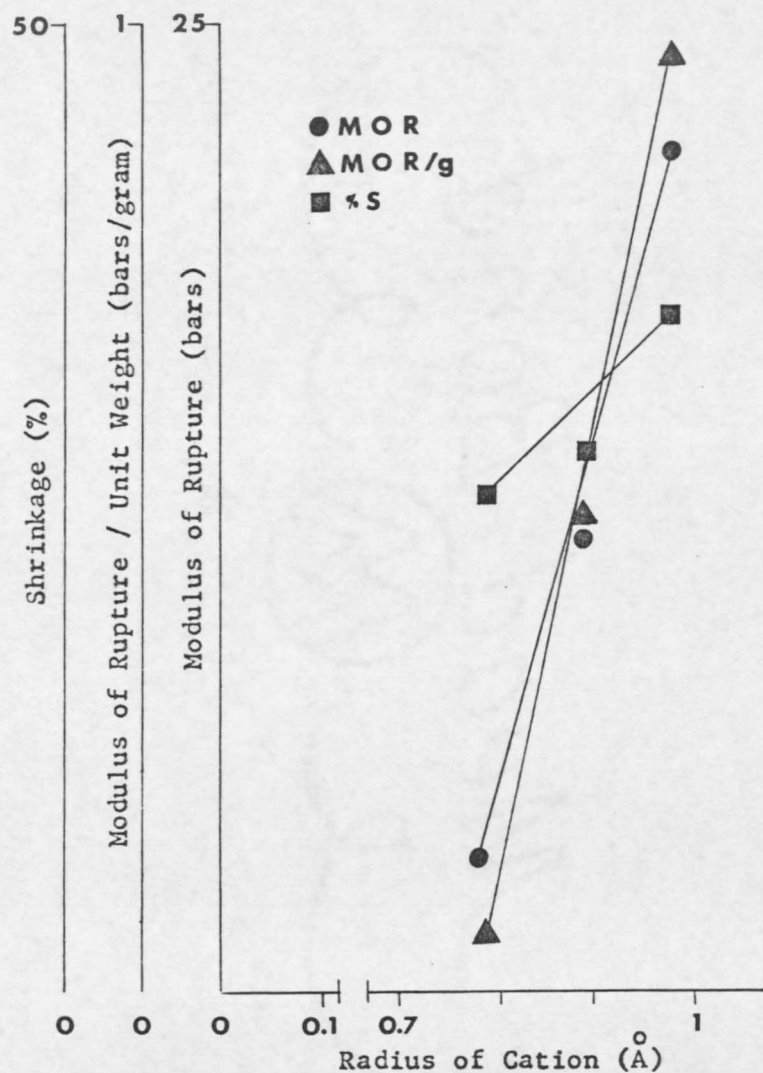


Figure IV.6 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Radius of Cation Relationships.

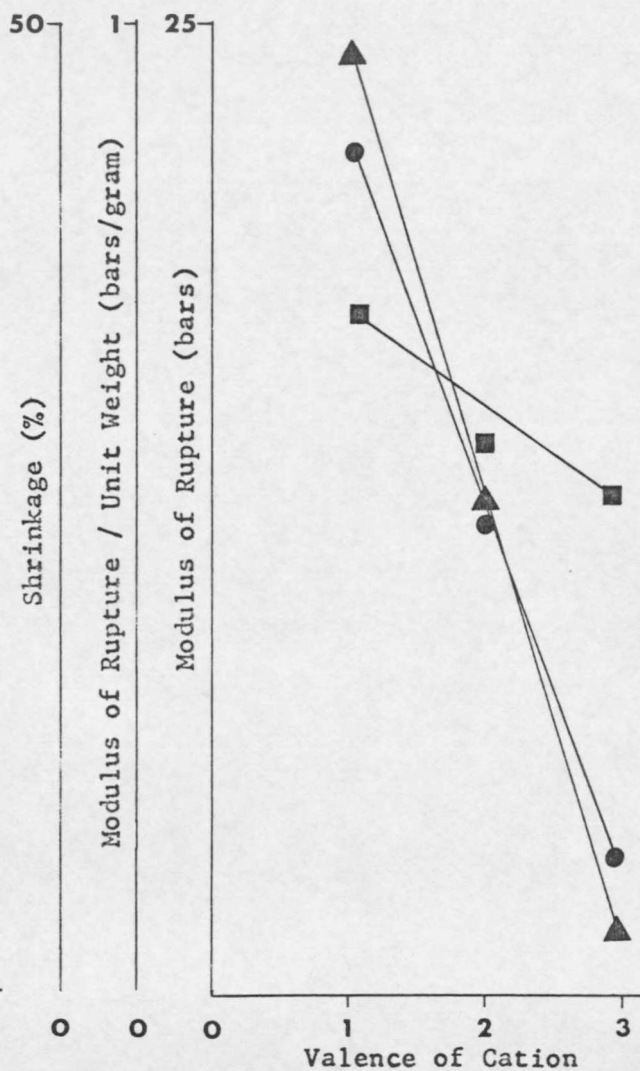


Figure IV.7 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Valence of Cation Relationships.

The net negative charge on the clay particle surface would be more effectively neutralized by higher-charged cations than lower-charged ones. Comparing Na^+ and Mg^{++} (+1, 0.98 Å and +2, 0.68 Å respectively), it would be expected that Mg^{++} would make a stronger crust than Na^+ by looking at the ionic radius alone. However, due to the charge on Mg^{++} , more effective aggregation is caused than if Na^+ were present (Fig. IV.7).

The potential energy of attraction and charge relationships are mathematically represented by the Born equation⁶:

$$\text{P.E.} = \frac{z_1 z_2 e^2}{d} + \frac{be^2}{d^n}$$

where z_1 and z_2 = charges of the cation and anion respectively (note: the anion in this case is the clay particle); e = charge on the electron (= 4.8029×10^{-10} e.s.u. = 1.6021×10^{-19} coulomb); d = distance between the nucleus of the cation and the nucleus of the negative species; n = Born exponent and b = repulsion coefficient. Potential energy P.E. is positive when d is small and increases as z_1 increases. An average value for n (value for cation and clay particle) is used to account for the differences in electron densities of both the positive and negative species⁶. If cation-saturated clays are considered to form a single crystal structure, b could serve as a constant characteristic of all cation-saturated clays.

⁶ B.E. Douglas and D.H. McDaniel, Concepts and Models of Inorganic Chemistry, (New York: Blaisdell Publishing Co., 1965).

The Born equation accomodates the differences observed in the modulus of rupture values of various cation-saturated soils. The potential energy P.E. is assumed to represent the interparticle forces within an aggregate. In explaining why Na^+ -saturated soils require a higher breaking force than K^+ -saturated soils, it is apparent that by looking at the sizes of both ions, the term d for Na^+ is smaller than for K^+ . Therefore, P.E. is higher for Na^+ -saturated soils than for K^+ -saturated soils. In comparing Na^+ to Ca^{++} (note: Na^+ and Ca^{++} are almost identical in size) as to the magnitude of the potential energy binding the particles to the cations, it would seem that Ca^{++} -saturated soils would yield a greater P.E. value. There is a tendency to rashly assume that Ca^{++} -saturated soils should have a higher modulus of rupture value than Na^+ -saturated soils, though modulus of rupture is actually lower for the former than for the later. This is the same discrepancy mentioned before for Na^+ and Mg^{++} , and leads to the question as to which bonding forces modulus of rupture breaks. Actual data (Appendix) show that Ca^{++} lowered the breaking strength of soil briquettes. If the modulus of rupture values are lower, the bonds broken must be weaker. It is therefore suggested that in Ca^{++} -saturated soils, and in other divalent cation-saturated soils for that matter, interparticle bonds are stronger and what modulus of rupture measures are the weaker forces that bind the aggregates of particles together. This reasoning can be extended to include the potential energy of attraction in trivalent cation-saturated soils.

In turbidimetry, when the system is in suspension, a Mg^{++} -saturated clay is dispersed to a certain extent. The behavior exhibited is very similar to a Na^{+} -saturated clay system. This could be explained by the hydration of cations: the smaller a cation, the more hydrated it is. Looking at Table IV for the radii of Na^{+} and Mg^{++} , the value for Mg^{++} is actually lower than the value for Na^{+} . However, the hydration of Mg^{++} is compensated for by its charge. In modulus of rupture, the unhydrated sizes of the cations are taken into consideration.

One of the earliest researchers on this behavior of sodium and other cations on soil crusting was Carnes. Carnes (1934) reported that alkali and sodic soils produced stronger crusts than normal soils. Modulus of rupture was higher in sodium-saturated soils than in potassium-saturated soils (Reeve, et al, 1954).

The interaction between different cations and clay surfaces are described earlier in this paper. In the dehydration process, cations become more and more oriented and confined towards the clay surface. They approach the negative charges they are neutralizing as closely as possible and "fit" into the hexagonal hole created by the silica tetrahedrons (cations compensating for lattice imbalance would tend to take a position as close to the negative charge as possible, Mering and Glaeser, 1954). The ease with which ions could fit into the oxygen hexagon is shown by a representation in Fig. IV.8.

The smaller the cation, the thinner the electron shell is

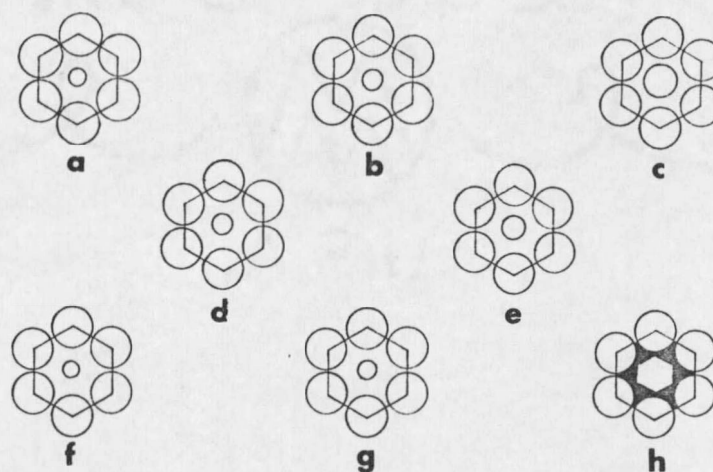


Figure IV.8 - Various cations and the oxygen hexagon. a, Li(+1); b, Na(+1); c, K(+1); d, Mg(+2); e, Ca(+2); f, Al(+3); g, Fe(+3) and h, unshaded portion represents a distance of 2.76 Å (side to side). For sizes of cations, refer to Table IV.

and the easier would the positive charge of the nucleus be available for positive-negative interactions with the negative clay surface. Although some divalent and trivalent cations are smaller than some monovalent cations, higher positive charges make polyvalent cations reside at the vicinity of not just one point charge but at a region where their charges are satisfied.

Monovalent cations could neutralize only a unit negative charge. Particles of Na^+ - or K^+ -saturated montmorillonite in a soil stack up on top of each other when dry, in a manner analogous to the arrangement of sheets in muscovite. A very high modulus of rupture was expected for muscovite. A value of 23,070.58 bars was obtained as an average. The use of excessive volumes of water is not only impractical but also almost un-

feasible. To compensate for this drawback, the quantity d in the formula $S = \frac{3}{2} \frac{Fl}{bd^2}$ was decreased. A second drawback was the flexibility of thin sheets of muscovite. This problem was lessened by decreasing the distance between the parallel supporting bars of the briquette-breaking apparatus.

Only a rough estimate of the modulus of rupture could be obtained for muscovite because of the contributions of shear and other related interactions. It was observed that although the balance swung indicating a break in the sample, the halves of the sample never detached completely from each other. Breaks were also found in spots which were lying on top of the supporting bars. Despite these difficulties, high modulus of rupture values (see Appendix) would place muscovite in a position above all soils in the order muscovite $\gg$ pressurized K^+ -saturated clay $>$ naturally-occurring soil crusts of Pylon soil.

Compression of K^+ -saturated soil increased its modulus of rupture by nearly a factor of two. A value of 16.72 bars was obtained as an average. It would seem that if application of higher pressures on montmorillonite were feasible and would actually happen, compressed K^+ -saturated montmorillonitic soils might attain a modulus of rupture value close to that of muscovite.

A slight upward curling in the Li^+ -, Na^+ - and K^+ -saturated soil briquettes indicates parallel stacking of clay plates. Curling is only possible in disc-shaped or plate-shaped particles and would occur after baking.

Divalent cations go into a position nearest the negative charges they neutralize, in a manner shown in Fig. IV.9. Clay particles and divalent cations arrange themselves in such a way that a cation is held between two hexagonal holes having a net charge of -2.

Curling was not observed in divalent cation-saturated soil briquettes.

Due to the phenomenon of aggregation, there is an increase in the size of floccules in these systems. On drying, extensive stacking does not occur because of the irregularity in shape of an individual aggregate. As in sand particles, weak bonds lead to the formation of planes of weaknesses throughout the entire crust which make such crusts easier to break. As in clay particles, strong interparticle bonds (within an aggregate) allow the modulus of rupture breaking force to break the weaker inter-aggregate bonds.

A consideration of the formation of Al and Fe hydroxides on clay-particle nuclei enters this phase of the discussion. It is suggested that hydroxide gels entrapping the particles dehydrate to the respective oxides and cement the particles in an aggregate. The formation of larger aggregates creates weaker bonds between aggregates and more planes of weaknesses. These make the crusts the easiest to break.

A schematic diagram of all three crusts is shown in Fig. IV.9.

One can now visualize an inner and outer force bonding the particles and aggregates in a soil crust respectively. The inner force is defined

by Born's equation and could be described as the electrostatic attractions between cations and oxides on one hand and clay particles on the other. The outer force could be the cohesion between particles and aggregates, or aggregates among themselves. The non-aggregating properties of monovalent cations leave the original sizes of the particles unchanged and since the particles remain small, the cohesive forces remain strong.

Cation-bridge type of bonding between divalent and trivalent cations and clay surfaces are stronger than cohesive forces between aggregates. These aggregates are larger in size compared to a single particle and less surface area is available for cohesive interactions. The fact that modulus of rupture values of aggregated soils are lower than those of unaggregated soils indicates that weaker cohesive bonds are broken.

The maxima in the modulus of rupture - added electrolyte concentration and modulus of rupture/unit weight - added electrolyte concentra-

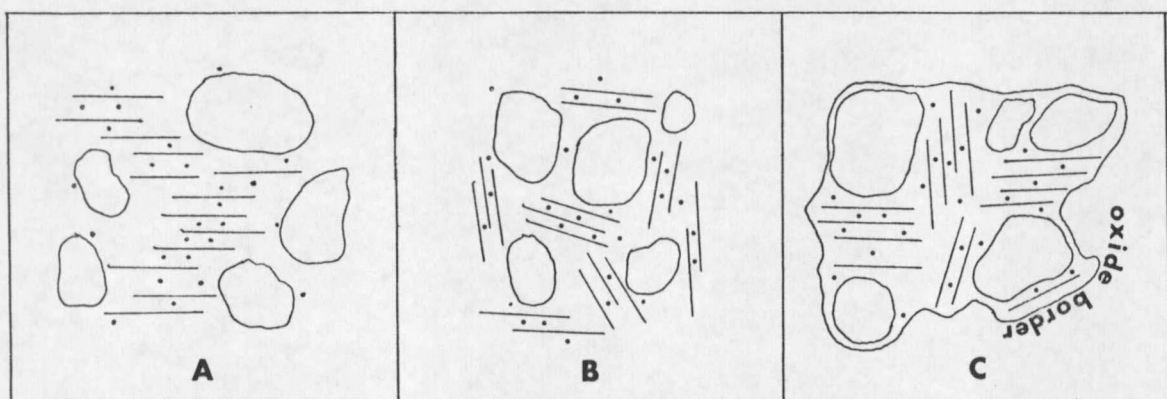


Figure IV.9 - A, stacking in a $\text{Li}(+1)$ -, $\text{Na}(+1)$ - or $\text{K}(+1)$ -saturated soil crust; B, in a $\text{Mg}(+2)$ - or $\text{Ca}(+2)$ -saturated soil crust; and C, in an $\text{Al}(+3)$ - or $\text{Fe}(+3)$ -saturated soil crust. Straight lines represent clay particles and dots are cations. Irregularly-shaped figures are silt and sand.

tion for soils saturated with Na^+ . Before these maxima are reached, the soil still contains cations unreplaced by Na^+ . A crust with a lower strength than the maximum is thereby obtained. After these maxima, the excess electrolyte act to repress the thickness of the double layer, lowering the zeta potential and consequently, the crust strength upon drying.

Although the double layer exists only in suspensions and therefore pertains only to the relations between cations and clay surfaces in a water system, the influence of the double layer is exerted on a dry soil system through a capacity to order or disorder particles. While still in water, the particular manner in which particles are arranged would be reflected by the magnitude of the force necessary to break the dried crust.

Reeve, et al (1954) expressed the relationship between modulus of rupture of Na^+ -saturated soils to the percentage of exchangeable Na^+ present in the system with the equation $y = mx + b$. y represents the modulus of rupture, m , the slope of the line, and x , the percentage of exchangeable Na^+ . This is presumed to occur before complete saturation of exchange sites on the clay surfaces; continuous incremental addition of Na^+ would increase the modulus of rupture until a particular point is reached. This point represents the maximum concentration of Na^+ that would cause the greatest modulus of rupture value and beyond this limit, the modulus of rupture would start to decrease upon addition of more Na^+ .

This last portion of the argument is what is supposed to have happened in the experiment, the result of which are in Fig. IV.10. The line can be described by the equation $y = -mx + b$ where y = modulus of rupture, x = concentration of exchangeable Na^+ and b = a parameter characteristic of the soil properties.

In the phosphate study (Fig. IV.11), it is believed that the lowering in crust strength was caused by one or more of several factors. $(\text{NaPO}_3)_6$ behaved like a polymer; its oxygens being available for H-bonding with $-\text{OH}$ groups on the clay surface and its sodium partially bonded with the negative sites. Several particles could be bonded together throughout the entire chain and can cause aggregation and disorientation. A second speculation would involve the same effect as in added electrolytes. It should be remembered that the addition of $(\text{NaPO}_3)_6$ involves the addition of Na^+ . Na^+ in $(\text{NaPO}_3)_6$ could have acted as excess electrolyte which could lower the crust strength as a result of the repression of the double layer thickness while in water suspension.

Phosphoric acid and monocalcium phosphate in small amounts (50-100 ppm) were effective in lowering the crust strength of soils (Lutz and Pinto, 1965). It was proposed that the formation of aluminum and iron phosphates and the consolidation of soil particles by these complexes were the reasons why crust strength of these soils was lowered. Small increments of phosphoric acid produced microaggregates as a probable result of particle linkage by the phosphate ion (Lutz, et al, 1960).

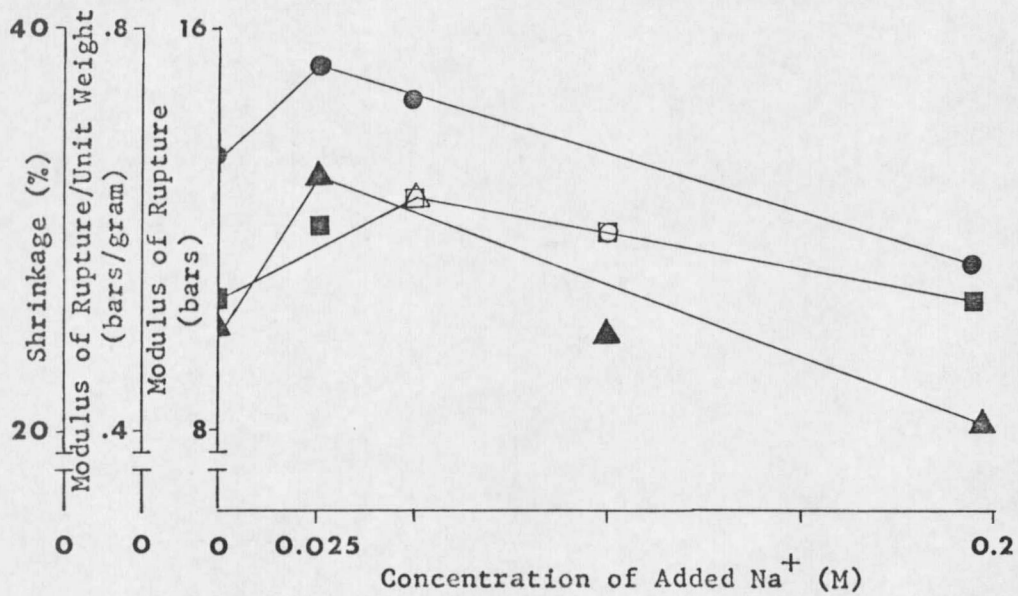


Figure IV.10 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Concentration of Added Electrolyte Relationships.

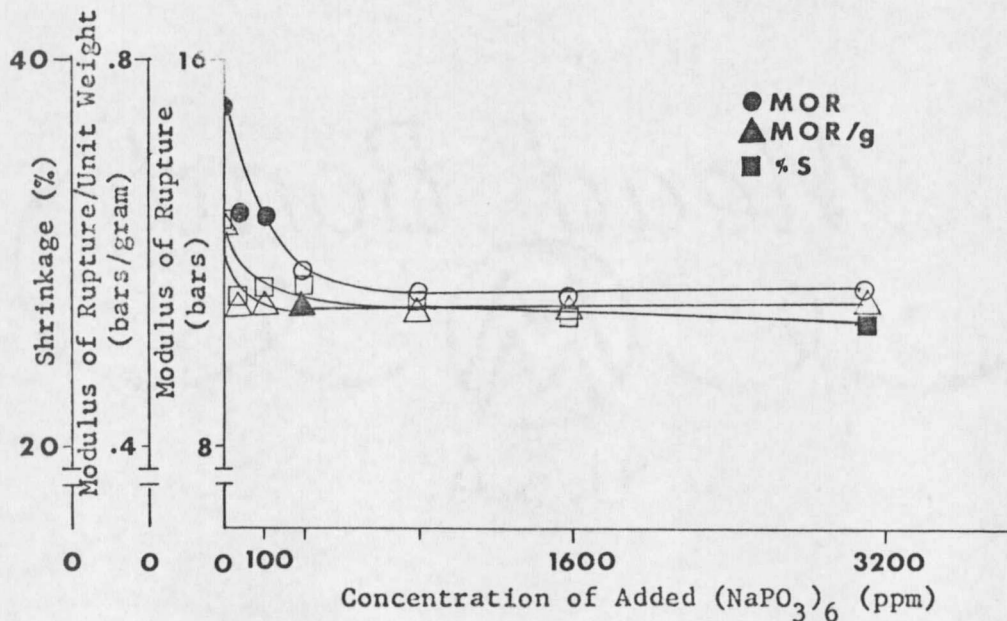


Figure IV.11 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Concentration of Added Phosphate Relationships.

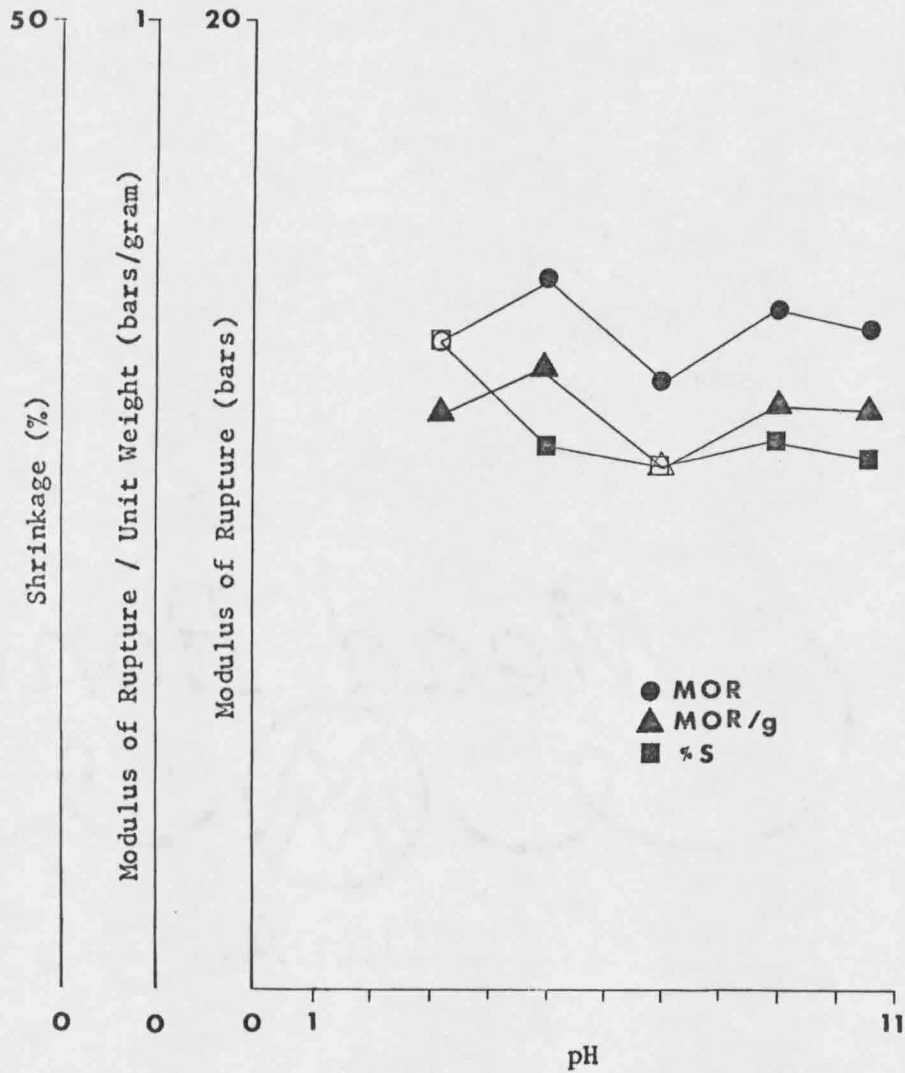


Figure IV.12 - Modulus of Rupture, Modulus of Rupture/ Unit Weight and Shrinkage, and pH Relationships.

However, the addition of phosphoric acid and monocalcium phosphate to a soil has its complications. The H^+ ion dissolves aluminum probably from aluminum oxides and hydroxides from the soil, or even aluminum from the octahedral layer. As a whole and depending upon the degree of dissolution of aluminum, the clay particles behave as if they were saturated with Al^{+++} . One of the manifestations of an Al^{+++} -saturated soil is the low modulus of rupture upon drying. Similarly, and again depending upon how much Ca^{++} is dissolved from monocalcium phosphate, the lowering of the modulus of rupture of soils with monocalcium phosphate might be due to the Ca^{++} and not to the phosphate ions.

The idea behind the pH study is the effect of increasing the positive and negative charges on the clay particles. It is a well-accepted notion that at lower pHs, an excess of positive charges exists and at higher pHs, an excess of negative charges exists. At both instances, the presence of similar charges should lower the crust strength of a dried sample. Since the changes in modulus of rupture did not reflect this, it is believed that there were side effects contributed by the H^+ and the Na^+ ions (Fig. IV.12).

Changes in pH might affect the Al and Fe oxides that might be present in the soil. It is the amphoteric behavior of these oxides which contributes to the buffer capacity of oxide-rich tropical soils (Sumner, 1963). At low pHs, iron hydroxide seems to be sorbed more readily on clay surfaces but with some clays and in some circumstances, sorption could

occur irrespective of the pH of the surrounding medium (Greenland and Oades, 1968). The commonly observed phenomenon of increasing positive charges at low pHs and increasing negative charges at increasing pHs was also presented by Deshpande, et al (1964) in their study of the effects of synthetic iron and aluminum oxides on the charges of soils and clays. Chesters, et al (1957) concluded that pH has little or no effect on soil aggregation. Evidently, most natural soils are neither too alkaline nor too saline for investigators to suspect low-charged cations to be the sole cause of crusting. Pylon soils that crust have a pH range of 5.6 to 7.3 in comparison to a range of 6.6 to 7.8 for other soils in the area (Clark, 1971).

Apparent discrepancies in the modulus of rupture of soils where sand has been added are due to the use of sand of a range of sizes and not just of a particular size. However, the modulus of rupture was greatest for soils without added sand. Modulus of rupture of soils with added fine sand (320-325 mesh) was greater than the modulus of rupture of soils with added coarse sand (60-120 and 50-200 mesh). The increase of interparticle distances upon addition of an inert material like sand affects the modulus of rupture, following the same line of reasoning as in increased interparticle distances due to aggregation (Fig. IV.13).

Al_2O_3 is considered an inert and fairly insoluble material. It would be expected that the behavior of soils upon addition of Al_2O_3 would mimic that of the addition of silica sand. The graph on Al_2O_3 percent

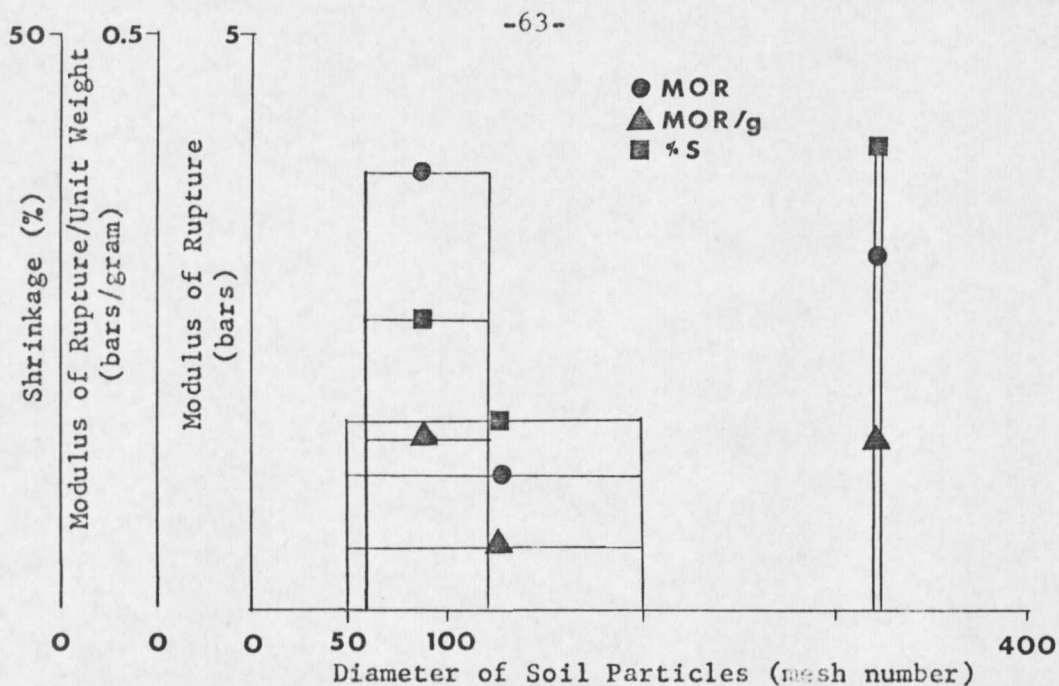


Figure IV.13 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Diameter of Sand Particles Relationships.

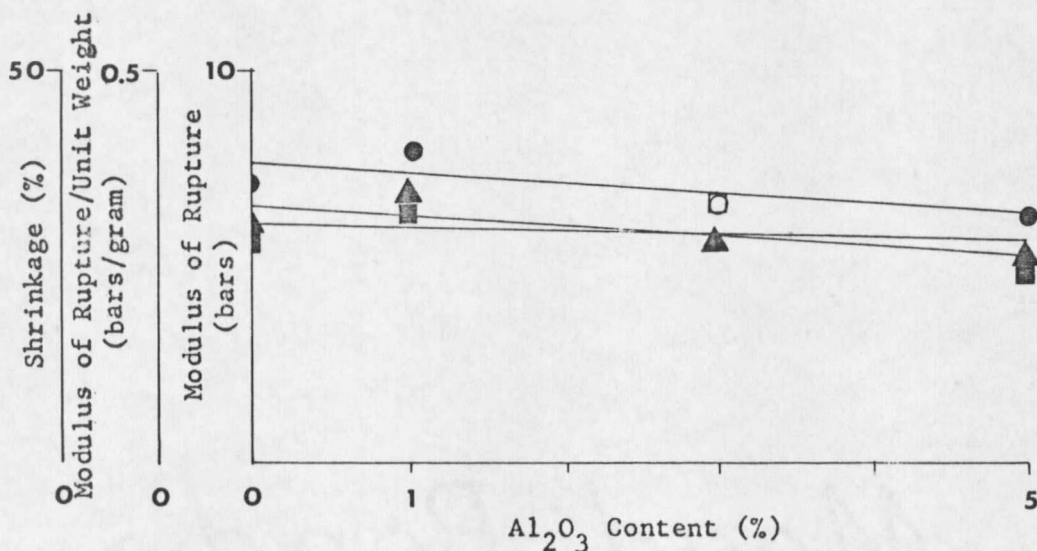


Figure IV.14 - Modulus of Rupture, Modulus of Rupture/Unit Weight and Shrinkage, and Al₂O₃ Content Relationships.

versus modulus of rupture again shows how the size of an inert material affects modulus of rupture due to increased interparticle distances. The decrease in modulus of rupture is greatest when sand or Al_2O_3 are added in large amounts (Fig. IV.14).

The modulus of rupture study had supported the model of soil crusting (i.e., crusting is a step in the reversion of the weathering process) in a number of ways. Crusting as believed to be caused by the arrangement of clay particles in the soil in a manner analogous to sheets of muscovite was shown by the high crust strengths of monovalent cation-saturated Pylon soils and compressed K^+ -saturated Pylon soil (as compared to modulus of rupture values of muscovite sheets). The parallel stacking of clay plates when a system is saturated with monovalent cations was evidenced by the curling of dry soil briquettes containing monovalent cations. Although large crystals of muscovite-like minerals are not formed, compaction by pressurization is assumed to cause higher breaking strengths. Conversely, polyvalent cation-saturated Pylon soil particles aggregate and assume sizes approaching the silt and fine sand category, or larger. As shown by the addition of sand, the increase in size of aggregates discourage compaction and the irregularity in the size and shape of the aggregates do not allow a close proximity when particles (now aggregated) come close together. Thus, low breaking strengths were obtained for soils treated with polyvalent cations.

Shrinkage. The degree of shrinkage of soil material is an indica-

tion of the type of clay mineral present. Montmorillonite, being of the expanding lattice type, would exhibit the greatest shrinkage of the clay minerals. Since Pylon soil is montmorillonitic, a considerable amount of shrinkage is expected.

Shrinkage is inversely proportional to the amount and size of interstitial spaces between soil particles. An indirect relationship between shrinkage and modulus of rupture is recognized in a physical standpoint in that a greater shrinkage of a soil bulk allows a greater compaction and consequently, an increased modulus of rupture. Shrinkage graphs have been shown in conjunction with modulus of rupture graphs.

In an effort to clarify modulus of rupture observations further, similar investigations dealing with strengths of consolidated material are explained:

Ca^{++} -montmorillonite had lower shear strength than Na^{+} -montmorillonite (Warkentin and Yong, 1960). In Na^{+} -montmorillonite, strength appeared to depend upon interparticle repulsion due to the osmotic activity of diffuse ion-layers, while in Ca^{++} -montmorillonite, forces of attraction and repulsion led to a particle arrangement that influenced the strength. They also found that increasing the salt concentration and the valence of exchangeable cations decreased interparticle repulsion and either increased or leaves unchanged the forces of attraction.

The tensile strengths of soils saturated with cations were such that $\text{Fe} > \text{K} \geq \text{Na} > \text{Al} > \text{Ca}$ (Dowdy and Larson, 1971). The controversial

position of iron in the order was suggested to have been caused by the cementation action of hydrous Fe oxides formed during cation saturation. In this arrangement, there is no way of grouping the cations as to the effects of ionic size or valency. An exact comparison between modulus of rupture on one hand and shear strength and tensile strength on the other cannot be made since these three measurements reflect different breaking planes and probably, the breaking of different types of bonding. Modulus of rupture determinations as applied to the soil represent the breaking strength of plantlets as they emerge through the soil to the surface.

Bulk Density. Although a separate chapter is devoted to Bulk Density, values for bulk density using the weights of the briquettes and their volumes as measured with calipers were obtained. Discussion on this will be found in the Bulk Density section. Data can be seen in the Appendix section, separate from the modulus of rupture, modulus of rupture per unit weight and shrinkage tables.

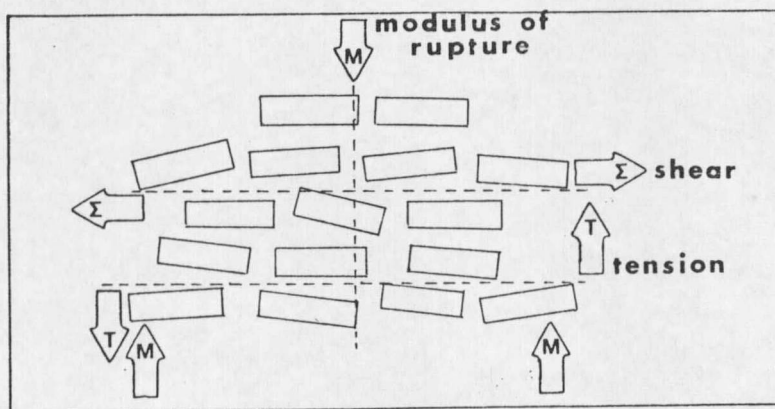


Figure IV.15 - A Comparison between Modulus of Rupture, Shear and Tensile Strengths. Arrows show the direction of applied forces; dotted lines, cleavage or breaking planes.

Chapter V

BULK DENSITY

Materials and Methods

The density of the soil was first determined by the pycnometer method. Two trials were made, one with boiling the sample to expel the air dissolved in the water and letting the sample cool, and another, without boiling the sample.

The formula

$$D_p = \frac{d_w (W_s - W_a)}{(W_s - W_a) - (W_{sw} - W_w)}$$

where D_p = density of the soil particles (in g/cm^3); d_w = density of water at a particular temperature; W_s = weight of pycnometer and soil (in g); W_a = weight of pycnometer; W_{sw} = weight of pycnometer, soil and water; and W_w = weight of pycnometer and water, was applied.

Broken briquettes of soil fractions, unwashed and washed soil, and cation-saturated soils from the modulus of rupture experiments were dessicated for 24 hours. Each briquette and 6-inch (15.24 cm)-long polymer-coated copper wires (with a diameter of 5.615 mils = 0.005615 inch = 0.014262 cm) were weighed. Each briquette was tied with a length of copper wire, reweighed, and dipped in molten paraffin for 15 seconds. The briquette was cooled for a minute, redipped for another 15 seconds, and cooled. Each briquette was weighed in air and in water.

Bulk density B.D. (in g/cm^3) was calculated from the formula

$$B.D. = \frac{W_{bsp} - (W_p + W_s)}{L_{bsp} - (V_p + V_s)}$$

where W_{bsp} = weight of briquettes, paraffin and strings (in g); W_p = weight of paraffin; W_s = weight of string; L_{bsp} = loss in weight of briquettes, paraffin and strings in water; V_p = volume of paraffin (W_p/ρ_p , weight divided by density, in cm^3) and V_s = volume of string (W_s/ρ_s).

Results and Discussion

The bulk density measurements yielded small differences among the different cation-saturated soils, but apparently showed the differences in compaction in soil, clay and silt (see Appendix) such that silt > soil > clay. Aggregation and cementation in clay caused a relatively smaller bulk density value when compared to silt. Air spaces between aggregates cause a low bulk density.

As a relationship is believed to exist between compaction and disorientation on one hand and the strength of crusts on the other, an indication of the sizes of the pores present in a dried soil could be obtained from bulk density measurements as long as the nature of the pores is preserved. Paraffin, by coating the surfaces of the briquettes, is presumed to do this, though the entire method itself may not be sensitive enough to detect small differences in bulk density. Apparent similarity or closeness in the bulk densities of the soils seems to show that very slight changes in bulk density, if any, could cause great changes in modulus of rupture.

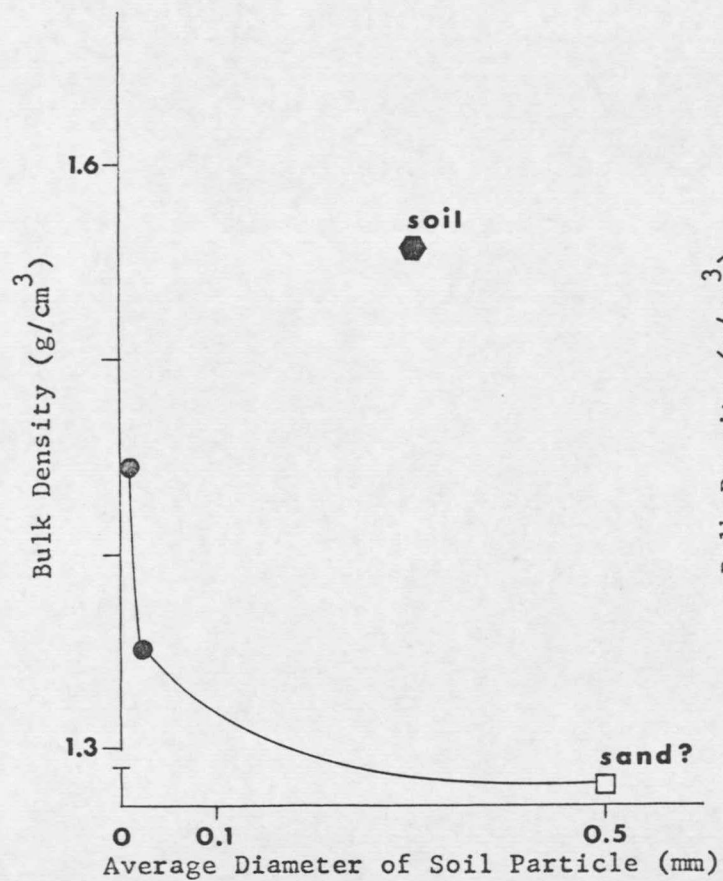


Figure V.1 - Bulk Density Relationships in Different Size Soil Particles.

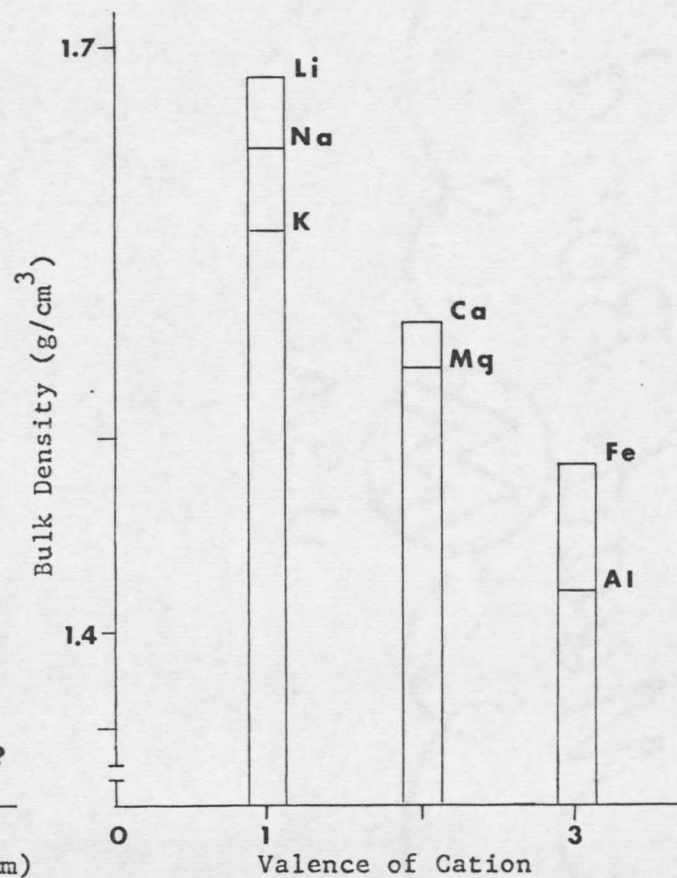


Figure V.2 - Bulk Density Relationships in Cation-Saturated Soils.

The bulk density as computed from the weights and volumes of the briquettes used in modulus of rupture may be found in the Appendix.

Fig. V.1 shows the relationships in soil fractions and Fig. V.2 shows the relationships in different cation-saturated soils.

Compactness could explain the high value for washed soil. Aggregation in clay gave a lower bulk density value, and the large size of silt particles caused an even lower bulk density. The trend for the cation-saturated soils are $Li > Na > K > Ca > Mg > Fe > Al$.

Should there be no real difference among the bulk densities of cation-saturated soils, an explanation as to what could be the mode of stacking of the parallel clay platelets is brought into consideration. Fig. V.3 shows how parallel stacking in monovalent cation-saturated clay differs from parallel stacking in polyvalent cation-saturated clay, yet give similar bulk density values. In congruence to modulus of rupture studies, the parallel stacking in polyvalent cation-saturated clay would indicate the presence of planes of weaknesses (broken lines), which would amount to low breaking strengths.

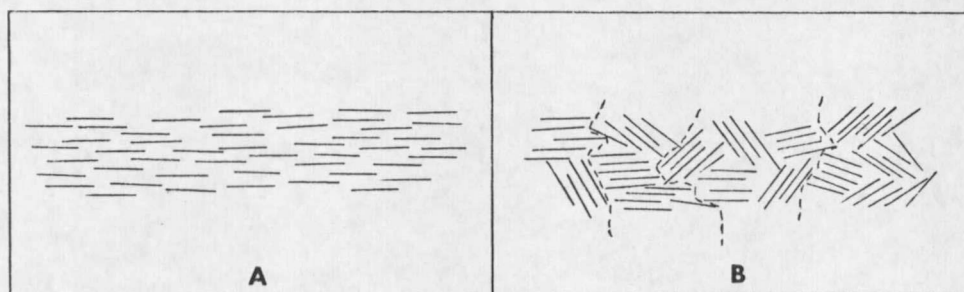


Figure V.3 - Parallel stacking in monovalent cation-saturated clay systems (A) and in polyvalent cation-saturated clay systems (B).

Chapter VI

THIN SECTIONING

Materials and Methods

Briquettes of soil fractions, unwashed and washed soil, and cation-saturated soils from the modulus of rupture experiments were impregnated with plastic¹. Thin slices were made and set in glass slides. The slides were studied under a polarizing petrographic microscope and photographed. The size of the pores and the degree of orientation and aggregation of particles were noted.

Results and Discussion

The visual proof of orientation of particles and aggregation in a soil which forms hard crusts should be seen in any of two methods: microscopy using polarized light and electron microscopy. The former method was employed in this paper. When a thin section of a soil is viewed through a microscope using ordinary light, the largest bodies seen are mineral grains (usually quartz and feldspars) and crop residues. Organic matter and pores appear dark and transparent respectively and are of varying sizes. Individual particles of clay are not seen but a soil matrix consisting mostly of clay appears as very fine fillings between large minerals. Silt is seen as small pellets interspersed with the clay and fine sand in the matrix. Coatings of organic matter or sesquioxides are usually darker than the mineral grains they are enveloping.

¹ Commercially prepared by Cal-Brea, Inc., Brea, California.

When viewed under crossed polarizers (Nicol prisms), particles which are parallel to the plane of polarization of light (0° angle with the plane of polarization) appear dark. Rotation of the microscope stage in such a way that the particles are at a position 45° to the plane of polarization of light brightens the images of those particles. If there is any clay orientation, dark "extinction bands" seem to sweep across the thin section, alternately brightening and darkening as the microscope stage is rotated.

Reproductions of the thin sections under 100x magnification (1 mm particles appear as 10 cm particles) are shown in ordinary light and polarized light. A third picture shows the same sample with the microscope stage rotated 45° . These photomicrographs can be seen in the Appendix.

The appearance of larger particles in washed soil as compared to unwashed soil indicates the loss of some clay particles upon washing. Aggregation is seen in the clay thin section. Definite borders of aggregates are apparent in the micrographs. Grinding did not break the aggregates, implying the good cementing properties of clay. The presence of aggregates could be a reason why the modulus of rupture of clay is greater than the modulus of rupture of washed soil, but not too great as was expected.

Silt appears aggregated to a lesser degree than clay.

The soils saturated with monovalent cations show small and few pores. There is no sign of extensive aggregation in any of these thin sections.

Ca^{++} - and Mg^{++} -saturated soils appear as mixtures of larger particles and some aggregates. Further evidence of aggregates in Ca^{++} -saturated montmorillonite was obtained using electron microscopy (Mathieu-Sicaud, et al, 1951). The aggregates appeared to increase in size after aging for several hours and days. Most interesting is the presence of very large aggregates in Al^{+++} - and Fe^{+++} -saturated soils. They are easily mistaken for mineral grains with a sole exception: a conglomerate suspected to be a clay aggregate would be composed of grains that alternately brighten and darken when the microscope stage is rotated under polarized light; a mineral grain would brighten or darken as a whole. The conglomerates found in the thin sections seem to twinkle as the stage of the microscope is rotated, and are therefore considered as clay aggregates.

The reddish-brown coloration of the iron-clay aggregates is a strong indication that iron oxides had coated the particles and had caused the aggregation. According to electron microscopy studies and data obtained by Greenland and Oades (1968), at pH 7, clay particles are actually observed as to be coated or enveloped by ferric hydroxide gels. Drying had transformed the hydroxides to oxides, still retaining the particles that had been trapped in the initial formation of conglomerates.

These aggregates are presumed to be composed of clay particles, silt and very fine sand held in firm bonding by iron oxides. As such,

an aggregate could act as a single large particle. This is an evidence of "clay domains" observed and explained by Emerson (1959). The intermingling of these large aggregates with the unaggregates silt and sand makes a soil crust behave like a sand consolidate, with low breaking strength. Appearance of planes of weaknesses is also expected, and was actually photographed (Fig. VI).

Evans and Buol (1968) have found numerous horizontally-oriented particles and platy structures along with the absence of large pores in some photomicrographs of natural crusts. The orientation of particles would be expected to contribute to the rigidity of the crusts. Large

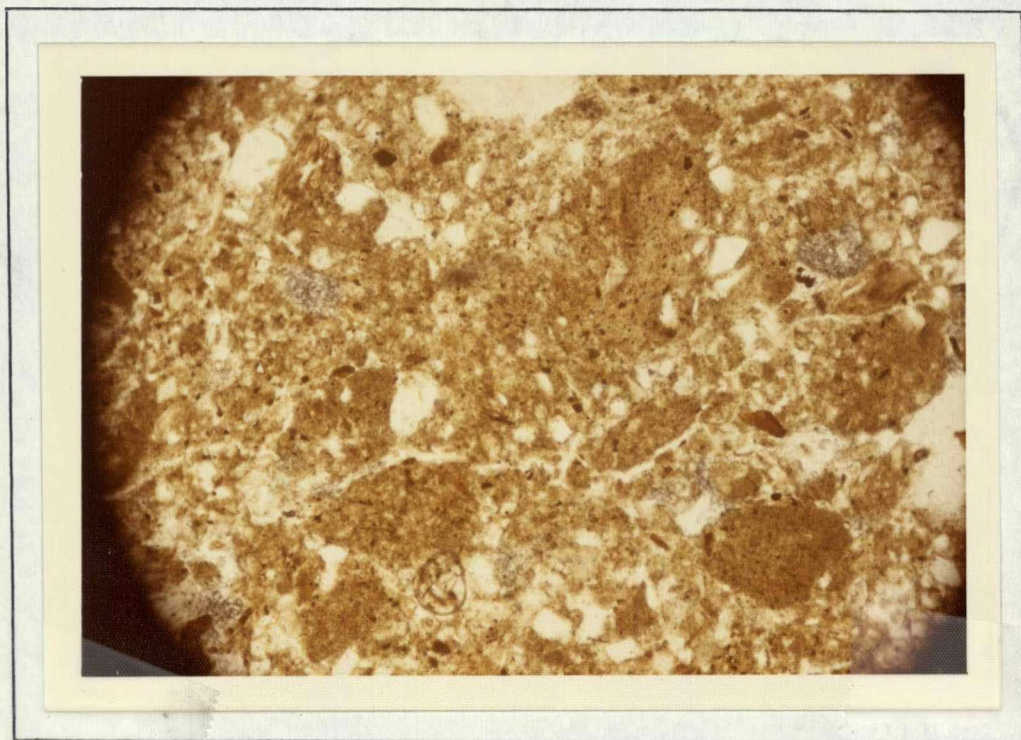


Figure VI - An apparent line of weakness in a soil aggregated by the presence of ferric ions.

pores were present in thin sections of weak crusts and small pores, in thin sections of strong crusts (Moe, et al, 1971).

To a certain extent, the thin sectioning study has shown that soils saturated with monovalent cations are more compact than soils saturated with polyvalent cations. Moreover, if the thought is extended, the particles in monovalent cation-saturated clayey soils are arranged in such a way that less pores are created. This ordering leads to a model of soil crusts approaching the arrangement of sheets in muscovite. On the other hand, the formation of irregular aggregates due to the presence of polyvalent cations, disorient the particles. Particles (now aggregates) which are almost sand-like in proportions, lower the crust strength due to the presence of large pores in between the aggregates.

Chapter VII

WATER AND OXYGEN PERMEABILITY

Water Permeability

Materials and Methods. Briquettes of soil fractions, unwashed and washed soil, and cation-saturated soils were prepared. They were dipped in pans of water and the time required for the water to completely wet the briquettes was recorded. Water permeability was expressed in sec/cm, the dimension of thickness being used.

Results and Discussion. The relationship between the diameter of a soil fraction and the rate of infiltration of water suggests the extent of sealing of the pores. Soil losses and crust formation are consequences of raindrop impact (Epstein and Grant, 1967); pores sealed by smaller clay particles and compaction prevent the seepage of water through the entirety of the soil. Numerous investigations have shown this (Duley, 1939; McIntyre, 1958a and b; Tackett and Pearson, 1965).

Figs. VII.1 and 2 show the water permeability of the samples: sand >> silt > clay; Fe > Al > Ca > Mg > K >> Na = Li. The speed with which water could penetrate a soil stratum, water permeability, as an interplay between surface tension and capillarity, depends upon the diameter of the pores present in a system.

Air and water permeability were lower for Na^+ - than for K^+ -saturated soils (Reeve, et al, 1954). In kaolinite systems, addition of cations influenced water permeability. It was greatest for H^+ -saturated samples, followed by control (Ca^{++} -saturated) > K^+ - > Na^+ -saturated sam-

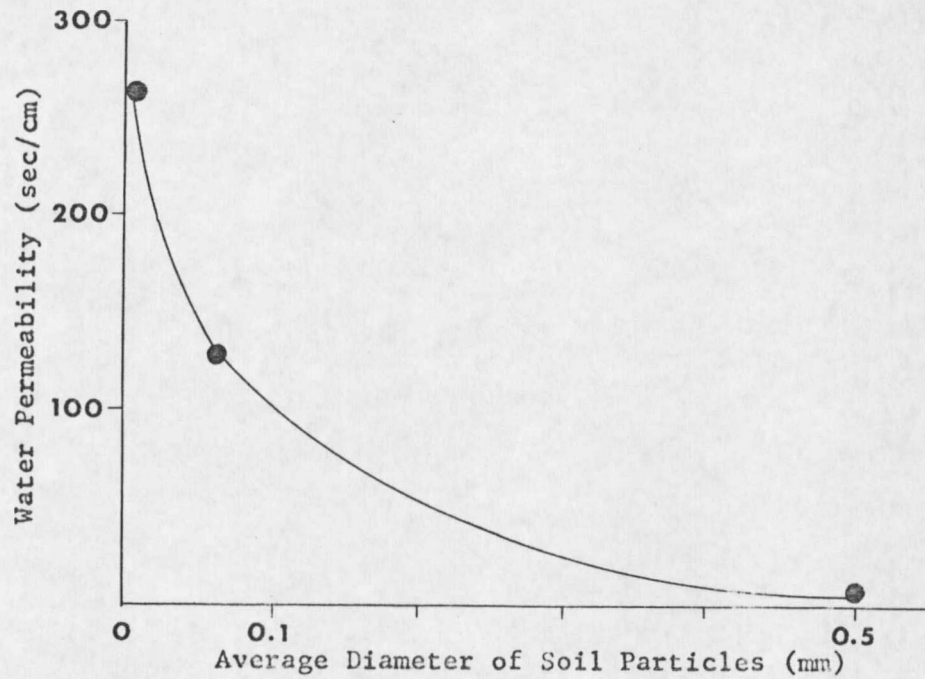


Figure VII.1 - Water Permeability and Size of Particles Relationships.

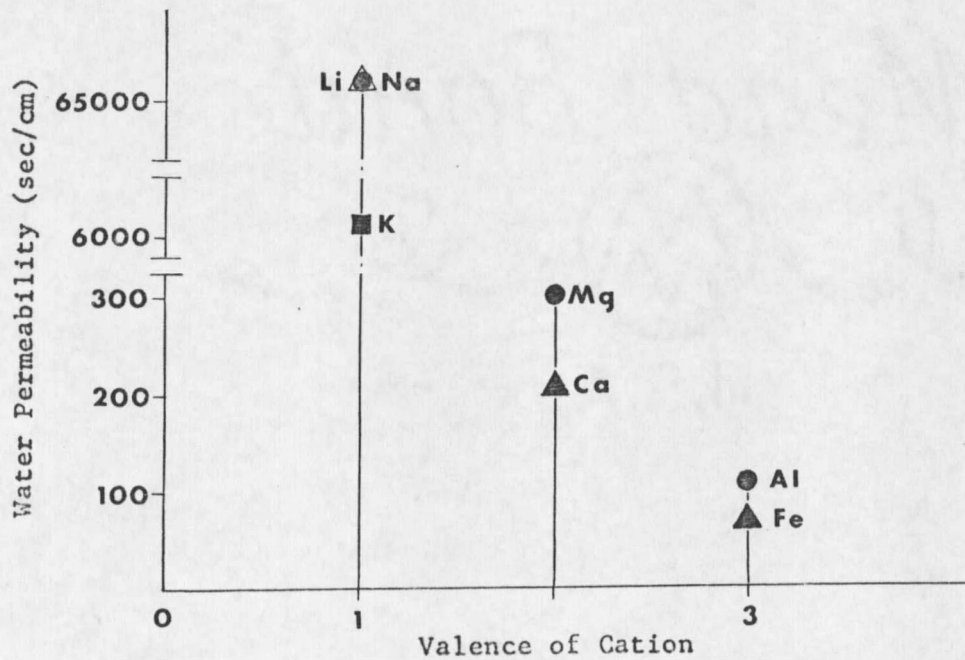


Figure VII.2 - Water Permeability and Valence of Saturating Cation Relationships.

ples (Elgabaly and Elghamry, 1970).

The model of soil crusts with the clay platelets lying horizontally and in parallel configuration is supported by the water permeability results of soils saturated with monovalent cations. Water seepage through the platelets was longer than water seepage through aggregates in random arrangement.

Oxygen Permeability

Materials and Methods. Fig. VII.3 represents the oxygen permeability apparatus used in the experiment. It consists of a diffusion chamber and a Beckmann Model D2 Oxygen Analyzer. The diffusion chamber is a filter flask over which a plastic plate with a hole $2\frac{1}{2}$ cm in diameter has been fused. The inlet of the flask has a 3-way stopcock; one branch was connected to a nitrogen tank and the other, to the sample outlet of the oxygen analyzer. The outlet of the flask has a Y-tube, one branch of which is provided with a 2-way stopcock. The other branch was hooked up to the sample inlet of the oxygen analyzer.

Dessicated, broken briquettes of soil fractions, unwashed and washed soil, and cation-saturated soils from the modulus of rupture studies were mounted, one at a time, on another plastic plate with a circular hole $2\frac{1}{2}$ cm in diameter. All exposed surfaces of the briquette, except those directly lying on top of the hole, were coated with petroleum jelly. The plastic plate-briquette set-up was fitted on the identical plate on the flask. All contact points between the two plates were coated with petroleum jelly.

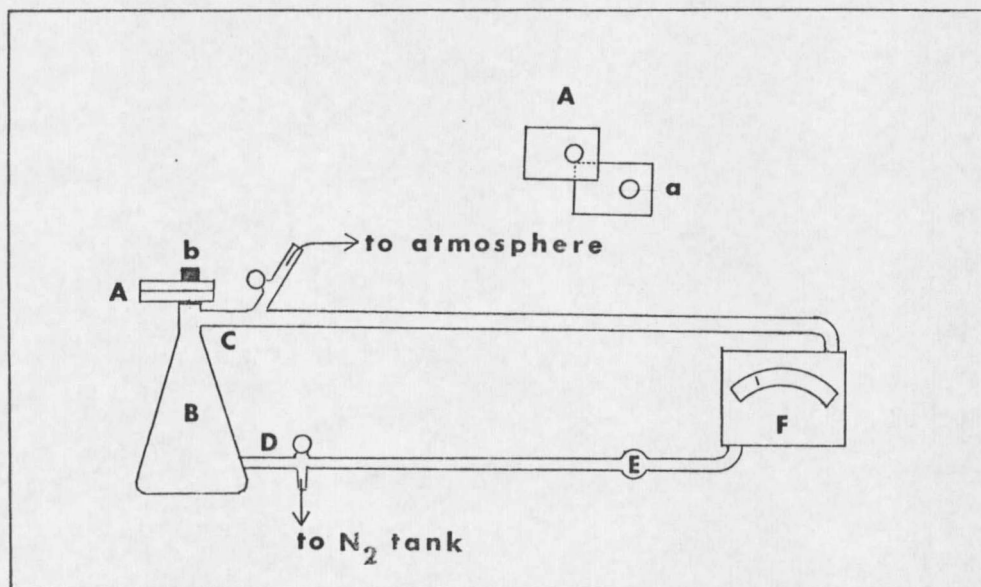


Figure VII.3 - Oxygen permeability apparatus. A, plastic plates; a, holes in plates; b, sample; B, diffusion chamber; C, flask outlet; D, flask inlet; E, rubber bulb for circulating gas; F, Beckmann Model D2 Oxygen Analyzer.

The hole of the plastic plate on the flask can be blocked by sliding the overlying plastic plate-briquette set-up. With stopcocks closed and all connections from the flask to the oxygen analyzer completed, a closed system is produced. Letting nitrogen through the 3-way stopcock and opening the 2-way stopcock flushes air out of the system. Residual oxygen, if any, is detected by the analyzer, which gives readings in mm Hg partial pressure.

The plastic plate-briquette set-up was carefully slid on the plastic plate of the diffusion chamber in such a way that both holes coincided. Air from the outside was allowed to diffuse through the samples, into the chamber for one minute. After the hole has been closed again, the analyzer bulb was squeezed for 30 seconds, at a rate of $\frac{1}{2}$ squeeze/sec.

A reading from the analyzer gave the amount of oxygen present in the system after the operation. The amount of diffused oxygen was taken as the difference between the final and the initial readings.

Oxygen permeability was expressed as atm partial pressure-cm-sec⁻¹.

The experiment was done in a constant-temperature room (37°F = about 3°C) since the rate of diffusion of oxygen into the system is directly proportional to the absolute temperature (Taylor, 1949). The partial pressure of oxygen in the air was determined by letting atmospheric air enter the analyzer. A sample of silt briquette was mounted on the plastic plate and the above procedure was repeated. To check for the validity of the equation

$$\ln \frac{P_o}{(P_o - P)} = \frac{D'A}{\lambda^2} t$$

(where P_o = partial pressure of oxygen in air; P = partial pressure of oxygen in the vessel; D' = diffusion coefficient; A = cross-sectional area of the sample; λ = a parameter with a value of unity when the system is free of soil and when diffusion is allowed to occur over a unit cross-sectional area where the entire area is available to the movement of gases) (Taylor, 1949), readings from this silt briquette were made at 1, 3, 5, 10, 30 and 120 minute intervals. $P_o/(P_o - P)$ values were plotted against t (in sec) in a semi-logarithmic paper, and the shape of the resulting curve was observed.

Results and Discussion. The method used is a modification of an earlier scheme by Taylor (1949).

The rate at which a gas diffuses through a porous medium can be a measure of the permeability of a system. The oxygen permeability of a soil sample gives an idea of the arrangement of particles in the sample. The amount of oxygen as detected by an oxygen analyzer would be small if the particles are oriented in a manner that would not permit the formation of pores and would be great if the particles are disordered in a manner that permits the formation of large pores.

The validity of the experiment is proven in Fig. VII.4, i.e., equilibration of a soil sample to atmospheric oxygen would yield a characteristic curve showing the rate of oxygen permeability. Taylor (1949) had done a similar experiment and had obtained similar results.

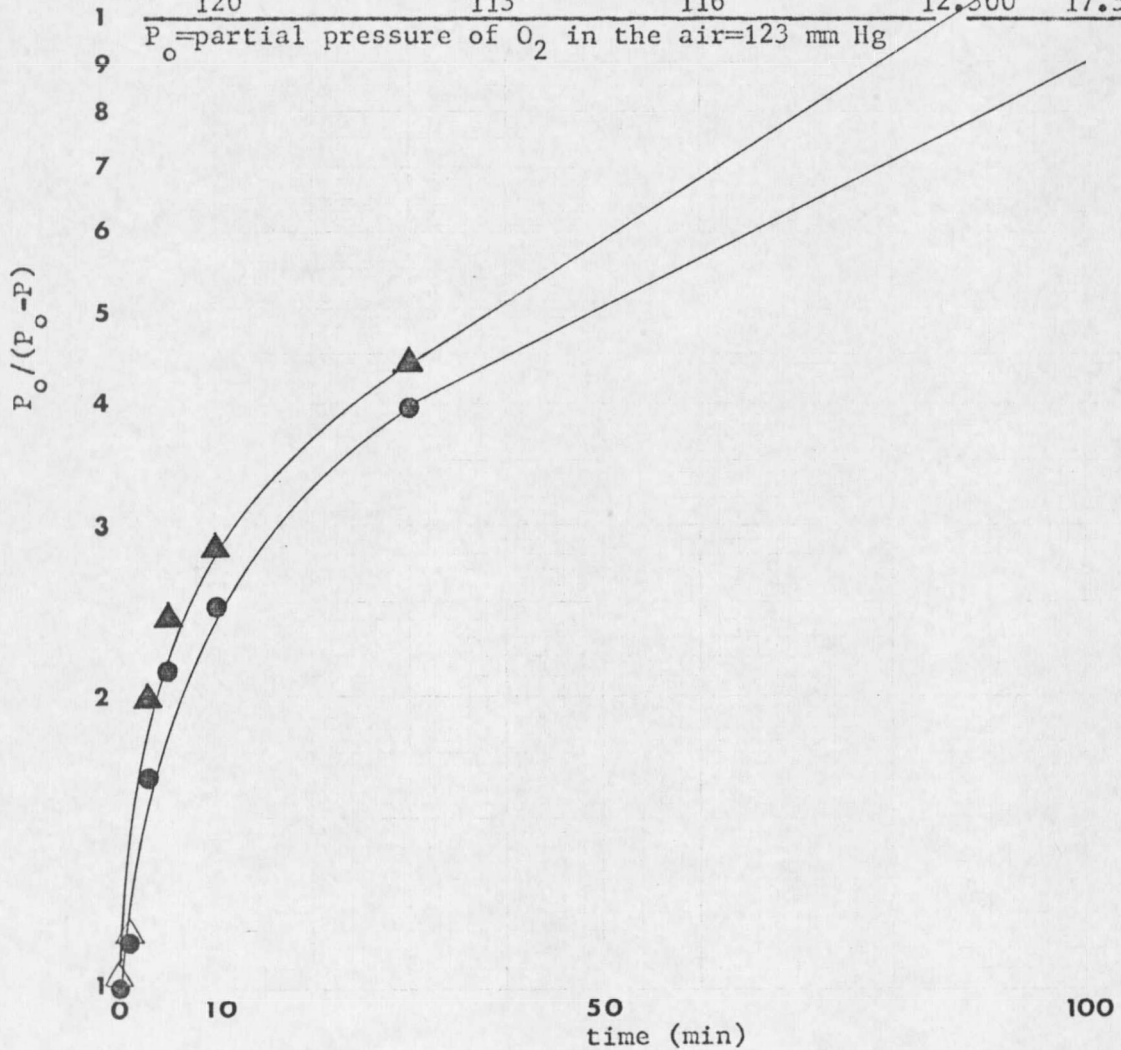
The oxygen permeability of soil fractions and cation-saturated soils are shown in the Appendix. Curves expressing the relationships between oxygen permeability and sizes of particles, and valency of cations are shown in Figs. VII.5 and 6. The general trend among soil fractions and cation-saturated soils is very similar to that obtained from the water permeability measurements.

Bulk density, water permeability and oxygen permeability measurements all point out the presence of pores, or the absence of pores, in a soil system. The model of soil crusting presented was greatly upheld by these three clear-cut determinations. Although bulk density values were

Figure VII.4 - Partial Pressure of O_2 versus Time

Relationships in Silt Crust.

Data				
2	time (min)	Partial Pressure of O_2 (mm Hg)		
		1	2	
				$\frac{P_o}{P_o - P}$
				$\frac{P_o}{P_o - P}$
	0	0	3	1
	1	23	26	1.230
	3	56	60	1.836
	5	65	72	2.121
	10	73	80	2.460
	30	92	95	3.968
	120	113	116	12.300
				17.571



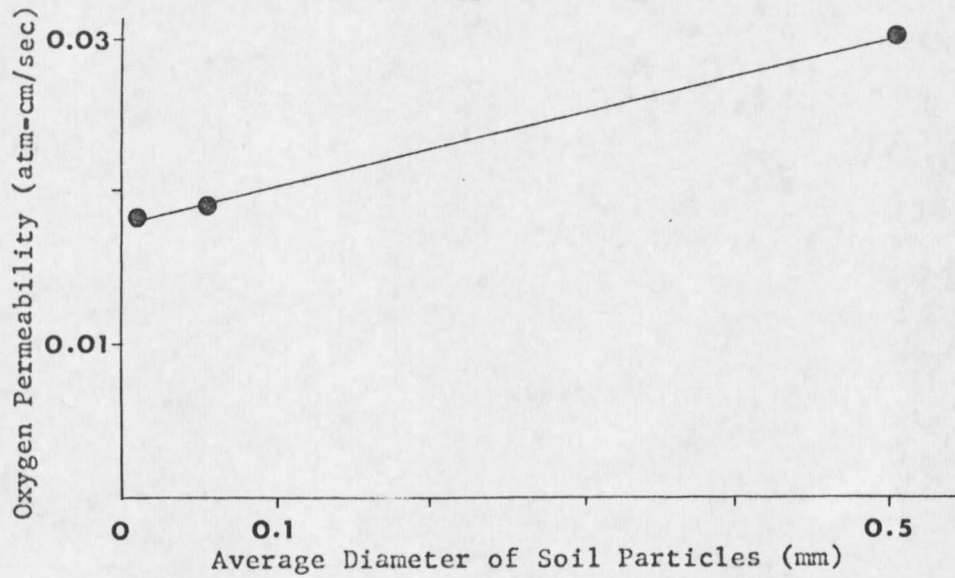


Figure VII.5 - Oxygen Permeability versus Average Diameter of Soil Particles Relationships.

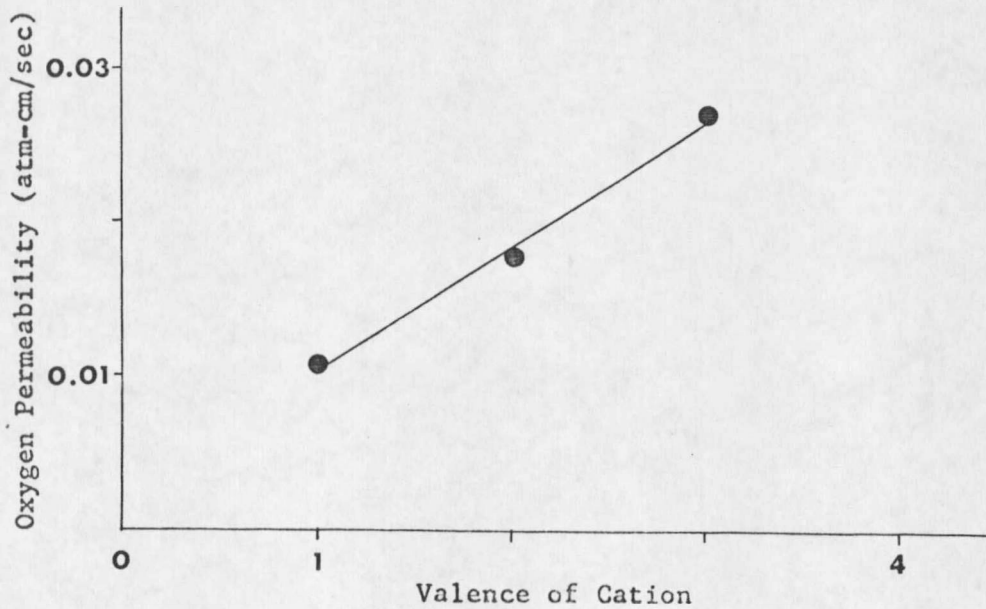


Figure VII.6 - Oxygen Permeability versus Valence of Saturating Cation Relationships.

not as clearly-defined as was expected, the permeability tests, together with thin sectioning, have shown the absence of pores in fine-size particles and the presence of large pores in large-size particles forming crusts. In muscovite, these measurements should have given very low values. Again, the model of soil crusting, i.e., layering of small particles and compaction resulting from influences of cations approximate the layering of sheets in muscovite, and that this could be avoided by causing more aggregation.

Chapter VIII

SOIL AGGREGATION

The presence of stable aggregates is an index of the tilth of the soil. There are materials which promote soil aggregation and these materials form crumbs which allow plant roots to penetrate, grow and anchor themselves well, provide stable traction for farm implements and maintain adequate drainage with moderate retention of water. Organic matter is one of the factors responsible for stable aggregation (Browning and Milam, 1944; Emerson, 1959; Mehta, et al, 1960; Greenland, et al, 1962; Allison, F.E., 1968; and others). Sugars (Greenland, 1956), carbohydrates and related compounds (Lynch, et al, 1956) and polysaccharides (Clapp, et al, 1968) are adsorbed on clay particles and from electron microscopy studies (Kroth and Page, 1946), organic matter is seen universally distributed throughout naturally-occurring soil aggregates.

Organic matter in the soil have been found to be comprised mostly of polysaccharides and polypeptides (see preceding references). They have been extracted and their components identified (Mehta, et al, 1960; Barker, et al, 1965 and 1967; Finch, et al, 1967; Swincer, et al, 1968). Several researches have proven the presence of such compounds in the soil as products of microbial activity (Chesters, et al, 1957; Mehta, et al, 1961; Clapp and Emerson, 1965; Clapp, et al, 1962; Martin, et al, 1965; Aspiras, et al, 1971). The identification of some proteins and lignins were also reported by Weldon and Hide (1942). The stability of these microbial excretions and residues is a measure of the stability of the

aggregates formed by them. Comprehensive summaries of the effects of polysaccharides on soils were given by Allison, F.E. (1968) and Martin (1971).

The second important aggregating or cementing agents are aluminum and iron oxides or hydroxides. Chesters, et al (1957) considered them to be the most important aggregating agent in some soils and their effect on all size particles is great (Arca and Weed, 1966). These two compounds are present as coatings on clay surfaces (Kroth and Page, 1946) and are usually the common oxide minerals.

Clay, in small quantities, acts as a cementing agent of silt and sand. Clay of smaller size limits contributes to the presence of more water-stable aggregates (Arca and Weed, 1966).

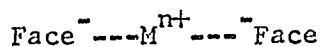
Harris, et al (1966) outlined the possible binding mechanisms in the table below:

Table VIII - Possible Aggregate Bonding Mechanisms

I. Clay Domain-Clay Domain^a

A. Domain face-Domain face

Cation^b bridge between negative faces. Mechanism similar to that for orientation of clay platelets into domains (E.W. Russell, 1935).



B. Domain edge-Domain face

Positive edge site to negative face (Emerson, 1959).

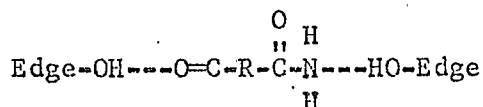
Table VIII - continued.

Edge Al-OH_2^+ --- Face

II. Clay Domain-Organic Polymer^c-Clay Domain

A. Domain edge-Organic polymer-(Domain)

1. Anion exchange: Positive edge site to polymer carboxyl (Ruehrwein and Ward, 1952; Packter, 1957; Warkentin and Miller, 1958; Mortensen, 1962; Emerson, 1963).
2. Hydrogen bonding between edge hydroxyl and polymer carbonyl or amide (Emerson, 1955; Holmes and Toth, 1957; Kohl and Taylor, 1961).



3. Cation-bridge between negative edge site and polymer carboxyl.



4. Van der Waals attraction between edge and polymer (Greenland, 1965).

B. Domain face-Organic polymer-(Domain)

1. Hydrogen bonding between polymer hydroxyl and external or internal (expanding lattice minerals) face silicate oxygens (Geoghegan, 1950; Emerson, 1960; Emerson and Raupach, 1964).

Table VIII - continued.

Face Si-O---HO-R-OH---

2. Cation-bridge between domain external face and polymer carboxyl or other polarizable group (E.W. Russell, 1935; Kroth and Page, 1946; Peterson, 1946; Emerson, 1963).

External Face⁻---Mⁿ⁺---⁻OOC-R-COO⁻

3. Van der Waals attraction between face and polymer (Greenland, 1965).

III. Quartz-(Silt, Inorganic and Organic Colloids)-Quartz

A. Chemical bonds established between quartz surface gels of hydrated alumino silicates and active groups of other aggregate constituents (Emerson, 1959).

B. Quartz grains held in a matrix of silt and clay stabilized primarily by:

1. Oriented clay particles (E.J. Russell, 1950; J.P. Martin, et al, 1955).
2. Irreversibly dehydrated silicates (Dutt, 1948), sesquioxides (Lutz, 1936), or humic-sesquioxide complexes (Filippovich, 1956).
3. Irreversibly dehydrated humic materials (Sokolovskii, 1931; Williams, 1935; Sideri, 1936).
4. Silt-size microaggregates stabilized by iron hu-

Table VIII - continued.

mates (Tiulin, 1954).

5. Organic colloids and clay domains bonded by mechanisms cited under I and II.
-

^aClay domain defined as a group of clay crystals oriented sufficiently close together by cations or hydrogen bonds between the crystal faces to behave as a single unit.

^b M^{n+} = free cation or positively-charged metal oxide or hydroxide.

^cR = organic polymer with axis horizontal or perpendicular to clay domain.

Formation of aggregates is caused by orientation of fine soil particles brought in close contact by physical forces which hold them together firmly even when in the dry state. These forces could be functions of particle size and properties, wetting and drying, freezing and thawing, other temperature changes, cultivation, plant growth and earthworm activity. Chemical and electrical forces also exist. Stability (resistance to pulling apart when wet) is brought about by organic matter and oxides.

Martin (1971) summarized the role of aggregating agents as follows: the length and linear structures of polymers bridge spaces between soil particles; their flexible nature allows a large number of points to be in close contact with each other so that the Van der Waals forces become effective; and -OH and -COOH groups allow hydrogen bonding and ionic bonding between the compounds and the exchange sites on clay surfaces.

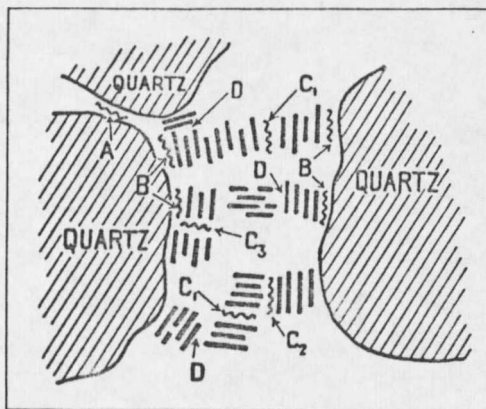


Figure VIII - Scheme of Aggregation. For explanations, see below. (Redrawn from Emerson, 1959).

A visual representation of soil aggregates is given by Emerson (1959) in Fig. VIII. A represents quartz-organic-matter-quartz interactions; B, quartz-organic matter-domain; C, domain-organic matter-domain; C₁, face-face; C₂, edge-face; C₃, edge-edge; D, D₁, domain-domain, edge-face.

Edwards and Bremner (1967) proposed a microaggregate theory saying that the basic structural units in soils of high base status are fine sand- and silt-sized microaggregates (250 μ in diameter) consisting largely of clay-polyvalent metal-organic matter complexes.

Chapter IX

CONCLUSION

The soil is subject to building-up and breaking-down processes just as the human body is subject to the anabolic-catabolic cycle of life. Destruction of soil aggregates induced by erosion, raindrop impact, overcultivation and drying produces tiny particles which together with the preexisting clay and silt, enter the pores. Through the action of water and cementing agents, cementation occurs. If a tract of land is located in a depression, the presence of standing water may encourage the smaller clay and silt particles to rise and the larger sand particles to sink. Puddling orients the particles; formation of small pores after slow drying induces crusting.

As has been elucidated in the preceding chapters, the crust which develops, especially in montmorillonitic soils, resembles the structure of the common primary minerals, muscovite and biotite. Crystals of mica are not formed by these crusting clay particles, but if given the chance to revert to such mineral structures under certain conditions (presence of favorable exchangeable cations, pressure, temperature, etc.), it is possible that clay particles would eventually become mica crystals.

Crusting can be prevented by adequate aggregation of particles. The grouping of small particles gives rise to crumbs which possess surfaces that do not fit well together, thus preventing compaction. The presence of pores and planes of weaknesses reduce the strength of these soil crusts.

The Role of Water

Water in a soil system has more than just a dispersing role. It is a vehicle in which ions and other soluble material reach the active clay surfaces which are available for bonding and cementation. The behavior of particles in water could be different from their behavior in the dry state. In water, particles are freely moving and when in the dry state, the particles are confined to a specific volume.

The bonding of positive ions to negative sites on clay surfaces when the soil system is in water suspension is governed by factors like the size of the cation, the magnitude of charge on the cation, the cation concentration, the temperature and pressure, and competition from other cations. Before dehydration, the surrounding water orients or disorients the particles, again, accordingly as the nature of the ions present. Loss of water also makes the particles come closer together and maintain a certain distance through which the forces of attraction grossly overcome the forces of repulsion. Together with mechanical interlocking of irregular particles and frictional forces, the above-mentioned forces contribute to the physical forces involved in the bonding of crusts.

Van der Waals forces of attraction, if considered to be physical forces, could not be strong enough to hold soil particles together. In a tightly-packed soil crust with a high modulus of rupture, the presence of forces superior to physical forces, is indicated. One possibility is extensive hydrogen-bonding within the crust.

Flakes of oriented clay (cation-saturated) do not disperse in

water unless disturbed. This is due to the presence of an energy barrier at a critical distance of separation between clay crystals. This distance varies as the kind of cation present. Emerson (1959) clearly defines a "clay domain" as a group of clay crystals having suitable exchangeable cations, where the particles are oriented, and are sufficiently close together for the group to act as one. Clay domains had been identified for Ca^{++} -saturated clays, but not for Na^{+} -saturated clays.

If the idea of a clay domain is extended, a Na^{+} - or any monovalent cation-saturated clay crust is one big clay domain. Breaking such a grouping would require great forces which could approach the breaking force necessary for primary minerals.

It is emphasized that aggregation, as opposed to crusting, contributes to the prevention of the formation of hard, cemented soil, by allowing the formation of pores through which water and air might circulate.

The Rock-Clay Cycle

A step-by-step transformation in the rock-clay cycle is presented in Chapter I as Fig. I.1. Fig. IX is another version.

Neither illite nor any of the micas is freely expansible. This limits the entry of water between the interlayers, making it quite difficult for the cation to be exchanged once it bonds to the clay surface as the water evaporates. Addition of a high level of potassium would tend to reverse the equilibrium towards the micas (especially muscovite). Upon drying, a semi-permanent intermediate between a K^{+} -montmorillonite and muscovite is apparently formed.

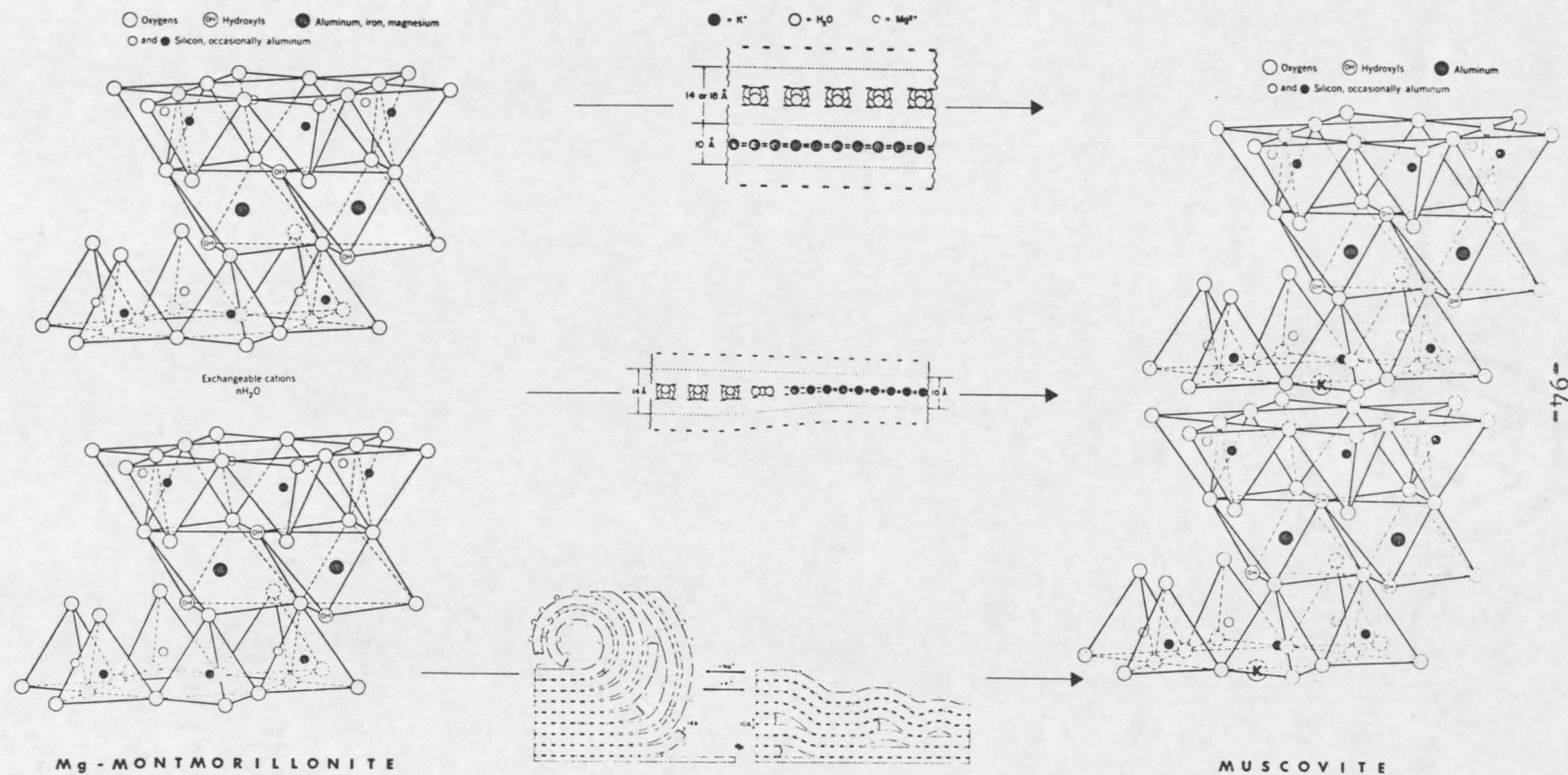


Figure IX - The Transformation of a Mg-Montmorillonite to Muscovite in the Reverse Weathering Process

In the process of crusting therefore, the formation of montmorillonite-muscovite intermediates cause the abnormally-high modulus of rupture, low water and oxygen permeability, and decreased stability of aggregates. Conditions that would favor aggregation, then, are recommended if a favorable soil is wanted.

Curbing Soil Crusting

In clayey soils, incorporation of sand would decrease the clay/sand ration; in silty soils, addition of clay in small amounts might alleviate objectionable soil crusting. Deep plowing, which allows the subsoil to emerge to the surface, could be a good alternative to the addition of either sand or clay.

The addition of divalent or trivalent cations, whichever is most economical and least toxic to plants, might be expected to reduce crust strength.

Animal manure, green manure, crop residues and related farm by-products provide the much-needed organic matter for aggregation.

Addition of synthetic soil conditioners, mostly polymers, have been recommended. Polyelectrolytes (Allison, 1952), polyvinyl alcohol (Greenland, 1963), hydrolyzed polyacrylonitrile (Mortensen, 1960), surface-active agents (Revut, et al, 1968) and soil conditioners HPAN (hydrolyzed polyacrylonitrile) and VAMA (vinyl acetate-maleic acid copolymer) (Martin, W.P., 1953; Sherwood and Engibous, 1953; Allison and Moore, 1956; and Allison, 1956) have been found to be adequately adsorbed by soil particles to favor aggregation.

Chapter X

H^+ -SATURATED CLAYS

The preparation of H^+ -saturated clays have mostly been through saturation of the clay with acid, usually HCl. It has been observed that acids have unfavorable effects on clay systems; acids dissolve either the oxides or the crystal lattice of the clay mineral itself.

Two alternative methods for preparing H^+ -saturated bentonite are proposed in this section. Both methods involve the preparation of a suspension of bentonite in water, and for that matter, a suspension of any clay preparation.

Procedure

In the first method, 100 ml of a 2% clay suspension was equilibrated with a 15-g portion of MB-3 (Amberlite) mixed-bed resin (pH = 6.28 in a 100-ml suspension). After an hour, the suspension was filtered through glass wool. The filtrate was reequilibrated for one hour with another 15-g portion of the same resin. After filtration, a third and a fourth equilibration were done for $1\frac{1}{2}$ and 1 hour respectively.

The pH of the filtrates was measured after each operation.

Blanks containing Al_2O_3 (15 g/300 ml), SiO_2 (5 g/300 ml), Al_2O_3 - SiO_2 mixture ($7\frac{1}{2}$ and $2\frac{1}{2}$ g/300 ml) and RSO_3Na resin (15 g/300 ml) were also treated with MB-3 resin to verify the lowering of pH of clays treated with the resin.

In the second method, a 0.025 M NaCl (= 1.46125 mg NaCl/ml = 0.575 mg Na^+ /ml - 575 ppm Na^+) in clay suspension (1000 ml contain 7.952

g clay; 1 g clay contains 0.0723 g Na^+) was prepared. A liter of the above solution was equilibrated with 50 g of MB-3 resin for 5 minutes. After filtration through glass wool, the clay suspension was passed through a 12-inch high, 4.5-inch in circumference MB-3 resin column at a rate of 200 ml/min, with the help of suction.

0.1 M NH_4Ac solution was added to coagulate the clay (100 ml clay suspension diluted to 500 ml with the NH_4Ac solution) in the eluate. 200 ml of the supernatant were centrifuged at 20,000 rpm for 20 minutes. Residual Na^+ in the eluate was determined by atomic absorption spectroscopy using a Beckman DB Prism Spectrometer with a Beckman Atomic Absorption Accessory.

The second method was repeated for a 0.25 M $\text{Ca}(\text{NO}_3)_2 \cdot 11_2\text{O}$ (45.5275 mg $\text{Ca}(\text{NO}_3)_2/\text{ml} = 10,020 \text{ ppm } \text{Ca}^{++}$) in clay suspension and a 0.25 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (64.1075 mg/ml = 6,078 ppm Mg^{++}) in clay suspension. Residual Ca^{++} and Mg^{++} in the eluates were determined by atomic absorption spectroscopy using a Varian Techtron Model AA5 Spectrometer.

Observations

Table X.1 outlines the results obtained from the first method.

The pH of bentonite (2% suspension) was greatly decreased after the first batch treatment, and continued to decrease after subsequent treatments. The pH of Pylon clay also decreased when treated similarly. Al_2O_3 and SiO_2 suspensions had increasing pHs due probably to increased dissolution and hydrolysis of the oxides to the respective hydroxides.

The pH of the RSO_3Na resin decreased, indicating a transformation from the sodium to the H^+ form.

Table X.1 - pHs of Suspensions Treated with MB-3 Resin

time (hour)	batch	Al_2O_3	SiO_2	Al-Si oxide	bentonite	Pylon clay	RSO_3Na
	0	7.7	4.3	6.95	9.7	6.4	9.1
1	1	9.85	4.9	9.25	3.4	6.0	5.6
2	2	9.85	4.9	9.25	3.5	5.45	4.4
$3\frac{1}{2}$	3	9.6	4.9	9.0	3.7	5.3	4.25
$4\frac{1}{2}$	4	9.85	4.9	9.1	3.8	5.3	4.25
	0	7.6	4.3	6.95	9.65	6.4	9.2
1	1	6.9	4.6	7.1	5.35	5.85	5.6
2	2	8.0	4.7	8.0	3.4	5.4	4.3
$3\frac{1}{2}$	3	9.4	4.75	9.0	3.5	5.3	4.25
$4\frac{1}{2}$	4	9.6	4.75	9.0	3.6	5.2	4.25

Table X.2 outlines the results obtained from the second method.

Concentrations of Na^+ , Mg^{++} and Ca^{++} were greatly diminished after the operations. A 250-, 650- and a 900-fold decrease were obtained for the three cation concentrations respectively. It is assumed that the bulk of the cations added was replaced by H^+ from the resin to form H^+ -saturated clays by ion exchange.

Table X.2 - Concentrations of Na^+ , Mg^{++} and Ca^{++} Remaining in the Clay Suspensions before and after Equilibration with and Passage through MB-3 Resin.

cation	concentration before operation (ppm)	concentration after operation (ppm)
Na^+	575	2.458*
		1.82*
Mg^{++}	10,020	12.2
		15.2
Ca^{++}	6,078	6.6
		8.1

* First and second trials respectively.

Conclusion

Treatment of clay suspensions by batch operation and elution through a column of resin are commendable procedures in preparing H^+ -saturated clays in the sense that the lowering of the pH of the clay indicated a transformation from a cation-saturated clay to a predominantly H^+ -saturated clay; MB-3 resin columns strip the suspensions of exchangeable cations, again suggesting that H^+ -saturated clays are formed.

The objections to these schemes are the repetitious nature of the batch operations and the clogging of pores and channels in the resin column by clay particles. The former could be eased with the development of a constant-feed and filtration system, followed by pH determination which is entirely mechanized. The latter could be eased with the application

of suction.

The stability of the H^+ -saturated clays is not assured. Aging might dissolve some of the alumina and an Al^{+++} -saturated clay might ensue. However, it is presumed that the clay crystals retain their properties better than in the older method of acid saturation.

REFERENCES

- Allison, F.E. (1968). Soil Aggregation-Some Facts and Fallacies as Seen by a Microbiologist. *Soil Sci.* 106: 136-143.
- Allison, L.E. (1952). Effect of Synthetic Polyelectrolytes on the Structure of Saline and Alkali Soils. *Soil Sci.* 73: 443-454.
- _____. (1956). Soil and Plant Responses to VAMA and HPAN Soil Conditioners in the Presence of High Exchangeable Sodium. *Soil Sci. Soc. Amer. Proc.* 20: 147-151.
- _____. & Moore, D.C. (1956). Effect of VAMA and HPAN Soil Conditioners on Aggregation, Surface Crusting, and Moisture Retention in Alkali Soils. *Soil Sci. Soc. Amer. Proc.* 20: 143-146.
- Allison, R.V. (1923). The Modulus of Rupture of a Soil as an Index of Its Physical Structure. *J. Amer. Soc. Agron.* 15: 409-415.
- Arca, M.N. & Weed, S.B. (1966). Soil Aggregation and Porosity in Relation to Contents of Free Iron Oxide and Clay. *Soil Sci.* 101: 164-170.
- Aspiras, R.B., Allen, O.N., Harris, R.F. & Chesters, G. (1971). Aggregate Stabilization by Filamentous Microorganisms. *Soil Sci.* 112: 282-284.
- Barker, S.A., Finch, P., Hayes, M.H.B., Simmonds, R.G. & Stacey, M. (1965). Isolation and Preliminary Characterization of Soil Polysaccharides. *Nature* 205: 68-69.
- _____, Hayes, M.H.B., Simmonds, R.G. & Stacey, M. (1967). Studies on Soil Polysaccharides, I. *Carbohydr. Res.* 5: 13-24.
- Baver, L.D. *Soil Physics*. 3rd ed. New York: John Wiley & Sons, Inc., 1956.
- Bear, F.E. (ed.). *Chemistry of the Soil*. 2nd ed. American Chemical Society Monograph Series, No. 160. New York: Reinhold Publishing Corp., 1964.
- Bower, C.A. & Truog, E. (1940) Base-exchange Capacity Determination Influenced by Nature of Cation Employed and Formation of Basic Exchange Salts. *Soil Sci. Soc. Amer. Proc.* 5: 86-89.
- Browning, G.M. & Milam, F.M. (1944). Effect of Different Types of Organic Materials and Lime on Soil Aggregation. *Soil Sci.* 57: 91-106.
- Buckman, H.O. & Brady, N.C. *The Nature and Properties of Soils*. 6th ed. New York: The MacMillan Co., 1960.

- Buol, S.W. & Fadness, D.M. (1961). New Method of Impregnating Fragile Material for Thin Sectioning. *Soil Sci. Soc. Amer. Proc.* 25: 253.
- Garnes, A. (1934). Soil Crusts-Methods of Study, Their Strength, and a Method of Overcoming Their Injury to Cotton Stand. *Agr. Engr.* 15: 167-171.
- Chang, C.W. & Anderson, J.U. (1968). Flocculation of Clays and Soils by Organic Compounds. *Soil Sci. Soc. Amer. Proc.* 32: 23-27.
- Chepil, W.S. (1955). Factors That Influence Clod Structure and Erodibility of Soil by Wind: IV. Sand, Silt, and Clay. *Soil Sci.* 80: 155-162.
- Chesters, G., Attoe, O.J. & Allen, O.N. (1957). Soil Aggregation in Relation to Various Soil Constituents. *Soil Sci. Soc. Amer. Proc.* 21: 272-277.
- Clapp, C.E., Davis, R.J. & Waugaman, S.H. (1962). The Effect of Rhizobial Polysaccharides on Aggregate Stability. *Soil Sci. Soc. Amer. Proc.* 26: 466-469.
- _____ & Emerson, W.W. (1965a). The Effect of Periodate Oxidation on the Strength of Soil Crumbs: I. Qualitative Studies. *Soil Sci. Soc. Amer. Proc.* 29: 127-130.
- _____ (1965b). The Effect of Periodate Oxidation on the Strength of Soil Crumbs: II. Quantitative Studies. *Soil Sci. Soc. Amer. Proc.* 29: 130-134.
- Clapp, C.E., Olness, A.E. & Hoffmann, D.J. (1968). Adsorption Studies of a Dextran on Montmorillonite. *Trans. 9th Int. Congr. Soil Sci. Adelaide, I*: 627-634.
- Clark, C., "Crusting Topsoil Problem", *Montana Farmer Stockman*, Feb. 19, 1970, p. 46.
- Davey, B.G. & Low, P.F. (1968). Clay-Water Interaction as Affected by Hydrous Aluminum Oxide Films. *Trans. 9th Int. Congr. Soil Sci. Adelaide, I*: 607-616.
- Day, P.R., "Particle Fractionation and Particle-Size Analysis", in Black, C.A. (ed.), *Methods of Soil Analysis*, Part I, Agronomy No. 9 (Madison: American Society of Agronomists, Inc., 1965), pp. 545-567.
- Deshpande, T.L., Greenland, D.J. & Quirk, J.P. (1964a). Role of Iron Oxides in the Bonding of Soil Particles. *Nature* 201: 107-108.

- Deshpande, T.L., Greenland, D.J. & Quirk, J.P. (1964b). Charges on Iron and Aluminum Oxides in Soils. Trans. 8th Int. Congr. Soil Sci. Bucharest, III: 1213-1225.
- ____ (1968). Changes in Soil Properties Associated with the Removal of Iron and Aluminum Oxides. J. Soil Sci. 19: 108-122.
- Dettmann, M.G. & Emerson, W.W. (1959). A Modified Permeability Test for Measuring the Cohesion of Soil Crumbs. J. Soil Sci. 10: 215-226.
- Douglas, B.E. & McDaniel, D.H. Concepts and Models of Inorganic Chemistry. New York: Blaisdell Publishing Co., 1965.
- Dowdy, R.H. & Larson, W.E. (1971). Tensile Strength of Montmorillonite as a Function of Saturating Cation and Water Content. Soil Sci. Soc. Amer. Proc. 35: 1010-1014.
- Duley, F.L. (1939). Surface Factors Affecting the Rate of Intake of Water by Soils. Soil Sci. Soc. Amer. Proc. 4: 60-64.
- Dutt, A.K. (1948). Certain Aspects of the Mechanism of Aggregate Stability in Water. Soil Sci. 65: 383-392.
- Edwards, A.P. & Bremner, J.M. (1967). Microaggregates in Soils. J. Soil Sci. 18: 64-73.
- Elgabaly, M.M. & Elghamry, W.M. (1970). Water Permeability and Stability of Kaolinite Systems as Influenced by Adsorbed Cation Ratio. Soil Sci. 110: 107-110.
- Emerson, W.W. (1955). Complex Formation between Montmorillonite and High Polymers. Nature 176: 461.
- ____ (1959). The Structure of Soil Crumbs. J. Soil Sci. 10: 235-244.
- ____ (1960). Complexes of Calcium-Montmorillonite with Polymers. Nature 186: 573-574.
- ____ (1963). The Effect of Polymers on the Swelling of Montmorillonite. J. Soil Sci. 14: 52-63.
- ____ & Raupach, M. (1964). The Reaction of Polyvinyl Alcohol with Montmorillonite. Aust. J. Soil Res. 2: 46-55.
- Epstein, E. & Grant, W.J. (1967). Soil Losses and Crust Formation as Related to Some Physical Properties. Soil Sci. Soc. Amer. Proc. 31: 547-550.

- Evans, D.D. & Buol, S.W. (1968). Micromorphological Study of Soil Crusts. Soil Sci. Soc. Amer. Proc. 32: 19-22.
- Filippovich, Z.S. (1956). The Adsorption of Colloids by Soils and Structure Formation. Pochvovedenie 2: 16-26.
- Finch, P., Hayes, M.H.B. & Stacey, M., "Studies on Soil Polysaccharides and on Their Interaction with Clay Preparations", Transactions of the International Society of Soil Science, Soil Chemistry and Fertility, Meeting of Commissions II & IV of the International Society of Soil Science, Sept. 1966 (Aberdeen: International Society of Soil Science, 1967), pp. 19-32.
- Geoghegan, M.J. (1950). Aggregate Formation in Soil-Influence of Some Microbial Products and Other Substances on Aggregation of Soil Particles. Trans. 4th Int. Congr. Soil Sci. Amsterdam, I: 198-201.
- Gerard, C.J. (1965). The Influence of Soil Moisture, Soil Texture, Drying Conditions, and Exchangeable Cations on Soil Strength. Soil Sci. Soc. Amer. Proc. 29: 641-645.
- Gill, W.R. (1959). The Effects of Drying on the Mechanical Strength of Lloyd Clay. Soil Sci. Soc. Amer. Proc. 23: 255-257.
- Glasstone, S. Textbook of Physical Chemistry. 2nd ed. New York: D. Van Nostrand Co., Inc., 1946.
- Greenland, D.J. (1956). The Adsorption of Sugars by Montmorillonite, II. Chemical Studies. J. Soil Sci. 7: 329-334.
- ____ (1963). Adsorption of Polyvinyl Alcohols by Montmorillonite. J. Colloid Sci. 18: 647-664.
- ____ (1965a). Interaction between Clays and Organic Compounds in Soils, Part I. Mechanism of Interaction between Clays and Defined Organic Compounds. Soils & Fertilizers 28: 415-425.
- ____ (1965b). Interaction between Clays and Organic Compounds in Soils, Part II. Adsorption of Soil Organic Compounds and Its Effect on Soil Properties. Soils & Fertilizers 28: 521-532.
- ____, Lindstrom, G.R. & Quirk, J.P. (1962). Organic Materials which Stabilize Natural Soil Aggregates. Soil Sci. Soc. Amer. Proc. 26: 366-371.
- ____ & Oades, J.M. (1968). Iron Hydroxides and Clay Surfaces. Trans. 9th

- Int. Congr. Soil Sci. Adelaide, I: 657-667.
- Grim, R.E. Clay Mineralogy. 2nd ed. New York: McGraw-Hill Book Co., 1968.
- Hanks, R.J. & Thorp, F.C. (1957). Seedling Emergence of Wheat, Grain Sorghum, and Soybeans as Influenced by Soil Crust Strength and Moisture Content. *Soil Sci. Soc. Amer. Proc.* 21: 357-359.
- Harris, R.F., Allen, O.N., Chesters, G. & Attoe, O.J. (1963). Evaluation of Microbial Activity on Soil Aggregate Stabilization and Degradation by the Use of Artificial Aggregates. *Soil Sci. Soc. Amer. Proc.* 27: 542-545.
- _____, Chesters, G. & Allen, O.N. (1966). Dynamics of Soil Aggregation. *Adv. Agron.* 18: 107-169.
- Hendricks, S.B. (1942). Lattice Structure of Clay Minerals and Some Properties of Clays. *J. Geol.* 50: 276-290.
- Holmes, R.M. & Toth, S.J. (1957). Physico-Chemical Behavior of Clay-Conditioner Complexes. *Soil Sci.* 84: 479-487.
- Jackson, M.L., Hseung, Y., Corey, R.B., Evans, E.J. & Van den Heuvel, R.C. (1952). Weathering Sequence of Clay-size Minerals in Soils and Sediments: II. Chemical Weathering of Layer Silicates. *Soil Sci. Soc. Amer. Proc.* 16: 3-6.
- Kirkham, D., de Boodt, M.F. & de Leenheer, L. (1959). Modulus of Rupture Determinations on Undisturbed Soil Core Samples. *Soil Sci.* 87: 141-144.
- Koehnke, H. Soil Physics. New York: McGraw-Hill Book Co., 1968.
- Kohl, R.A. & Taylor, S.A. (1961). Hydrogen Bonding between the Carbonyl Group and Wyoming Bentonite. *Soil Sci.* 91: 223-227.
- Kolthoff, I.M., Sandell, E.B., Meehan, E.J. & Bruckenstein, S. Quantitative Chemical Analysis. 4th ed. Toronto: The MacMillan Co., 1969.
- Kroth, E.M. & Page, J.B. (1946). Aggregate Formation in Soils with Special Reference to Cementing Substances. *Soil Sci. Soc. Amer. Proc.* 11: 27-34.
- Lauritzen, C.W. (1948). Apparent Specific Volume and Shrinkage Characteristics of Soil Materials. *Soil Sci.* 65: 155-179.
- Lemos, P. & Lutz, J.F. (1957). Soil Crusting and Some Factors Affecting

It. Soil Sci. Soc. Amer. Proc. 21: 485-491.

Lutz, J.F. (1936). The Relation of Free Iron in the Soil to Aggregation. Soil Sci. Soc. Amer. Proc. 1: 43-45.

_____, Garcia-Lagos, R. & Hilton, H.G. (1960). The Effect of Phosphate Fertilizers on Some Physical Properties of Soil. Trans. 7th Int. Congr. Soil Sci. Madison, VI: 241-248.

Lutz, J.F. & Pinto, R.A. (1965). Effect of Phosphorus on Some Physical Properties of Soils: I. Modulus of Rupture. Soil Sci. Soc. Amer. Proc. 29: 458-460.

Lynch, D.L., Wright, L.M. & Cotnoir, L.J., Jr. (1956). The Adsorption of Carbohydrates and Related Compounds on Clay Minerals. Soil Sci. Soc. Amer. Proc. 20: 6-9.

McIntyre, D.S. (1958a). Permeability Measurements of Soil Crusts Formed by Raindrop Impact. Soil Sci. 85: 185-189.

_____. (1958b). Soil Splash and the Formation of Surface Crusts by Rain-drop Impact. Soil Sci. 85: 261-266.

Marshall, C.E. (1935). Layer Lattices and Base-Exchange Clays. Z. Krist. 91: 433-449.

_____. The Colloid Chemistry of the Silicate Minerals, Agronomy No. 1 (New York: Academic Press, Inc., 1949).

_____. The Physical Chemistry and Mineralogy of Soils, Vol. I-Soil Materials. New York: John Wiley & Sons, Inc., 1964.

Martin, J.P. (1971). Decomposition and Binding Action of Polysaccharides in Soil. Soil Biol. & Biochem. 3: 33-41.

_____, Ervin, J.O. & Shepherd, R.A. (1965). Decomposition and Binding Action of Polysaccharides from Azotobacter Indicus (Beijerinckia) and Other Bacteria in the Soil. Soil Sci. Soc. Amer. Proc. 29: 397-400.

_____, Martin, W.P., Page, J.B., Raney, W.A. & de Ment, J.D. (1955). Soil Aggregation. Adv. Agron. 7: 1-37.

Martin, W.P. (1953). Status Report on Soil Conditioning Chemicals, I. Soil Sci. Soc. Amer. Proc. 17: 1-9.

Mathieu-Sicaud, A., Mering, J. & Perrin-Bonnet, I. (1951). Etude au Micro-

scope Electronique de la Montmorillonite et de l'Hectorite Saturées par Différents Cations. Bull. Soc. Franç. Mineral. Cristal. 74: 439-466.

Mehta, N.C., Dubach, P. & Deuel, H. (1961). Carbohydrates in the Soil. Adv. Carb. Chem. 16: 335-355.

_____. Streuli, H. Müller, M. & Deuel, H. (1960). Role of Polysaccharides in Soil Aggregation. J. Sci. Food Agric. 11: 40-47.

Mering, J. & Glaeser, R. (1954). Sur le Rôle de la Valence des Cations Echangeables dans le Montmorillonite. Bull. Soc. Franç. Mineral. Cristal. 77: 519-530.

Moe, R.A., "Thinsections and Bulk Density Determinations of Pore Space in Some Crusted Agricultural Soils and Some Forest and Meadow Soils", Soils 201 Special Project under Dr. J.R. Sims, Montana State University, Dec. 16, 1968.

_____, "Modulus of Rupture-Pylon Soils", A Summary of Results, An unpublished paper submitted to the Plant and Soil Science Department, Montana State University, Bozeman, Aug. 8, 1969.

_____, Nielsen, G.A. & Choriki, R.T., "Soil Crust Studies-Evaluation of Chemical and Physical Treatments Using Modulus of Rupture Techniques", Research Report No. 6, Montana Agricultural Experiment Station, Montana State University, Bozeman, April 1971.

Moore, W.J. Physical Chemistry. 3rd ed. Englewood Cliffs: Prentice-Hall, Inc., 1962.

Mortensen, J.L. (1962). Adsorption of Hydrolyzed Polyacrylonitrile on Kaolinite. Proc. 9th Nat. Conf. Clays & Clay Min. Lafayette: 530-545.

Myhrman, M.A. & Evans, D.D. (1969). Hexadecanol in Soil-Its Locational Stability and Influence on Modulus of Rupture. Soil Sci. Soc. Amer. Proc. 33: 203-205.

Norrish, K. (1954). The Swelling of Montmorillonite. Disc. Faraday Soc. 18: 120-134.

Ottewill, R.H., "Attractive Forces between Surfaces", in Alner, D.J. (ed.), Aspects of Adhesion. London: University of London Press, 1966.

Packter, A. (1957). Interaction of Montmorillonite Clays with Polyelec-

- trolyte. Soil Sci. 83: 335-343.
- Peterson, J.B. (1946). The Role of Clay Minerals in the Formation of Soil Structure. Soil Sci. 61: 247-256.
- Pilpel, N. (1969). The Cohesiveness of Powders. Endeavour 28: 73-76.
- _____ (1971). Crumb Formation. Endeavour 30: 77-81.
- Radoslovich, E.W. (1963). The Cell Dimensions and Symmetry of Layer-Lattice Silicates. IV. Interatomic Forces. The Amer. Mineral. 48: 76-99.
- Reeve, R.C., "Modulus of Rupture", in Black, C.A. (ed.) Methods of Soil Analysis, Part I, Agronomy No. 9 (Madison: American Society of Agronomists, Inc. 1965), pp. 466-471.
- _____, Bower, C.A., Brooks, R.H. & Gschwend, F.B. (1954). A Comparison of the Effects of Exchangeable Sodium and Potassium upon the Physical Conditions of Soils. Soil Sci. Soc. Amer. Proc. 18: 130-132.
- Revut, I.B., Maslenkova, G.L. & Ionavichus, A.A. (1968). Polymers and Surface Active Substances for Stabilizing Soil Conditions. Trans. 9th Int. Congr. Soil Sci. Adelaide, I: 503-513.
- Richards, L.A. (1953). Modulus of Rupture as an Index of Crusting of Soil. Soil Sci. Soc. Amer. Proc. 17: 321-323.
- Ruehrwein, R.A. & Ward, D.W. (1952). Mechanisms of Clay Aggregation by Polyelectrolytes. Soil Sci. 73: 485-492.
- Russell, E.J. Soil Conditions and Plant Growth. 9th ed. New York: John Wiley & Sons, Inc. 1971.
- Russell, E.W. (1935). The Binding Forces between Clay Particles in a Soil Crumb. Trans. 3rd Int. Congr. Soil Sci. Oxford, I: 26-29.
- Sawhney, B.L. (1960). Aluminum Interlayers in Clay Minerals. Trans. 7th Int. Congr. Soil Sci. Madison, IV: 476-481.
- Schnitzer, M. (1968). Reactions between Organic Matter and Inorganic Soil Constituents. Trans. 9th Int. Congr. Soil Sci. Adelaide, I: 635-644.
- Schwertmann, U., Fischer, W.R. & Papendorf, H. (1968). The Influence of Organic Compounds on the Formation of Iron Oxide. Trans. 9th Int. Congr. Soil Sci. Adelaide, I: 645-653.
- Sherwood, L.V. & Engibous, J.C. (1953). Status Report on Soil Conditio-

- ning Chemicals, II. Soil Sci. Soc. Amer. Proc. 17: 9-16.
- Sideri, D.I. (1936). On the Formation of Structure in Soil: II. Synthesis of Aggregates on the Bonds Uniting Clay with Sand and Clay with Humus. Soil Sci. 42: 461-481.
- Singleton, P.C. & Harward, M.E. (1971). Iron Hydroxy Interlayers in Soil Clay. Soil Sci. Soc. Amer. Proc. 35: 838-842.
- Soil Survey Staff. Soil Survey Manual, U.S.D.A. Handbook No. 18. Washington: U.S. Government Printing Office, 1951.
- _____. Soil Classification-A Comprehensive System. 7th Approximation. Washington: U.S. Government Printing Office, 1960.
- Sokolovskii, A.N. (1931). ---. Contrib. Ukr. Inst. Soil Res. 3: 189-193. Title not available. Main reference: Harris, et al (1966).
- Stefanson, R.C. (1968). Factors Determining Seasonal Changes in the Stabilities of Soil Aggregates. Trans. 9th Int. Congr. Soil Sci. Adelaide, I: 395-401.
- Sumner, M.E. (1963). Effect of Iron Oxides on Positive and Negative Charges on Clays and Soils. Clay Min. Bull. 5: 218-235.
- Swincer, G.D., Oades, J.M. & Greenland, D.J. (1968). Studies on Soil Polysaccharides. Aust. J. Soil Res. 6: 225-235.
- _____. (1969). The Extractions, Characterization and Significance of Soil Polysaccharides. Adv. Agron. 21: 195-235.
- Tackett, J.L. & Pearson, R.W. (1965). Some Characteristics of Soil Crusts Formed by Simulated Rainfall. Soil Sci. 99: 407-413.
- Taylor, S.A. (1949). Oxygen Diffusion in Porous Media as a Measure of Soil Aeration. Soil Sci. Soc. Amer. Proc. 14: 55-61.
- Tiulin, A.F. (1954). Problems of Structure Forest Soils. Pochvovedenie 1: 30-44.
- U.S. Department of Agriculture, Soil Conservation Service, Selected Chapters from the Unedited Text of the Soil Taxonomy of the National Cooperative Soil Survey, Washington: U.S. Government Printing Office, 1970, Chaps. 8 & 9.
- U.S. Salinity Laboratory Staff. Diagnosis and Improvement of Saline and Alkali Soils, U.S.D.A. Handbook No. 60. Washington: U.S. Government

Printing Office, 1954.

Volk, G.M. & Hensel, D.R. (1970). Aggregation of Mineral and Organic Matter in Rutlege, Ona, and Leon Fine Sands of the Southeastern Coastal Plains. Soil Sci. 110: 333-338.

Warkentin, B.P., "Bonding between Montmorillonite Clay Particles", Ph.D. Thesis, Cornell University, 1956.

_____ & Miller, R.D. (1958). Conditions Affecting Formation of the Montmorillonite-Polyacrylic Acid Bond. Soil Sci. 85: 14-18.

Warkentin, B.P. & Yong, R.N. (1960). Shear Strength of Montmorillonite and Kaolinite Related to Interparticle Forces. Clays and Clay Min. 9: 210-218.

Weldon, T.A. & Hide, J.C. (1942). Some Physical Properties of Soil Organic Matter and of Sesquioxides Associated with Aggregation in Soils. Soil Sci. 54: 343-351.

Williams, V.R. (1935). ---. Pochvovedenie 5-6: 755-762. Title not available. Main reference: Harris, et al (1966).

Appendix A

PYLON SOILS

Two classifications of the crusting Pylon soils of Montana are as follows:

Table A.1 - Classifications of Pylon Soils¹

	I ^a	II ^b
Order:	Aridisol	Alfisol
Suborder:	Argid	Boralf
Great Soil Group:	Paleargid	Eutroboralf
Subgroup:	Borollic Paleargid	Typic Eutroboralf
Family:	fine, montmorillonitic	
Series:	Pylon	

a, ^b Early and current classifications.

The physical and chemical analyses and description of Pylon soils are given below:

Table A.2 - An Outline of the Physico-Chemical
Characteristics of Pylon Soil²

Soil: Pylon silty clay loam

Area (origin of samples): Cascade County, Montana

¹Based on the Soil Survey, U.S.D.A. Soil Conservation Service system.

²From the analyses made by the Soil Survey Laboratory Staff, U.S.D.A. Soil Conservation Service, Lincoln, Nebraska, May 13, 1971.

Table A.2 - continued.

Climate: Cool, semi-arid, continental, with long, cold, dry winters and moist springs and summers (Mean precipitation: 32 cm; Apr.-Oct., 22-25 cm; Average temperature: annual, 6°C; Jan., -7°C; July, 20.5°C; winter, -4°C; summer, 19.5°C)

Elevation: about 1000 meters

Parent materials^{*}: Silty clay glacial meltwater sediments deposited on a sedimentary bedrock surface

Physiography: Sedimentary uplands

Vegetation: Small grain and summer fallow

Slope: 1%

Relief: Less than 60 cm, local

Drainage: Well-drained

Ground water: Below 3 meters

Permeability: Very slow

Infiltration: Very slow

Run-off: Medium to rapid

Salt and Alkali: Slight

Moisture: Dry to 65 cm, slightly moist below

Stoniness: None

^{*}Refers to the initial state of the soil.

Only the topsoil was subjected to the studies in this paper. It is described in Table A.3.

Table A.3 - Physico-Chemical Characteristics of
Pylon Topsoil from Cascade County, Montana³

Depth: 0-1 cm

Horizon^a: A2pl^b

Color: Light brownish gray (2.5 Y, 6/2 rubbed, 6/1 unrubbed)^c, silty
clay loam, dark grayish brown (2.5 Y, 4/2), moist

Texture and Appearance: Massive and cloddy when dry, very weak granular
when moist; extremely hard, very friable, slightly sticky and
slightly plastic; abundance of unstained sand grains; the surface
of clods and of crusts has a continuous light gray unglazed surface
with distinctive evidence of siltflow on underside of clods and in
cracks in the crusts; abrupt wavy boundary

Size Class and Particle Diameter (mm):

Coarse fragments: trace

Sand (2-0.05): 24.6%

Very coarse (2-1): 0.5%

Coarse (1-0.5): 0.7%

Medium (0.5-0.25): 1.2%

Fine (0.25-0.1): 5.8%

Very fine (0.1-0.05): 16.3%

Silt (0.05-0.002): 42.3%

Clay (0.002 and below): 33.1%

Int. II (0.2-0.02): 39.2%

Table A.3 - continued.

Int. III (0.02-0.002): 23.5%

(2-0.1): 8.3%

Remarks: Cracks up to 2.5 cm wide in surface crusts. These cracks extend to 88 cm long when they are 5 mm wide. Roots are mainly compressed along vertical surfaces of prisms. The solum^d appears to have developed in nonconforming materials over sedimentary rock. Surface is covered by extremely durable tillage clods of varying sizes and by a continuous vesicular massive crust.

Water content (15-bar): 10.7%

Organic C: 1.38%

Nitrogen: 0.137%

C/N: 10

Available P (Bray): 55 ppm^e

Carbonates (as CaCO₃): trace

Electrical Conductance (Saturation Extract): 0.7 mmhos/cm^e

Extractable Cations: 19.5 meq/100 g

Extractable bases: 15.2 meq/100 g

Ca (NH₄OAc extract): 8.6 meq/100 g

Mg (NH₄OAc extract): 4.8 meq/100 g

Na: 0.1 meq/100 g

K: 1.7 meq/100 g

Extractable acidity: 4.3 meq/100 g

Table A.3 - continued.

pH: about 6.5

Cation-exchange Capacity (NH_4OAc extract): 17.1 meq/100 g

^a Defined as a layer within a soil that is approximately parallel to the soil surface and that has properties that are produced by soil-forming processes but that are unlike those of adjoining layers.

^b A2: mineral horizons in which the feature emphasized is loss of clay, iron or aluminum, with resultant concentration of quartz or other resistant minerals in sand and silt sizes; p: indicates disturbance by cultivation or pasturing at, or adjacent to the surface.

^c Refer to hue symbols of the Munsell color classification system.

^d Defined as the horizons above the parent material.

^e Moe, et al, "Soil Crust Studies-Evaluation of Chemical and Physical Treatments Using Modulus of Rupture Techniques", Research Report No. 6, Montana Agricultural Experiment Station, Montana State University, Bozeman, April 1971.

Appendix B

ORIGINAL DATA

Table B.1 - Turbidimetry Study of Pylon Clay with Added Electrolyte

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I ¹	Ratio II ²
LiCl	Standard		9:45	2.71			
	0	6.43	9:58	12.02	2.9845	4.026	1
	0.05	6.08	10:01	11.37	2.9750	3.822	0.9493
	0.1	6.04	10:03	11.20	2.9680	3.774	0.9374
	0.5	6.08	10:09	10.70	2.9477	3.630	0.9016
	Standard		10:12	2.96			
NaCl	Standard		12:50	2.90			
	0	6.43	12:53	11.82	2.8475	4.152	1
	0.05	6.12	12:57	11.60	2.8350	4.091	0.9853
	0.1	6.08	12:59	11.49	2.8320	4.059	0.9776
	Standard		1:06	2.78			
KCl	Standard		3:17	2.55			
	0	6.43	3:20	12.60	2.4735	5.094	1
	0.05	6.28	3:22	12.53	2.4675	5.078	0.9969

Table B.1 - continued.

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I	Ratio II
MgCl ₂	0.1	6.14	3:25	12.65	2.4600	5.140	1.009
	0.5	6.05	3:30	12.12	2.4475	4.950	0.9717
	Standard		3:40	2.77			
	Standard		1:53	2.63			
	0	6.43	2:14	12.42	2.6390	4.706	1
	0.05	6.06	2:17	12.26	2.6315	4.657	0.9896
	0.1	6.00	2:20	12.30	2.6255	4.685	0.9955
	0.5	5.90	2:24	11.95	2.6150	4.570	0.9711
	Standard		2:27	2.54			
CaCl ₂	Standard		3:32	2.68			
	0	6.43	3:41	13.57	2.713	5.001	1
	0.05	5.90	3:47	13.54	2.7030	5.010	1.0018
	0.1	6.06	3:50	13.48	2.6985	4.997	0.9992
	0.5	6.00	3:55	13.60	2.6900	5.057	1.0112
	Standard		4:12	2.69			
AlCl ₃	Standard		10:37	2.67			
	0	6.43	10:41	17.27	2.6470	6.525	1
	0.05	5.48	10:45	18.50	2.6400	7.009	1.0742

Table B.1 - continued.

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I	Ratio II
FeCl ₃	0.1	4.84	10:49	18.75	2.6325	7.121	1.0913
	0.5	4.78	10:57	18.64	2.6160	7.125	1.0920
	Standard		11:00	2.60			
	Standard		1:45	2.45			
	0	6.43	1:52	15.82	2.4316	6.505	1
	0.05	5.60	1:55	17.02	2.4313	7.000	1.0761
	0.1	4.80	1:57	17.33	2.4311	7.127	1.0956
	0.5	4.48	2:02	17.51	2.4310	7.201	1.1070
	Standard		2:04	2.52			

¹ galvanometer reading for the clay
corrected galvanometer reading for the standard

² galvanometer reading for the clay with added electrolyte
corrected galvanometer reading for the standard

galvanometer reading for the clay without added electrolyte
corrected galvanometer reading for the standard

Table B.2 - Turbidimetry Study of Bentonite with Added Electrolyte

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I ¹	Ratio II ²
LiCl	Standard		8:50	1.18			
	0	5.97	8:54	2.15	1.1900	1.807	1
	0.01	6.02	8:57	1.80	1.1900	1.513	0.837
	0.05	5.98	9:01	1.65	1.1900	1.387	0.768
	0.1	5.99	9:03	1.58	1.1900	1.328	0.735
	0.2	5.98	9:06	1.55	1.1900	1.303	0.721
	0.5	6.04	9:08	1.38	1.1900	1.160	0.642
	Standard		9:09	1.18			
NaCl	Standard		9:27	1.18			
	0	5.97	8:54	2.15	1.1900	1.807	1
	0.01	6.20	9:31	1.80	1.1900	1.513	0.837
	0.05	6.18	9:33	1.80	1.1900	1.513	0.837
	0.1	6.19	9:35	1.60	1.1900	1.345	0.744
	0.2	6.10	9:37	1.55	1.1900	1.303	0.721
	0.5	6.03	9:39	1.43	1.1900	1.202	0.665
	Standard		9:40	1.20			
KCl	Standard		9:37	1.17			

Table B.2 - continued.

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I	Ratio II
MgCl ₂	0	6.45	9:41	1.95	1.1935	1.634	1.634
	0.01	6.30	9:43	2.10	1.1901	1.765	1.080
	0.05	6.16	9:46	1.90	1.1896	1.597	0.977
	0.1	6.18	9:49	1.80	1.1865	1.517	0.928
	0.2	5.95	9:52	1.65	1.1845	1.393	0.853
	0.5	5.85	9:54	1.55	1.1820	1.311	0.802
	Standard		9:55	1.20			
	Standard		10:09	1.17			
	0	6.45	9:41	1.95	1.1935	1.634	1
	0.01	5.99	10:12	1.83	1.1680	1.551	0.949
	0.05	5.90	10:15	1.72	1.1660	1.475	0.903
	0.1	5.87	10:17	1.70	1.1640	1.460	0.894
	0.2	5.86	10:19	1.78	1.1625	1.531	0.937
	0.5	5.85	10:21	1.90	1.1615	1.636	1.001
CaCl ₂	Standard		10:22	1.14			
	Standard		10:35	1.15			
	0	6.45	9:41	1.95	1.1935	1.634	1
	0.01	6.28	10:37	1.87	1.1475	1.630	0.998

Table B.2 - continued.

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I	Ratio II
AlCl ₃	0.05	5.95	10:39	1.91	1.1465	1.666	1.020
	0.1	5.89	10:41	2.00	1.1460	1.745	1.068
	0.2	5.82	10:45	2.00	1.1420	1.751	1.072
	0.5	5.80	10:47	2.00	1.1400	1.754	1.073
	Standard		10:51	1.21			
	Standard		10:19	1.12			
	0	5.93	10:24	1.75	1.1185	1.565	1
	0.01	5.88	10:26	2.32	1.1180	2.075	1.326
	0.05	4.84	10:29	3.35	1.1165	3.000	1.917
	0.1	4.64	10:32	3.25	1.1150	2.915	1.863
	0.2	4.55	10:35	3.50	1.1145	3.140	2.006
	0.5	4.48	10:37	3.70	1.1125	3.326	2.125
	Standard		10:38	1.11			
	Standard		9:41	1.14			
FeCl ₃	0	5.93	9:45	1.80	1.1365	1.584	1
	0.01	5.63	9:47	2.40	1.1350	2.115	1.335
	0.05	4.94	9:50	2.15	1.1340	1.896	1.197
	0.1	4.49	9:52	2.00	1.1325	1.766	1.115

Table B.2 - continued.

Electrolyte	Volume of Electrolyte Added (ml)	pH	Time	Galvanometer Reading	Corrected Standard Reading	Ratio I	Ratio II
	0.2	4.13	9:55	1.90	1.1315	1.679	1.060
	0.5	3.73	9:58	2.10	1.1299	1.859	1.174
	Standard		9:59	1.08			

^{1,2} Refer to Table B.1.

Table B.3 - Modulus of Rupture and Shrinkage of Artificial Crusts of Soil Fractions

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Briquette Density (g/cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>washed soil</u>											
1	23.013	6.43	3.22	0.75	15.53	1.482	2035	1,994,300	8.26	0.36	29.57
2	23.886	6.43	3.22	0.71	14.70	1.625	2070	2,028,600	9.37	0.39	33.33
3	23.056	6.43	3.18	0.71	14.52	1.588	1985	1,945,300	9.10	0.39	34.15
4	23.103	6.43	3.22	0.71	14.70	1.572	1995	1,955,100	9.03	0.39	33.33
5	23.521	6.43	3.22	0.75	15.53	<u>1.515</u>	2065	2,023,700	<u>8.38</u>	<u>0.36</u>	<u>29.57</u>
Average						1.556			8.83	0.38	31.99
<u>clay fraction</u>											
1	17.754	5.95	2.90	0.71	12.25	1.449	1740	1,705,200	8.75	0.49	44.44
2	17.272	5.86	2.90	0.71	12.07	1.431	1645	1,612,100	8.27	0.48	45.26
3	15.361	5.83	2.86	0.64	10.67	1.440	1400	1,372,000	8.66	0.56	51.61
4	16.905	5.83	2.90	0.71	12.00	1.409	1700	1,666,000	8.55	0.51	45.58
5	17.527	5.86	2.90	0.71	12.07	<u>1.452</u>	1725	1,690,500	<u>8.67</u>	<u>0.49</u>	<u>45.26</u>
Average						1.436			8.58	0.51	46.43
<u>silt fraction</u>											
1	16.354	6.63	3.29	0.56	12.22	1.338	618	605,640	4.40	0.27	44.58
2	16.059	6.63	3.28	0.56	12.18	1.318	535	524,300	3.82	0.24	44.76
3	16.677	6.63	3.25	0.57	12.28	1.358	630	617,400	4.39	0.26	44.31
4	16.424	6.63	3.27	0.56	12.14	1.353	610	597,800	4.37	0.27	44.94
5	16.746	6.63	3.25	0.56	12.07	<u>1.387</u>	590	578,200	<u>4.25</u>	<u>0.25</u>	<u>45.26</u>
Average						1.351			4.25	0.26	44.77
<u>sand fraction</u>											
parameters immeasurable, briquettes crumbled at slightest touch											

Table B.4 - Modulus of Rupture and Shrinkage of Artificial Crusts
of Soils Saturated with Cations

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Briquette Density (g/cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>unwashed soil</u>											
1	23.083	6.47	3.22	0.83	17.29	1.335	530	519,400	1.77	0.08	21.59
2	23.681	6.47	3.22	0.83	17.29	1.370	495	485,100	1.64	0.07	21.59
3	24.503	6.47	3.22	0.87	18.13	1.352	565	553,700	1.70	0.07	17.77
4	24.493	6.51	3.22	0.87	18.24	1.343	600	588,000	1.81	0.07	17.28
5	23.934	6.47	3.22	0.83	17.29	<u>1.384</u>	510	499,800	<u>1.69</u>	<u>0.07</u>	<u>21.59</u>
Average						1.357			1.72	0.07	19.96
<u>washed soil</u>											
1	24.203	6.45	3.25	0.79	16.56	1.462	1530	1,499,400	5.54	0.23	24.90
2	24.486	6.45	3.18	0.75	15.38	1.592	1480	1,450,400	6.08	0.25	30.25
3	23.855	6.47	3.22	0.75	15.63	1.526	1440	1,411,200	5.84	0.24	29.12
4	23.414	6.45	3.18	0.71	14.56	1.608	1375	1,347,500	6.30	0.27	33.97
5	23.742	6.43	3.18	0.71	14.52	<u>1.635</u>	1375	1,347,500	<u>6.30</u>	<u>0.27</u>	<u>34.15</u>
Average						1.565			6.01	0.25	30.48
<u>Li-soil</u>											
1	23.540	6.27	3.12	0.71	13.89	1.695	4665	4,571,700	21.80	0.93	37.00
2	24.102	6.27	3.14	0.71	13.98	1.724	4540	4,449,200	21.08	0.87	36.60
3	24.583	6.29	3.14	0.75	14.81	1.660	4500	4,410,000	18.73	0.76	32.83
4	23.303	6.29	3.12	0.71	13.93	1.673	4200	4,116,000	19.63	0.84	36.83
5	23.259	6.33	3.10	0.71	13.93	<u>1.670</u>	4155	4,071,900	<u>19.54</u>	<u>0.84</u>	<u>36.83</u>
Average						1.684			20.16	0.85	36.02
<u>Na-soil</u>											
1	22.956	6.19	3.08	0.71	13.54	1.695	5190	5,086,200	24.57	1.07	38.59
2	23.194	6.19	3.06	0.75	14.21	1.632	5215	5,110,700	22.27	0.96	35.56
3	22.942	6.17	3.06	0.71	13.40	1.712	4780	4,684,400	22.78	0.99	39.23
4	23.060	6.23	3.08	0.75	14.39	1.603	5165	5,061,700	21.91	0.95	34.74
5	23.003	6.23	3.08	0.75	14.39	<u>1.599</u>	4470	4,380,600	<u>18.96</u>	<u>0.82</u>	<u>34.74</u>
Average						1.648			22.10	0.96	36.57

Table B.4 - continued.

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Briquette Density (g/cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>K-soil</u>											
1	23.579	6.35	3.14	0.71	14.16	1.665	2345	2,298,100	10.89	0.46	35.78
2	22.714	6.35	3.14	0.71	14.16	1.604	2110	2,067,800	9.80	0.43	35.78
3	22.145	6.35	3.12	0.71	14.07	1.574	2185	2,141,300	10.21	0.46	36.19
4	22.445	6.35	3.15	0.71	14.20	1.581	2000	1,960,000	9.26	0.41	35.60
5	23.064	6.35	3.18	0.71	14.34	<u>1.608</u>	2085	2,043,300	<u>9.56</u>	<u>0.41</u>	<u>34.97</u>
Average						1.606			9.94	0.43	35.66
<u>Mg-soil</u>											
1	23.788	6.430	3.18	0.79	16.15	1.473	3035	2,974,300	11.24	0.47	26.76
2	24.195	6.39	3.22	0.77	15.84	1.527	3057	2,995,860	11.77	0.49	28.16
3	24.303	6.35	3.18	0.79	15.95	1.524	3240	3,175,200	12.00	0.49	27.66
4	24.785	6.35	3.18	0.79	15.95	1.554	3262	3,196,760	12.08	0.49	27.66
5	24.322	6.35	3.22	0.75	15.34	<u>1.586</u>	3050	2,989,000	<u>12.38</u>	<u>0.51</u>	<u>30.43</u>
Average						1.533			11.89	0.49	28.13
<u>Ca-soil</u>											
1	24.268	6.33	3.18	0.79	15.90	1.526	2855	2,797,900	10.57	0.44	27.89
2	24.917	6.31	3.12	0.79	15.55	1.602	3050	2,989,000	11.51	0.46	29.48
3	24.139	6.29	3.14	0.79	15.60	1.547	2882	2,824,360	10.81	0.45	29.25
4	24.059	6.31	3.11	0.79	15.50	1.552	2847	2,790,060	10.78	0.45	29.71
5	24.537	6.29	3.14	0.79	15.60	<u>1.573</u>	2897	2,839,060	<u>10.87</u>	<u>0.44</u>	<u>29.25</u>
Average						1.560			10.91	0.45	29.12
<u>Al-soil</u>											
1	22.603	6.43	3.18	0.79	16.15	1.400	880	862,400	3.26	0.14	26.76
2	23.423	6.47	3.25	0.79	16.61	1.410	947	928,060	3.43	0.15	24.67
3	22.734	6.43	3.22	0.79	16.36	1.390	869	851,620	3.18	0.14	25.80
4	23.661	6.47	3.22	0.79	16.46	1.437	930	911,400	3.40	0.14	25.35
5	24.028	6.43	3.22	0.79	16.36	<u>1.469</u>	979	959,420	<u>3.58</u>	<u>0.15</u>	<u>25.80</u>
Average						1.421			3.37	0.14	25.68

Table B.4 - continued.

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Briquette Density (g/cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>Fe-soil</u>											
1	24.111	6.43	3.24	0.79	16.46	1.465	915	896,700	3.33	0.14	25.35
2	23.121	6.39	3.18	0.79	16.05	1.441	870	852,600	3.22	0.14	27.21
3	23.716	6.43	3.18	0.75	15.34	1.546	870	852,600	3.57	0.15	30.43
4	23.932	6.41	3.18	0.79	16.10	1.486	835	818,300	3.09	0.13	26.98
5	24.071	6.43	3.18	0.79	16.15	<u>1.490</u>	855	837,900	<u>3.17</u>	<u>0.13</u>	<u>26.76</u>
Average						1.486			3.28	0.14	27.35

Table B.5 - Modulus of Rupture and Shrinkage of Artificial Crusts of Sodium-Saturated Soil with Added Na⁺

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>Na-soil</u>										
1	24.250	6.43	3.18	0.83	16.97	3950	3,871,000	13.25	0.52	23.04
2	23.606	6.43	3.18	0.79	16.15	3590	3,518,200	13.30	0.56	26.76
3	23.657	6.43	3.18	0.75	15.34	3455	3,385,900	14.20	0.60	30.43
4	24.247	6.43	3.18	0.79	16.15	3850	3,773,000	14.26	0.59	26.76
5	24.733	6.43	3.18	0.79	16.15	3920	3,841,600	<u>14.52</u>	<u>0.59</u>	<u>26.76</u>
Average								13.91	0.57	26.75
<u>Na-soil + 2.5 x 10⁻² M Na⁺</u>										
1	24.523	6.39	3.18	0.83	16.87	3920	3,841,600	13.15	0.54	23.49
2	22.670	6.43	3.14	0.71	14.34	3750	3,675,000	17.41	0.77	34.97
3	22.469	6.39	3.18	0.71	14.43	3605	3,532,900	16.53	0.74	34.56
4	23.676	6.43	3.18	0.79	16.15	3520	3,449,600	13.04	0.55	26.76
5	23.283	6.47	3.18	0.71	14.61	3875	3,797,500	<u>17.77</u>	<u>0.76</u>	<u>33.74</u>
Average								15.58	0.67	30.70
<u>Na-soil + 5 x 10⁻² M Na⁺</u>										
1	23.167	6.39	3.14	0.71	14.25	3620	3,547,600	16.81	0.73	35.37
2	22.963	6.35	3.14	0.79	15.75	3775	3,699,500	14.16	0.62	28.57
3	23.431	6.39	3.14	0.71	14.25	3480	3,410,400	16.16	0.69	35.37
4	23.475	6.39	3.14	0.75	15.05	3320	3,253,600	13.82	0.59	31.75
5	24.375	6.43	3.14	0.79	15.95	3670	3,596,600	<u>13.76</u>	<u>0.56</u>	<u>27.66</u>
Average								14.94	0.64	31.74
<u>Na-soil + 1 x 10⁻¹ M Na⁺</u>										
1	24.386	6.35	3.14	0.79	15.75	3160	3,096,800	11.85	0.49	28.57
2	24.104	6.35	3.14	0.75	15.75	2930	2,871,400	12.19	0.51	28.57
3	23.451	6.39	3.22	0.71	14.61	2900	2,842,000	13.13	0.56	33.74
4	23.774	6.39	3.14	0.75	15.05	3000	2,940,000	12.48	0.52	31.75
5	23.631	6.39	3.14	0.75	15.05	3055	2,993,900	<u>12.71</u>	<u>0.54</u>	<u>31.75</u>
Average								12.47	0.52	30.88
<u>Na-soil + 2 x 10⁻¹ M Na⁺</u>										
1	24.363	6.39	3.18	0.79	16.05	3050	2,989,000	11.30	0.46	27.21
2	24.529	6.39	3.18	0.79	16.05	3165	3,101,700	11.72	0.48	27.21
3	24.838	6.39	3.18	0.79	16.05	3110	3,047,800	11.52	0.46	27.21
4	24.566	6.39	3.18	0.79	16.05	3090	3,028,200	11.44	0.47	27.21
5	24.992	6.35	3.18	0.79	16.05	3205	3,140,900	<u>11.87</u>	<u>0.47</u>	<u>27.21</u>
Average								11.57	0.47	27.21

Table B.6 - Modulus of Rupture and Shrinkage of Artificial Crusts
of Sodium-Saturated Soil with Added $(\text{NaPO}_3)_6$

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>Na-soil</u>										
1	22.310	6.35	3.18	0.75	15.14	3260	3,194,800	13.40	0.60	31.34
2	21.674	6.35	3.18	0.71	14.34	3635	3,562,300	16.67	0.77	34.97
3	22.105	6.35	3.18	0.71	14.34	3000	2,940,000	13.76	0.62	34.97
4	22.923	6.35	3.18	0.75	15.14	3610	3,537,800	14.83	0.65	31.34
5	22.100	6.35	3.18	0.75	15.14	3320	3,253,600	<u>13.64</u>	<u>0.62</u>	<u>31.34</u>
Average								14.46	0.65	32.79
<u>Na-soil + 8.2×10^{-6} M $(\text{NaPO}_3)_6$</u>										
1	22.640	6.35	3.18	0.79	15.95	3465	3,395,700	12.83	0.57	27.66
2	23.159	6.35	3.18	0.79	15.95	3570	3,498,600	13.22	0.57	27.66
3	22.595	6.35	3.18	0.75	15.14	3000	2,940,000	12.33	0.55	31.34
4	22.892	6.35	3.18	0.79	15.95	3110	3,047,800	11.52	0.50	27.66
5	22.901	6.35	3.18	0.79	15.95	3320	3,253,600	<u>12.30</u>	<u>0.54</u>	<u>27.66</u>
Average								12.44	0.55	28.40
<u>Na-soil + 1.64×10^{-5} M $(\text{NaPO}_3)_6$</u>										
1	23.861	6.35	3.18	0.79	15.95	3160	3,096,800	11.70	0.49	27.66
2	22.118	6.35	3.18	0.71	14.34	3390	3,322,200	15.54	0.70	34.97
3	22.891	6.35	3.18	0.79	15.95	3335	3,268,300	12.35	0.54	27.66
4	22.292	6.35	3.18	0.75	15.14	2750	2,695,000	11.30	0.51	31.34
5	23.272	6.35	3.18	0.79	15.95	3100	3,038,000	<u>11.48</u>	<u>0.49</u>	<u>27.66</u>
Average								12.47	0.55	29.86
<u>Na-soil + 3.28×10^{-5} M $(\text{NaPO}_3)_6$</u>										
1	23.475	6.35	3.18	0.79	15.95	3185	3,121,300	11.80	0.50	27.66
2	22.227	6.35	3.18	0.79	15.95	3240	3,175,200	12.00	0.54	27.66
3	21.906	6.35	3.18	0.71	14.34	2775	2,719,500	12.72	0.58	34.97
4	21.821	6.35	3.18	0.75	15.14	2550	2,499,000	10.48	0.48	31.34
5	22.202	6.35	3.18	0.79	15.95	3005	2,944,900	<u>11.13</u>	<u>0.50</u>	<u>27.66</u>
Average								11.63	0.52	29.86

Table B.6 - continued.

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>Na-soil + 1.312 x 10⁻⁴ M (NaPO₃)₆</u>										
1	21.982	6.35	3.18	0.75	15.14	2535	2,484,300	10.42	0.47	31.34
2	21.893	6.35	3.18	0.75	15.14	2875	2,817,500	11.81	0.54	31.34
3	21.849	6.35	3.18	0.75	15.14	2790	2,734,200	11.46	0.52	31.34
4	22.771	6.35	3.18	0.79	15.95	2980	2,920,400	11.04	0.48	27.66
5	21.999	6.35	3.18	0.75	15.14	2645	2,592,100	<u>10.87</u>	<u>0.49</u>	<u>31.34</u>
Average								11.12	0.50	30.60
<u>Na-soil + 2.624 x 10⁻⁴ M (NaPO₃)₆</u>										
1	22.808	6.35	3.18	0.79	15.95	2980	2,920,400	11.04	0.48	27.66
2	22.777	6.35	3.18	0.79	15.95	3100	3,038,000	11.48	0.50	27.66
3	22.875	6.35	3.18	0.79	15.95	3075	3,013,500	11.39	0.50	27.66
4	22.959	6.35	3.18	0.79	15.95	3090	3,028,200	11.44	0.50	27.66
5	22.802	6.35	3.18	0.79	15.95	3000	2,940,000	<u>11.11</u>	<u>0.49</u>	<u>27.66</u>
Average								11.29	0.49	27.66
<u>Na-soil + 5.248 x 10⁻⁴ M (NaPO₃)₆</u>										
1	23.047	6.35	3.18	0.79	15.95	2745	2,690,100	10.17	0.44	27.66
2	22.923	6.35	3.18	0.79	15.95	3280	3,214,400	12.15	0.53	27.66
3	22.967	6.35	3.18	0.79	15.95	3280	3,214,400	12.15	0.53	27.66
4	22.903	6.35	3.18	0.79	15.95	2920	2,861,600	10.81	0.47	27.66
5	22.929	6.35	3.18	0.79	15.95	3020	2,959,600	11.18	<u>0.49</u>	<u>27.66</u>
Average								11.29	0.49	27.66

Table B.7 - Modulus of Rupture and Shrinkage of Artificial Crusts
of Soil with Added Sand (4 soil : 1 sand)

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>unwashed soil</u>										
1	23.895	6.43	3.22	0.79	16.36	1930	1,891,400	7.06	0.30	25.80
2	24.163	6.35	3.22	0.79	16.15	1935	1,896,300	7.08	0.29	26.76
3	23.679	6.43	3.18	0.79	16.15	1925	1,886,500	7.13	0.30	26.76
4	23.145	6.43	3.18	0.79	16.15	1905	1,866,900	7.06	0.31	26.76
5	23.969	6.43	3.18	0.79	16.15	1920	1,881,600	<u>7.11</u>	<u>0.30</u>	<u>26.76</u>
Average								7.09	0.30	26.57
<u>soil + 320-325 mesh sand</u>										
1	21.165	6.55	3.25	0.71	15.11	500	490,000	2.24	0.11	31.47
2	21.826	6.55	3.22	0.60	12.65	535	524,300	3.39	0.16	42.63
3	21.321	6.51	3.25	0.56	11.85	520	509,600	3.75	0.17	46.26
4	21.391	6.55	3.25	0.56	11.92	500	490,000	3.61	0.17	45.94
5	20.879	6.59	3.29	0.68	14.74	485	475,300	<u>2.34</u>	<u>0.11</u>	<u>33.15</u>
Average								3.07	0.14	39.89
<u>soil + 60-120 mesh sand</u>										
1	26.331	6.59	3.29	0.83	18.00	1030	1,009,400	3.34	0.13	18.37
2	24.475	6.55	3.25	0.75	15.97	925	906,500	3.72	0.15	27.57
3	24.921	6.55	3.25	0.79	16.82	1050	1,029,000	3.80	0.15	23.72
4	24.477	6.55	3.25	0.75	15.97	980	960,400	3.94	0.16	27.57
5	24.674	6.51	3.25	0.75	15.87	975	955,500	<u>3.92</u>	<u>0.16</u>	<u>28.03</u>
Average								3.74	0.15	25.05
<u>soil + 50-200 mesh sand</u>										
1	20.010	6.75	3.37	0.83	18.88	300	294,000	0.95	0.05	14.38
2	19.877	6.71	3.37	0.79	17.86	340	333,200	1.19	0.06	19.00
3	19.822	6.71	3.33	0.79	17.65	315	308,700	1.11	0.06	19.95
4	20.702	6.71	3.33	0.83	18.55	345	338,100	1.11	0.05	15.87
5	20.164	6.71	3.33	0.79	17.65	320	313,600	<u>1.13</u>	<u>0.06</u>	<u>19.95</u>
Average								1.10	0.06	17.83

Table B.8 - Modulus of Rupture and Shrinkage of Artificial Crusts of Soil with Added Al₂O₃

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage
<u>unwashed soil</u>										
1	23.895	6.43	3.22	0.79	16.36	1930	1,891,400	7.06	0.30	25.80
2	24.163	6.35	3.22	0.79	16.15	1935	1,896,300	7.08	0.29	26.76
3	23.679	6.43	3.18	0.79	16.15	1925	1,886,500	7.13	0.30	26.76
4	23.145	6.43	3.18	0.79	16.15	1905	1,866,900	7.06	0.31	26.76
5	23.969	6.43	3.18	0.79	16.15	1920	1,881,600	<u>7.11</u>	<u>0.30</u>	<u>26.76</u>
Average								7.09	0.30	26.57
<u>soil, 1% Al₂O₃</u>										
1	23.332	6.39	3.22	0.71	14.61	1820	1,783,600	8.24	0.35	33.74
2	23.974	6.43	3.18	0.75	15.34	2000	1,960,000	8.22	0.34	30.43
3	23.978	6.43	3.18	0.75	15.34	1915	1,876,700	7.87	0.33	30.43
4	24.172	6.43	3.18	0.79	16.15	2030	1,989,400	7.52	0.31	26.76
5	23.730	6.43	3.22	0.75	15.53	1850	1,813,000	<u>7.51</u>	<u>0.32</u>	<u>29.57</u>
Average								7.87	0.33	30.19
<u>soil, 3% Al₂O₃</u>										
1	23.282	6.43	3.18	0.75	15.34	1650	1,617,000	6.78	0.29	30.43
2	24.427	6.47	3.18	0.75	15.43	1645	1,612,100	6.76	0.28	30.02
3	23.414	6.47	3.18	0.79	16.25	1600	1,568,000	5.93	0.25	26.30
4	23.768	6.43	3.22	0.79	16.37	1620	1,587,600	5.93	0.25	25.76
5	23.347	6.43	3.18	0.75	15.34	1590	1,558,200	<u>6.53</u>	<u>0.28</u>	<u>30.43</u>
Average								6.39	0.27	34.67
<u>soil, 5% Al₂O₃</u>										
1	24.233	6.47	3.22	0.79	16.46	1580	1,548,400	5.78	0.24	25.35
2	23.888	6.47	3.22	0.79	16.46	1585	1,553,300	5.80	0.24	25.35
3	23.672	6.47	3.22	0.75	15.63	1550	1,519,000	6.29	0.27	29.12
4	23.580	6.47	3.22	0.75	15.63	1480	1,450,400	6.01	0.25	29.12
5	23.347	6.47	3.22	0.75	15.63	1520	1,489,600	<u>6.17</u>	<u>0.26</u>	<u>29.12</u>
Average								6.01	0.25	27.61

Table B.9 - Modulus of Rupture and Shrinkage of Artificial Crusts of Sodium-Saturated Soil at Different pHs

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)	MOR/g (bars/g)	Shrinkage (%)
<u>Na-soil, pH = 3.05</u>										
1	22.635	6.31	3.10	0.71	13.89	3010	2,949,800	14.16	0.63	37.01
2	23.282	6.27	3.10	0.79	15.36	3325	3,258,500	12.63	0.54	30.34
3	22.873	6.27	3.06	0.79	15.16	3340	3,273,200	12.85	0.56	31.25
4	22.503	6.27	3.10	0.75	14.58	3140	3,077,200	13.24	0.59	33.88
5	22.754	6.27	3.10	0.75	14.58	3300	3,234,000	<u>13.91</u>	<u>0.61</u>	<u>33.88</u>
Average								13.36	0.59	33.27
<u>Na-soil, pH = 4.8</u>										
1	23.170	6.35	3.14	0.79	15.75	3935	3,856,300	14.76	0.64	28.57
2	22.853	6.35	3.14	0.79	15.75	3990	3,910,200	14.96	0.65	28.57
3	23.653	6.35	3.14	0.79	15.75	4025	3,944,500	15.10	0.64	28.57
4	23.161	6.35	3.14	0.79	15.75	3060	3,782,800	14.48	0.61	28.57
5	23.005	6.35	3.14	0.79	15.75	3940	3,861,200	<u>14.78</u>	<u>0.64</u>	<u>28.57</u>
Average								14.82	0.64	28.57
<u>Na-soil, pH = 6.9</u>										
1	23.328	6.35	3.18	0.79	15.95	3080	3,018,400	11.41	0.49	27.66
2	24.097	6.35	3.18	0.79	15.95	3505	3,434,900	12.98	0.54	27.66
3	23.176	6.35	3.18	0.79	15.95	3600	3,528,000	13.33	0.58	27.66
4	23.051	6.35	3.18	0.79	15.95	3645	3,572,100	13.50	0.59	27.66
5	23.519	6.35	3.18	0.79	15.95	3200	3,136,000	<u>11.85</u>	<u>0.50</u>	<u>27.66</u>
Average								12.61	0.54	27.66
<u>Na-soil, pH = 9</u>										
1	23.051	6.39	3.18	0.79	16.05	3250	3,185,000	12.04	0.52	27.21
2	24.059	6.39	3.18	0.79	16.05	3905	3,826,900	14.46	0.60	27.21
3	24.029	6.35	3.18	0.75	15.14	3800	3,724,000	15.61	0.65	31.34
4	22.718	6.43	3.18	0.75	15.34	3480	3,410,400	14.30	0.63	30.43
5	23.652	6.35	3.18	0.79	15.95	3970	3,890,600	<u>14.70</u>	<u>0.62</u>	<u>27.66</u>
Average								14.22	0.60	28.77
<u>Na-soil, pH = 10.5</u>										
1	24.001	6.35	3.22	0.79	16.15	3950	3,871,000	14.59	0.61	26.76
2	22.908	6.35	3.18	0.79	15.95	3795	3,719,100	14.05	0.61	27.66
3	24.027	6.35	3.18	0.79	15.95	3650	3,577,000	13.52	0.56	27.66
4	23.053	6.35	3.18	0.79	15.95	3620	3,547,600	13.41	0.58	27.66
5	23.289	6.35	3.18	0.79	15.95	3675	3,601,500	<u>13.61</u>	<u>0.58</u>	<u>27.66</u>
Average								13.84	0.59	27.48

Table B.10 - Modulus of Rupture of Artificial Crusts
of Potassium-Saturated Soil Prepared
with Applied Pressure

Replication	Briquette Width (cm)	Briquette Thickness (cm)	Volume of Water Used (cm ³)	Breaking Force (dynes)	MOR (bars)
1	3.41	0.60	2900	2,842,000	17.36
2	3.45	0.60	2650	2,597,000	15.68
3	3.41	0.60	2855	2,797,900	17.09
4	3.41	0.64	2890	2,832,200	15.21
5	3.41	0.60	3050	2,989,000	<u>18.26</u>
Average					16.72

Table B.11 - Modulus of Rupture of Muscovite Sheets

Replication	Sheet Width (cm)	Sheet Thickness (cm)	Volume of Water Used (cm ³)	Breaking Force (dynes)	
1	3.4	0.008	3200	3,136,000	17,294.12
2	3.4	0.008	3200	3,136,000	17,294.12
3	3.4	0.007	4500	4,410,000	31,879.52
4	3.4	0.0075	3450	3,381,000	21,214.12
5	3.4	0.005	2000	1,960,000	<u>27,670.59</u>
Average					23,070.58

Table B.12 - Bulk Density of Artificial Crusts of Soil Fractions

Replication	Weight of Briquette, String & Paraffin	Weight of Dry Briquette	Weight of Paraffin	Weight of String	Weight of Briquette, String & Paraffin in Water	Loss in Weight	Volume of Paraffin	Volume of String	Volume of Briquette	Bulk Density
<u>washed soil</u>										
1	13.191	11.944	1.225	0.022	5.523	7.668	1.531	0.002	6.135	1.947
2	13.261	12.019	1.220	0.022	5.559	7.702	1.525	0.002	6.175	1.946
Average										1.947
<u>clay fraction</u>										
1	8.897	8.068	0.807	0.022	3.670	5.227	1.009	0.002	4.216	1.914
2	10.052	9.001	1.029	0.022	4.002	6.050	1.286	0.002	4.762	1.890
Average										1.902
<u>silt fraction</u>										
1	9.350	7.860	1.468	0.022	3.696	5.654	1.835	0.002	3.817	2.059
2	10.384	789	1.573	0.022	4.936	6.348	1.966	0.002	4.380	2.007
Average										2.033
<u>sand fraction</u> parameters unmeasurable, briquettes crumbled at slightest touch										

Table B.13 - Bulk Density of Artificial Crusts of Soils Saturated with Cations

Replication	Weight of Briquette, String & Paraffin	Weight of Dry Briquette	Weight of Paraffin	Weight of String	Weight of Briquette, String & Paraffin in Water	Loss in Weight	Volume of Paraffin	Volume of String	Volume of Briquette	Bulk Density
<u>unwashed soil</u>										
1	14.149	12.011	2.116	0.022	5.663	8.486	2.645	0.002	5.839	2.057
2	13.041	11.166	1.853	0.022	5.348	7.693	2.316	0.002	5.375	<u>2.077</u>
Average										2.067
<u>washed soil</u>										
1	13.191	11.944	1.225	0.022	5.523	7.668	1.531	0.002	6.135	1.947
2	13.261	12.019	1.220	0.022	5.559	7.702	1.525	0.002	6.175	<u>1.946</u>
Average										1.947
<u>Li-soil</u>										
1	11.893	11.168	0.703	0.022	5.309	6.584	0.879	0.002	5.703	1.958
2	13.086	12.265	0.799	0.022	5.840	7.246	0.999	0.002	6.245	<u>1.964</u>
Average										1.961
<u>Na-soil</u>										
1	12.285	11.493	0.770	0.022	5.632	6.653	0.963	0.002	5.688	2.021
2	12.721	11.822	0.877	0.022	5.846	6.875	1.096	0.002	5.777	<u>2.046</u>
Average										2.034
<u>K-soil</u>										
1	12.272	11.279	0.971	0.022	5.418	6.854	1.214	0.002	5.638	2.001
2	12.876	11.862	0.992	0.022	5.662	7.214	1.240	0.002	5.972	<u>1.986</u>
Average										

Table B.13 - continued.

Replication	Weight of Briquette, String & Paraffin	Weight of Dry Briquette	Weight of Paraffin	Weight of String	Weight of Briquette, String & Paraffin in Water	Loss in Weight	Volume of Paraffin	Volume of String	Volume of Briquette	Bulk Density
<u>Mg-soil</u>										
1	12.627	11.532	1.073	0.022	5.608	7.019	1.341	0.002	5.676	2.032
2	12.728	11.689	1.017	0.022	5.655	7.073	1.271	0.002	5.800	<u>2.015</u>
Average										2.024
<u>Ca-soil</u>										
1	14.233	12.795	1.415	0.022	6.329	7.904	1.769	0.002	6.187	2.068
2	13.301	11.943	1.336	0.022	5.910	7.391	1.670	0.002	5.719	<u>2.088</u>
Average										2.078
<u>Al-soil</u>										
1	12.624	11.270	1.332	0.022	5.128	7.196	1.665	0.002	5.529	2.038
2	12.727	11.340	1.365	0.022	5.152	7.575	1.706	0.002	5.867	<u>1.933</u>
Average										1.986
<u>Fe-soil</u>										
1	13.700	12.236	1.442	0.022	5.803	7.897	1.803	0.002	6.092	2.009
2	13.624	12.191	1.411	0.022	5.681	7.943	1.764	0.002	6.177	<u>1.974</u>
Average										1.992

Table B.14 - Water Permeability of Artificial Crusts of Soil Fractions

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Time of Wetting (sec)	Water Permeability (sec/cm)
<u>washed soil</u>							
1	23.916	6.43	3.18	0.75	15.34	189.0	252.00
2	23.869	6.47	3.18	0.79	16.25	<u>155.0</u>	<u>196.20</u>
Average						172.0	224.10
<u>clay fraction</u>							
1	19.213	6.19	3.02	0.71	13.27	190.0	267.61
2	19.009	6.19	3.02	0.68	12.71	<u>182.0</u>	<u>267.65</u>
Average						186.0	267.63
<u>silt fraction</u>							
1	19.651	6.63	3.33	0.68	15.01	82.0	120.59
2	19.738	6.63	3.33	0.71	15.68	<u>83.2</u>	<u>117.18</u>
Average						82.6	118.89
<u>sand fraction</u>							
1	26.719	6.75	3.37	0.83	18.88	10.0	12.05
2	26.852	6.75	3.37	0.83	18.88	<u>10.3</u>	<u>12.41</u>
Average						10.2	12.23

Table B.15 - Water Permeability of Artificial Crusts
of Soils Saturated with Cations

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Time of Wetting (sec)	Water Permeability (sec/cm)
<u>unwashed soil</u>							
1	24.321	6.51	3.22	0.79	16.56	214.9	272.03
2	23.036	6.47	3.25	0.71	14.93	<u>221.0</u>	<u>311.27</u>
Average						217.9	291.65
<u>washed soil</u>							
1	23.916	6.43	3.18	0.75	15.34	189.0	252.00
2	23.869	6.47	3.18	0.79	16.25	<u>155.0</u>	<u>196.20</u>
Average						172.0	224.10
<u>Li-soil</u>							
1	20.991	6.19	3.02	0.64	11.96	> 43,200	67,500
2	22.588	6.27	3.18	0.64	12.76	<u>> 43,200</u>	<u>67,500</u>
Average						> 43,200	67,500
<u>Na-soil</u>							
1	19.215	6.07	3.02	0.64	11.73	> 43,200	67,500
2	20.239	6.11	3.02	0.64	11.81	<u>> 43,200</u>	<u>67,500</u>
Average						> 43,200	67,500
<u>K-soil</u>							
1	22.154	6.35	3.18	0.64	12.92	4.084.0	6381.25
2	21.236	6.35	3.18	0.64	12.92	<u>4,080.0</u>	<u>6375.00</u>
Average						4,082.0	6378.13

Table B.15 - continued.

Replication	Briquette Weight (g)	Briquette Length (cm)	Briquette Width (cm)	Briquette Thickness (cm)	Briquette Volume (cm ³)	Time of Wetting (sec)	Water Permeability (sec/cm)
<u>Mg-soil</u>							
1	23.153	6.31	3.10	0.71	13.89	215.0	302.82
2	23.538	6.35	3.10	0.71	13.98	<u>200.1</u>	<u>281.83</u>
Average						207.6	292.33
<u>Ca-soil</u>							
1	23.752	6.27	3.10	0.71	13.80	153.6	216.34
2	24.954	6.31	3.10	0.75	14.67	<u>155.0</u>	<u>206.67</u>
Average						154.3	211.51
<u>Al-soil</u>							
1	21.329	6.47	3.18	0.71	14.61	80.2	112.96
2	22.118	6.47	3.22	0.71	14.79	<u>75.2</u>	<u>105.92</u>
Average						77.7	109.44
<u>Fe-soil</u>							
1	22.544	6.55	3.18	0.79	16.45	54.0	68.35
2	22.467	6.55	3.18	0.79	16.45	<u>52.0</u>	<u>65.82</u>
Average						53.0	67.09

Table B.16 - Oxygen Permeability of Artificial Crusts
of Soil Fractions

Replication	Thickness of Briquette (cm)	Partial Pressure of O ₂ , initial (atm)	Partial Pressure of O ₂ , final (atm)	Amount of O ₂ Diffused (atm Partial Pressure)	Oxygen Permeability ($\frac{\text{atm-cm}}{\text{sec}}$)
<u>unwashed soil</u>					
1	0.876	0.0105	0.0434	0.0329	0.0288
2	0.876	0.0013	0.0355	0.0342	0.0300
3	0.867	0	0.0342	0.0342	0.0297
4	0.867	0	0.0355	0.0355	<u>0.0308</u>
Average					0.0298
<u>washed soil</u>					
1	0.782	0	0.0316	0.0316	0.0247
2	0.782	0.0066	0.0395	0.0329	0.0257
3	0.796	0	0.0316	0.0316	0.0252
4	0.796	0.0276	0.0566	0.0290	<u>0.0231</u>
Average					0.0247
<u>clay</u>					
1	0.660	0	0.0263	0.0263	0.0174
2	0.660	0	0.0276	0.0276	0.0182
3	0.740	0	0.0263	0.0263	0.0195
4	0.740	0	0.025	0.025	<u>0.0185</u>
Average					0.0184
<u>silt</u>					
1	0.591	0.0039	0.0342	0.0303	0.0179
2	0.591	0	0.0316	0.0316	0.0187
3	0.581	0.0053	0.0368	0.0315	0.0183
4	0.581	0.0026	0.0355	0.0329	<u>0.0191</u>
Average					0.0185
<u>sand</u>					
1	0.849	0.0316	0.0645	0.0329	0.0279
2	0.849	0.0342	0.0684	0.0342	0.0290
3	0.850	0.0263	0.0632	0.0369	0.0314
4	0.850	0.0132	0.0513	0.0381	<u>0.0324</u>
Average					0.0302

Table B.17 - Oxygen Permeability of Artificial Crusts
of Cation-Saturated Soils

Replication	Thickness of Briquette (cm)	Partial Pressure of O ₂ , initial (atm)	Partial Pressure of O ₂ , final (atm)	Amount of O ₂ Diffused (atm Partial Pressure)	Oxygen Permeability ($\frac{\text{atm-cm}}{\text{sec}}$)
<u>Li-soil</u>					
1	0.765	0.0197	0.0316	0.0119	0.0091
2	0.765	0.025	0.0368	0.0118	0.0090
3	0.766	0	0.0118	0.0118	0.0090
4	0.766	0.0105	0.0237	0.0132	<u>0.0101</u>
Average					0.0093
<u>Na-soil</u>					
1	0.759	0	0.0145	0.0145	0.0110
2	0.759	0.0092	0.025	0.0158	0.0120
3	0.758	0.0105	0.0224	0.0119	0.0090
4	0.758	0.0053	0.0211	0.0158	<u>0.0120</u>
Average					0.0110
<u>K-soil</u>					
1	0.760	0	0.0132	0.0132	0.0100
2	0.760	0.0105	0.0276	0.0171	0.0130
3	0.765	0	0.0158	0.0158	0.0121
4	0.765	0.0118	0.0289	0.0171	<u>0.0131</u>
Average					0.0121
<u>Mg-soil</u>					
1	0.788	0.0132	0.0368	0.0236	0.0186
2	0.788	0.0105	0.0355	0.025	0.0197
3	0.777	0.0066	0.0303	0.0237	0.0184
4	0.777	0.0013	0.0237	0.0224	<u>0.0174</u>
Average					0.0185

Table B.17 - continued.

Replication	Thickness of Briquette (cm)	Partial Pressure of O ₂ , initial (atm)	Partial Pressure of O ₂ , final (atm)	Amount of O ₂ Diffused Partial Pressure)	Oxygen Permeability ($\frac{\text{atm-cm}}{\text{sec}}$)
<u>Ca-soil</u>					
1	0.822	0.0105	0.0408	0.0303	0.0249
2	0.822	0	0.0289	0.0289	0.0238
3	0.836	0	0.0289	0.0289	0.0242
4	0.836	0.0132	0.0421	0.0289	<u>0.0242</u>
Average					0.0243
<u>Al-soil</u>					
1	0.776	0.0263	0.0605	0.0342	0.0265
2	0.776	0.0329	0.0697	0.0368	0.0286
3	0.822	0.0158	0.0474	0.0316	0.0260
4	0.822	0.0132	0.0447	0.0315	<u>0.0259</u>
Average					0.0268
<u>Fe-soil</u>					
1	0.800	0.0026	0.0395	0.0369	0.0295
2	0.800	0	0.0355	0.0355	0.0284
3	0.808	0.0158	0.0500	0.0342	0.0276
4	0.808	0	0.0342	0.0342	<u>0.0276</u>
Average					0.0283

Appendix C

PLATES

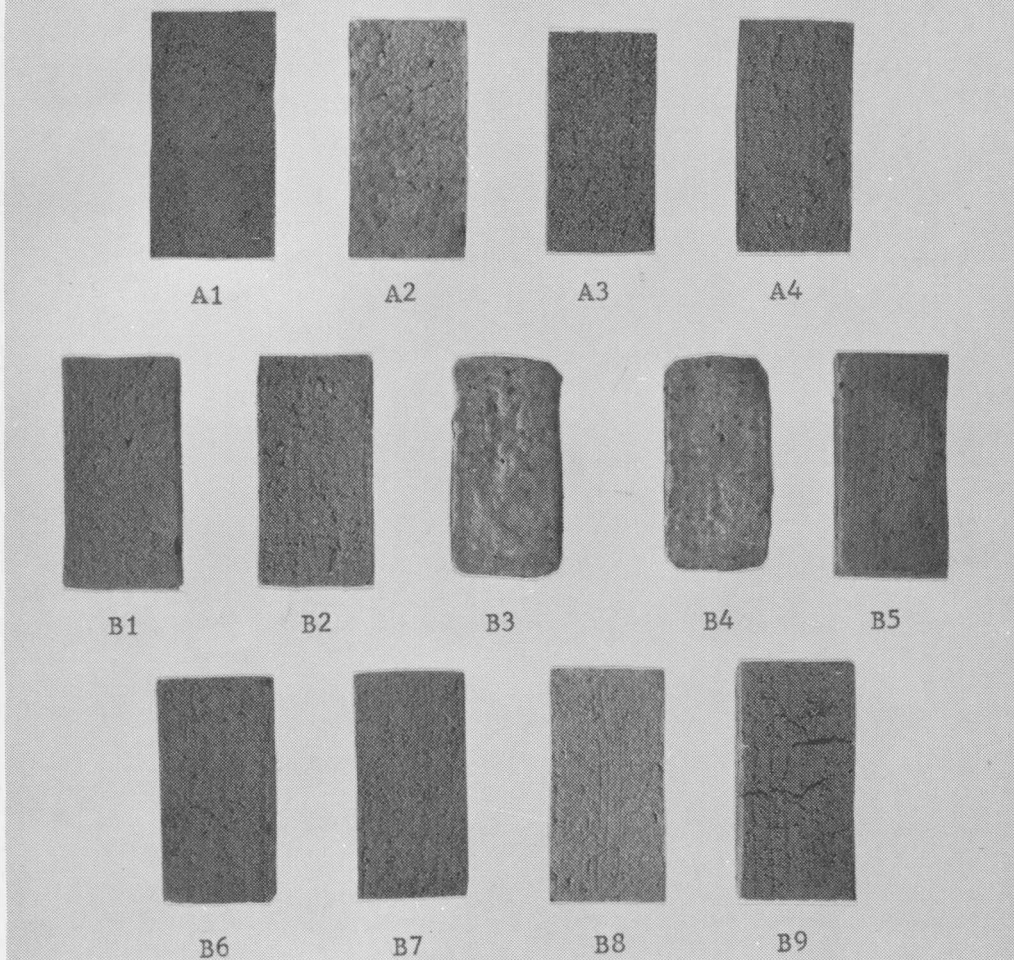


Plate C.1 - Briquettes of Artificial Pylon Crusts. A1, washed soil A2, clay; A3, silt; A4, sand; B1, unwashed soil; B2, washed soil; B3, Li-soil; B4, Na-soil; B5, K-soil; B6, Mg-soil; B7, Ca-soil; B8, Al-soil B9, Fe-soil.

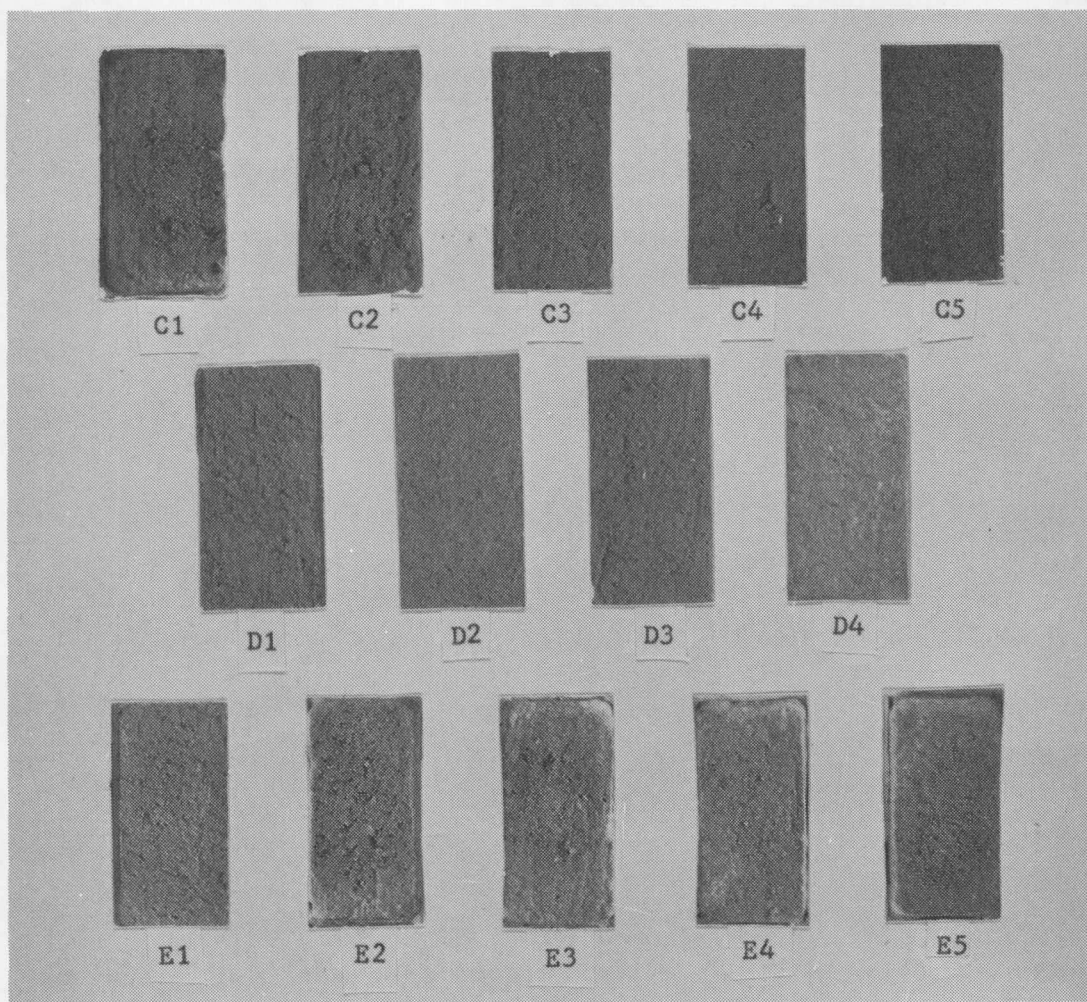


Plate C.1 - continued. C1, Na-soil; C2, Na-soil + 0.025 M NaCl; C3, Na-soil + 0.05 M NaCl; C4, Na-soil + 0.1 M NaCl; C5, Na-soil + 0.2 M NaCl; D1, unwashed soil; D2, soil + 50-200 mesh sand; D3, soil + 60-120 mesh sand; D4, soil + 320-325 mesh sand; E1, Na-soil at pH 3.05; E2, Na-soil at pH 4.8; E3, Na-soil at pH 6.9; E4, Na-soil at pH 9; E5, Na-soil at pH 10.5.

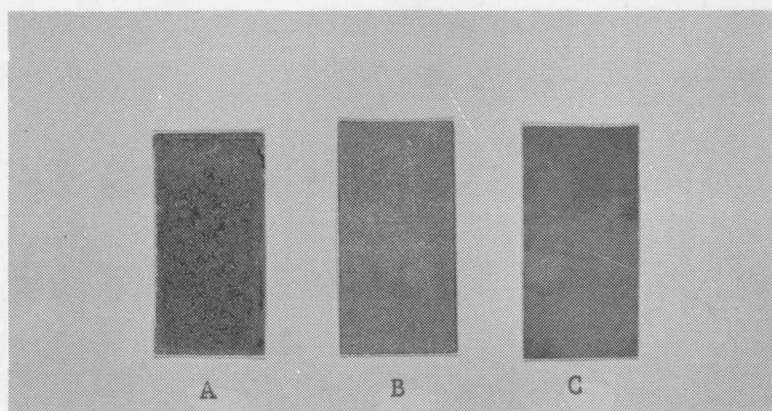


Plate C.2 - Briquettes of: A, K-soil; B, K-soil prepared with applied pressure; C, muscovite.

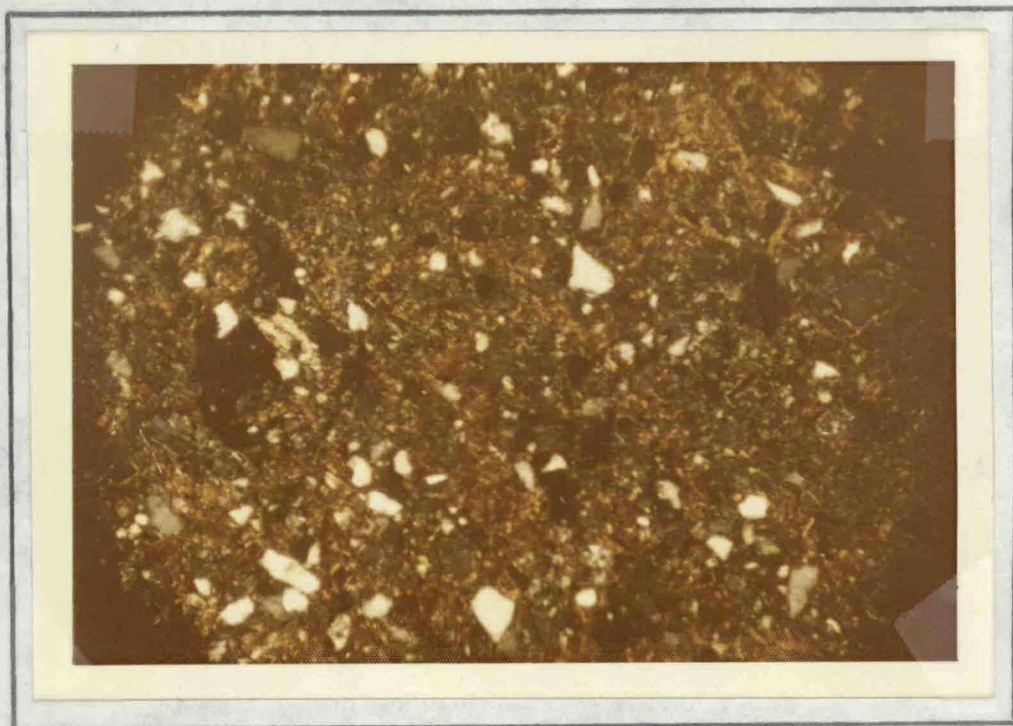
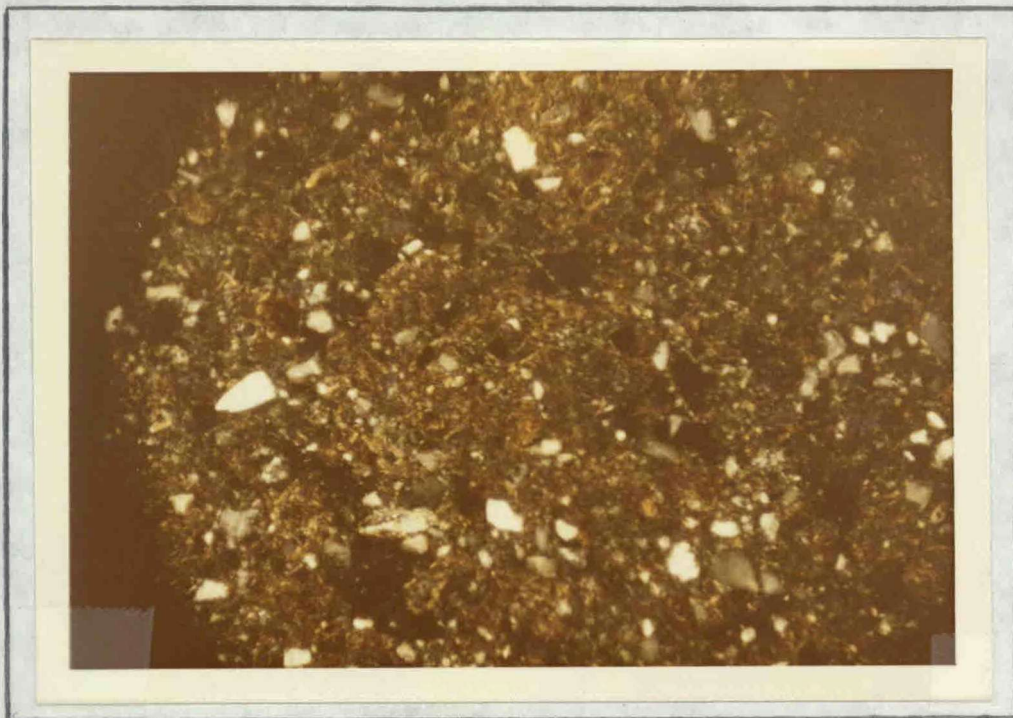
Appendix D

PHOTOMICROGRAPHS OF THIN SECTIONS

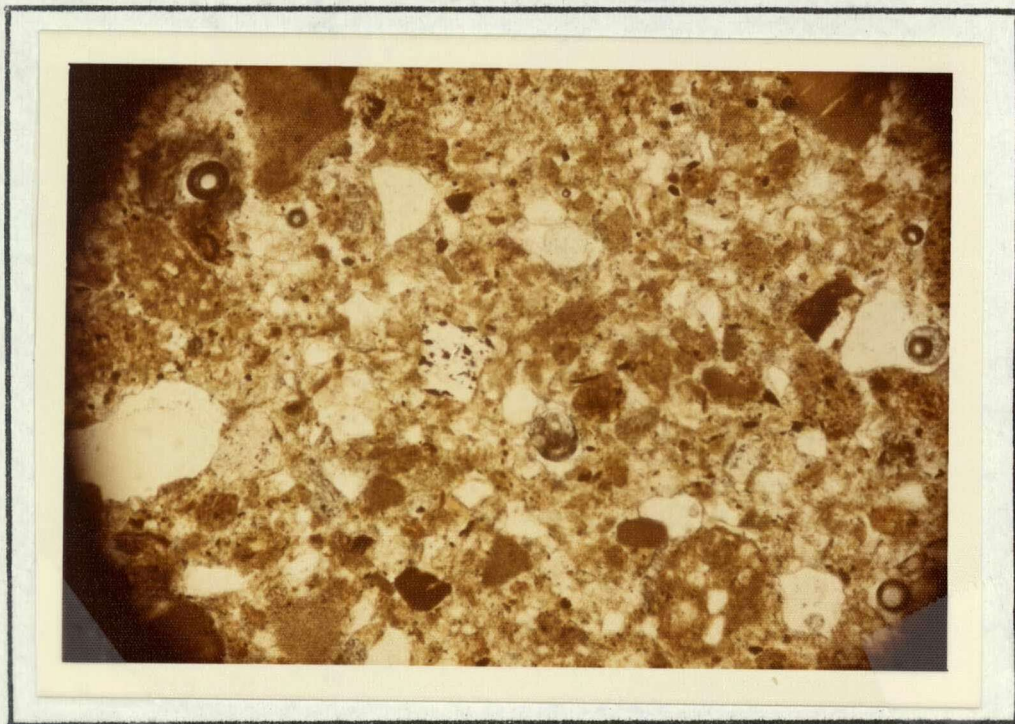
Explanation: The following photomicrographs are arranged in sets of three. The first print shows a thin section photographed under ordinary light; the next two prints show the same thin section photographed under polarized light. The first two pictures were taken at 0° angle of rotation of the microscope stage; the third picture was taken at 45° angle of rotation of the microscope stage, clockwise. The kind of soil or soil fraction is labelled at the first print of each set only.

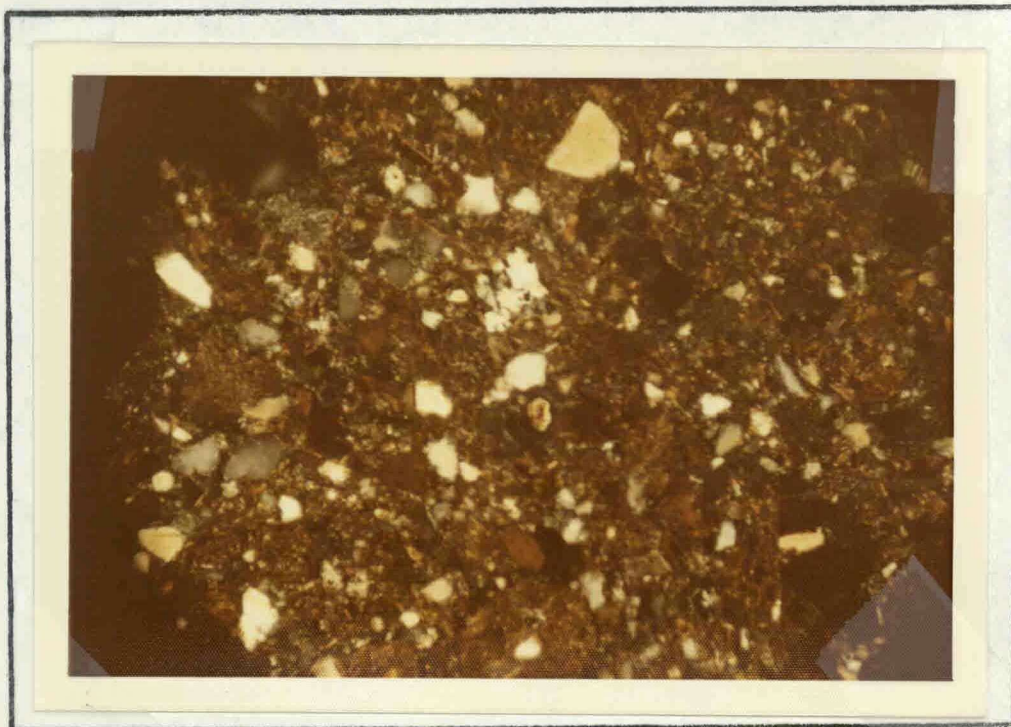
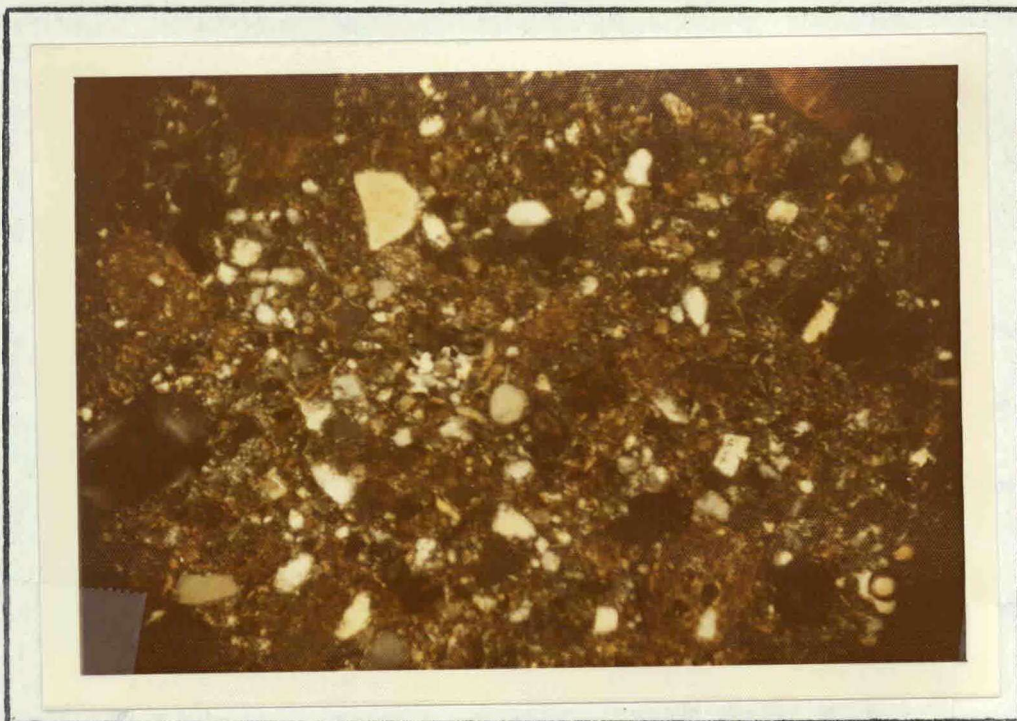
unwashed soil





washed soil

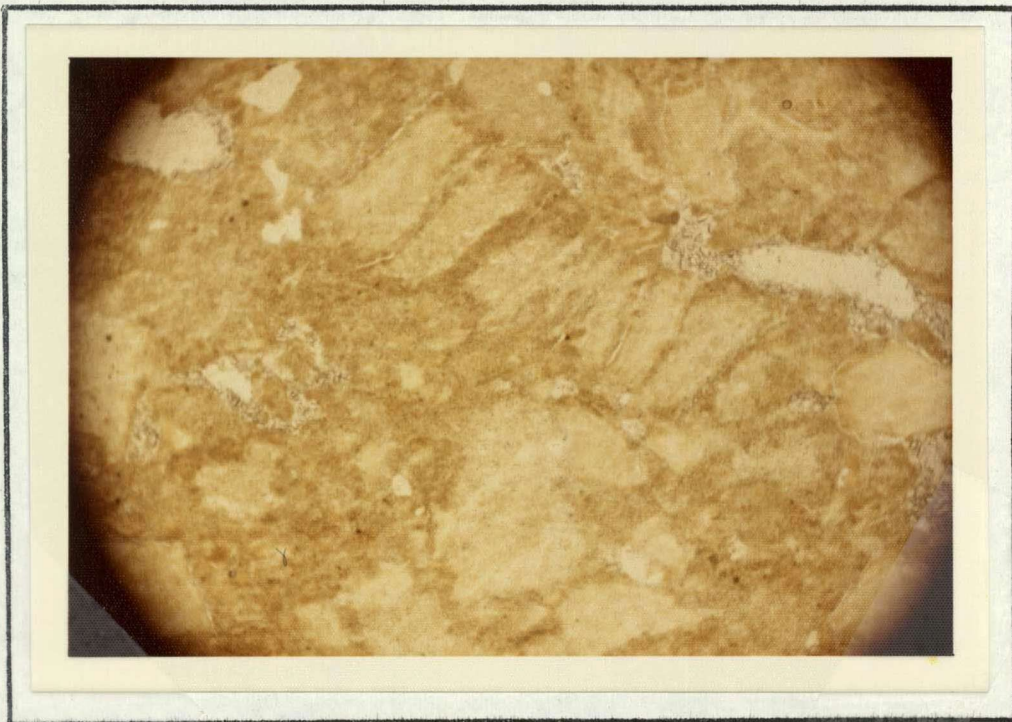


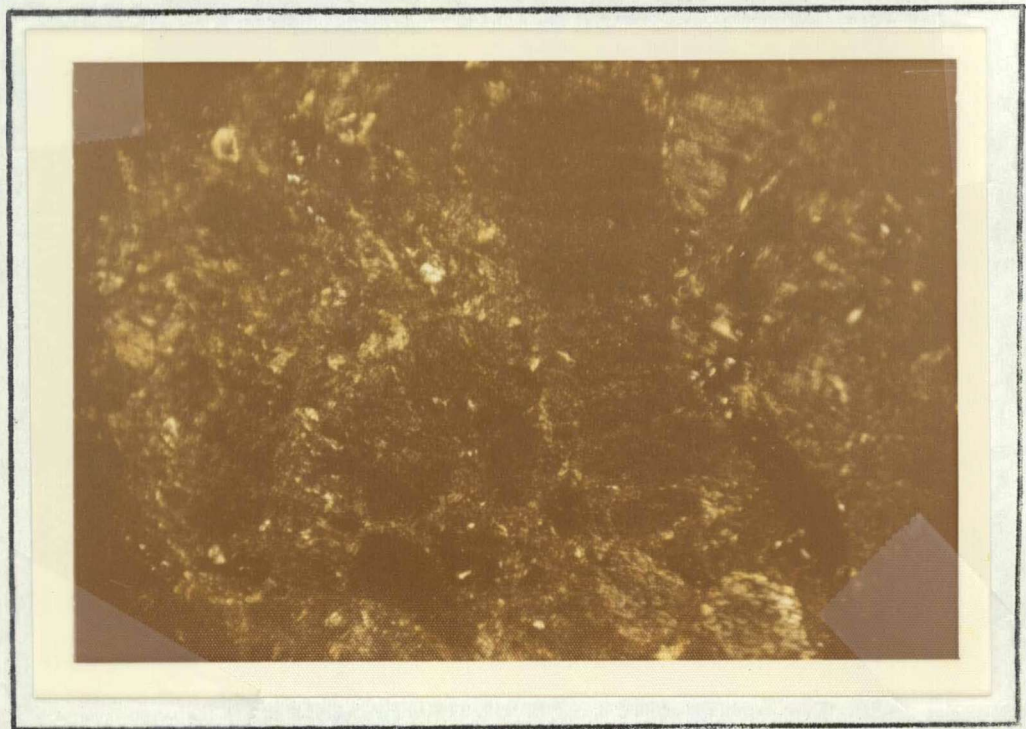
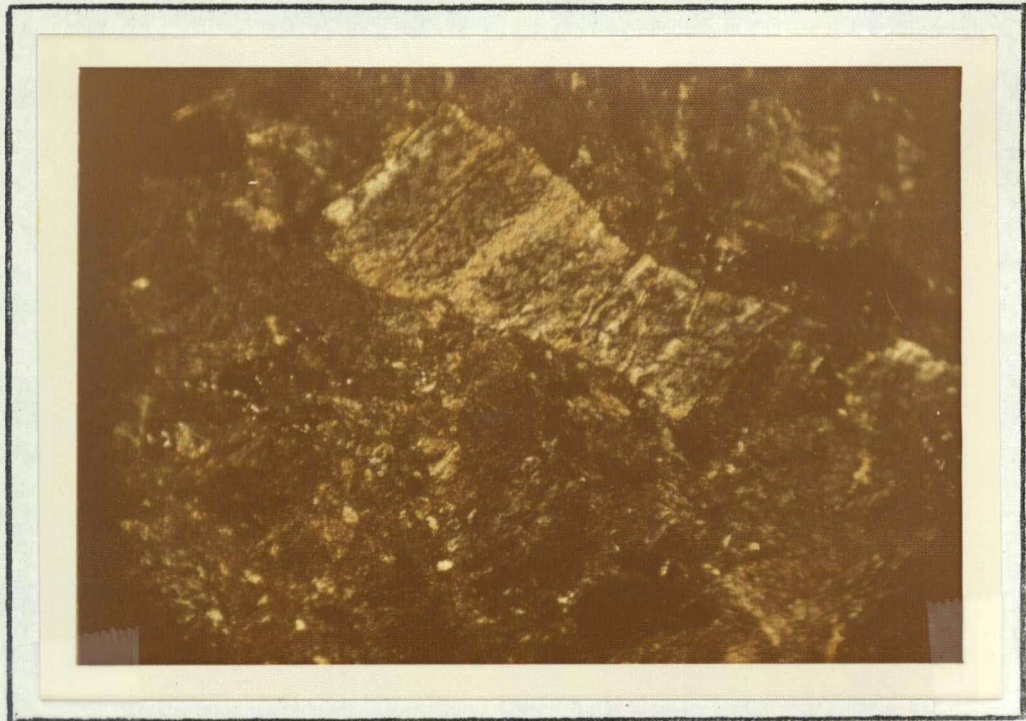


H
2

-151-

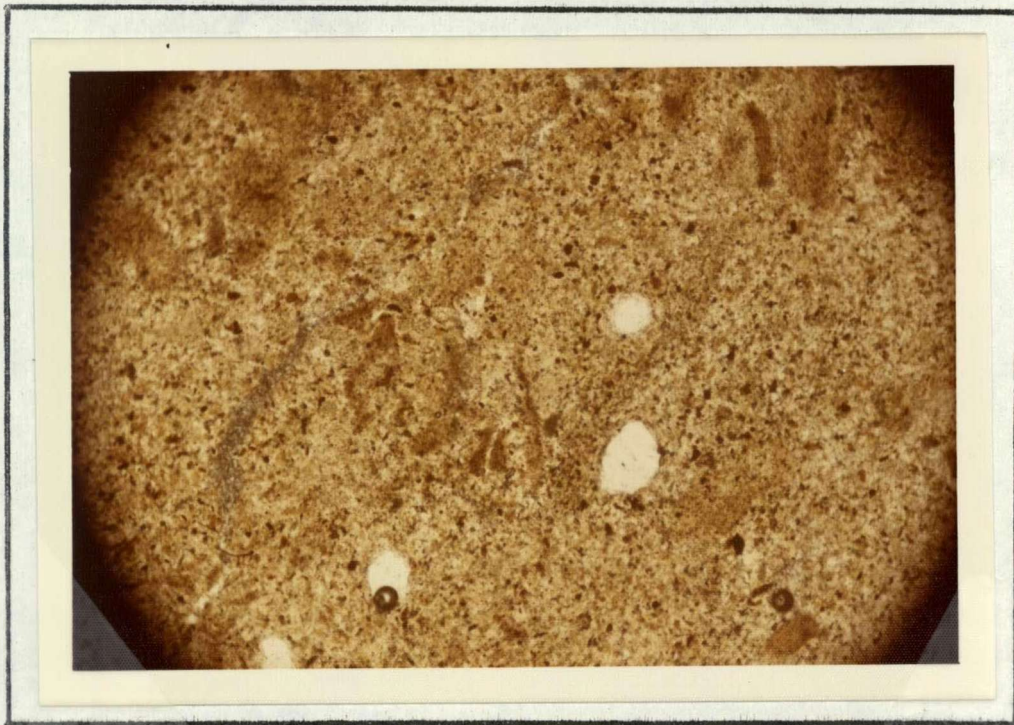
clay

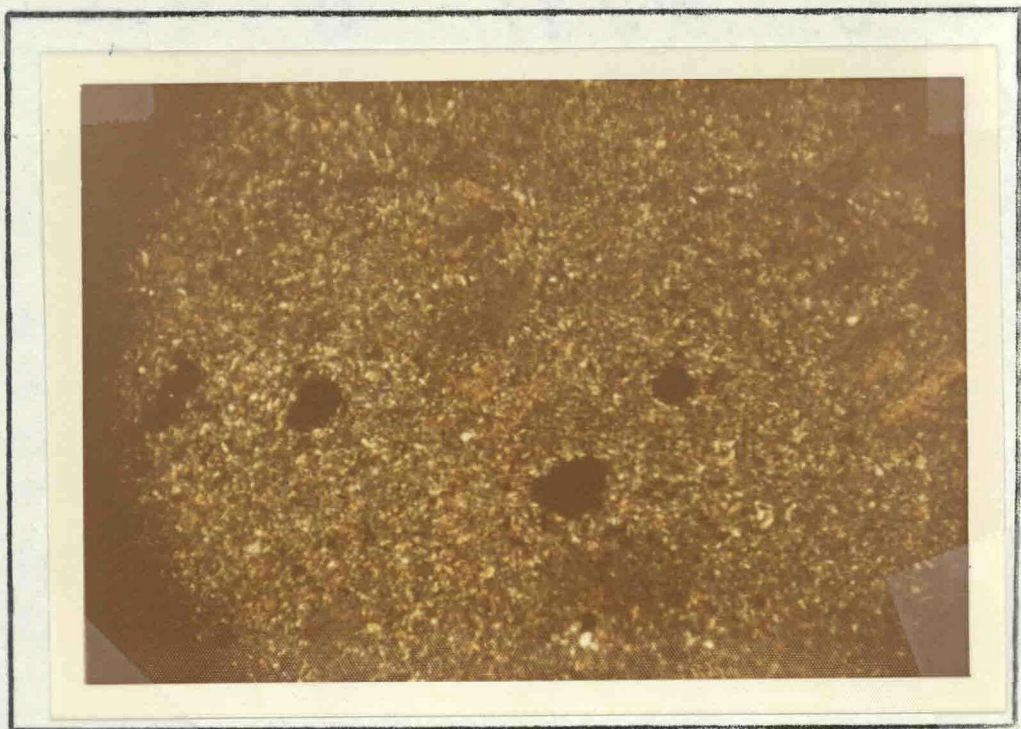
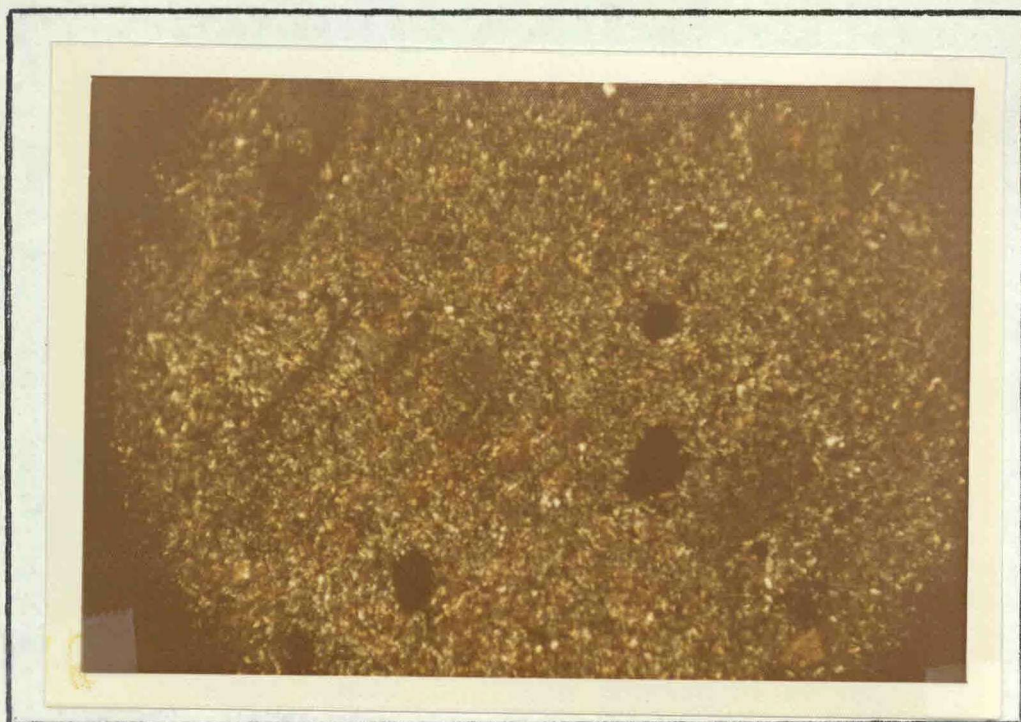




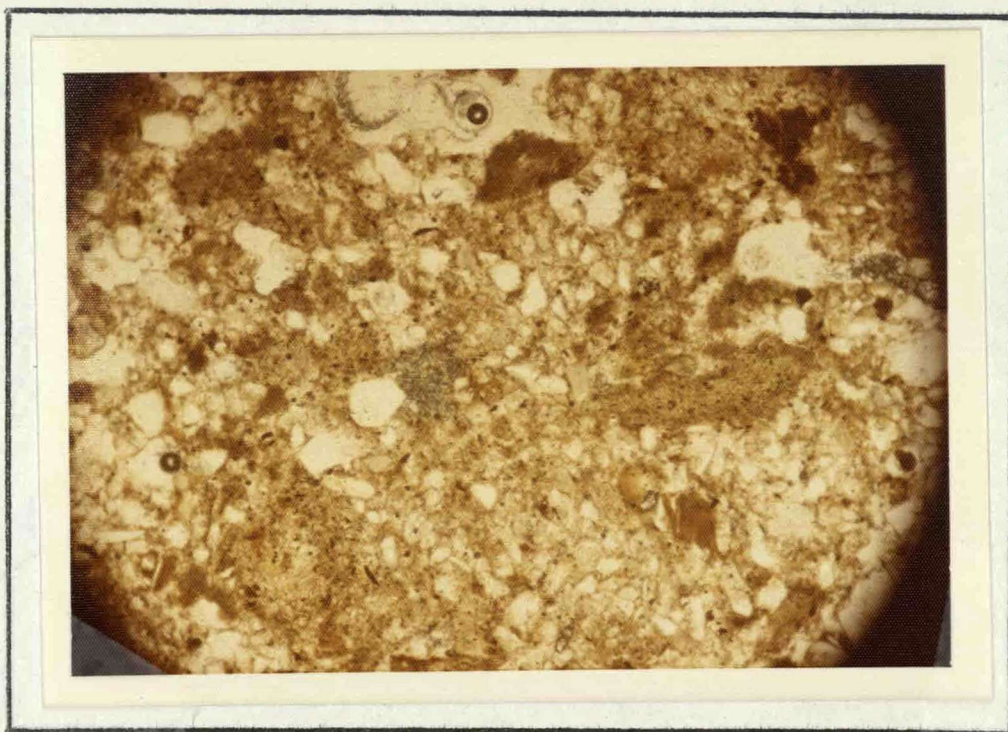
-153-

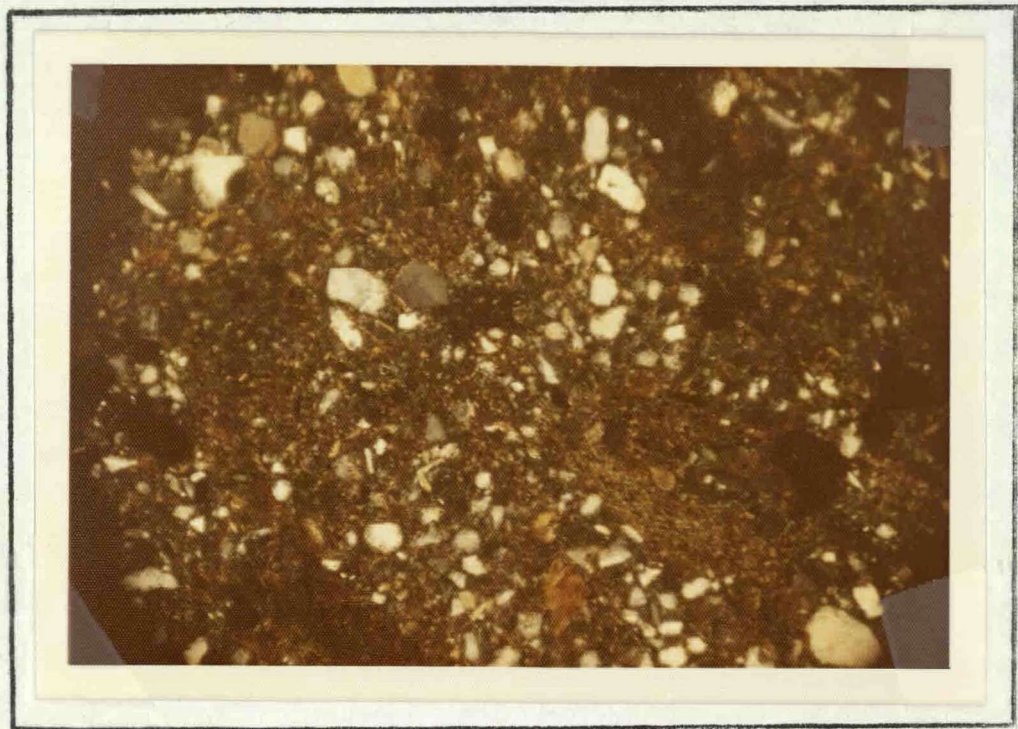
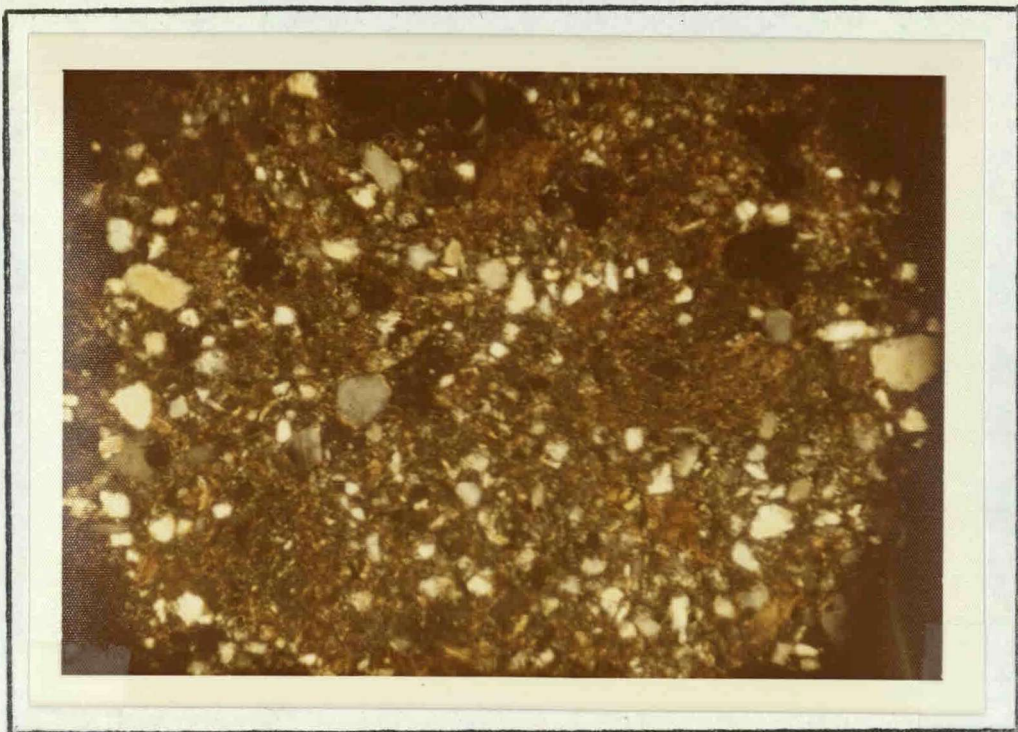
silt





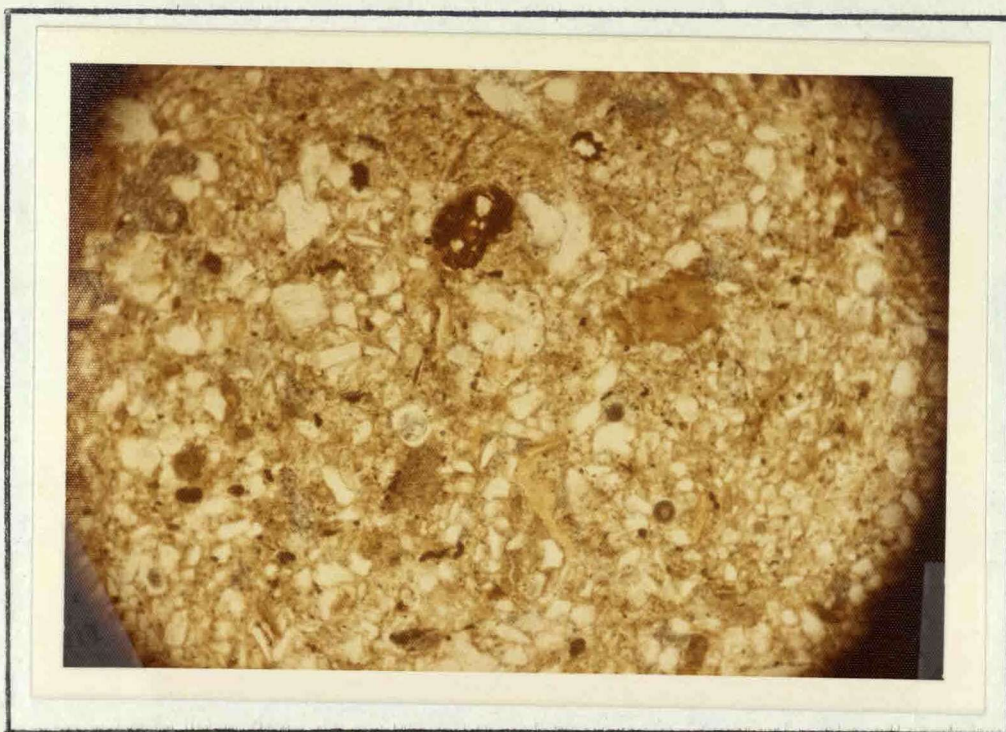
Li

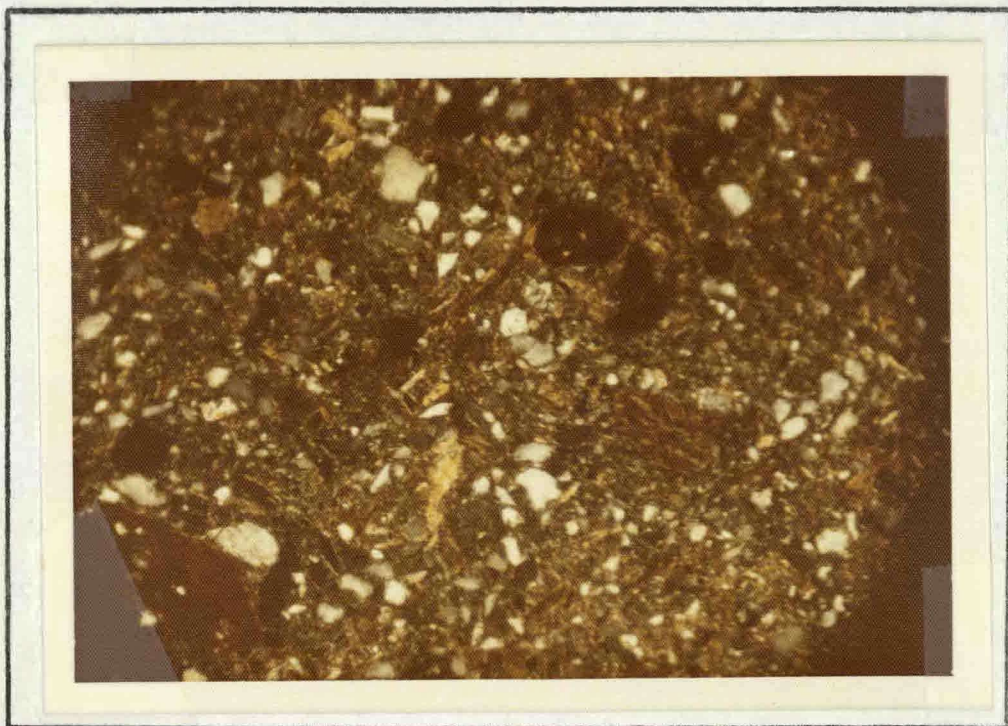
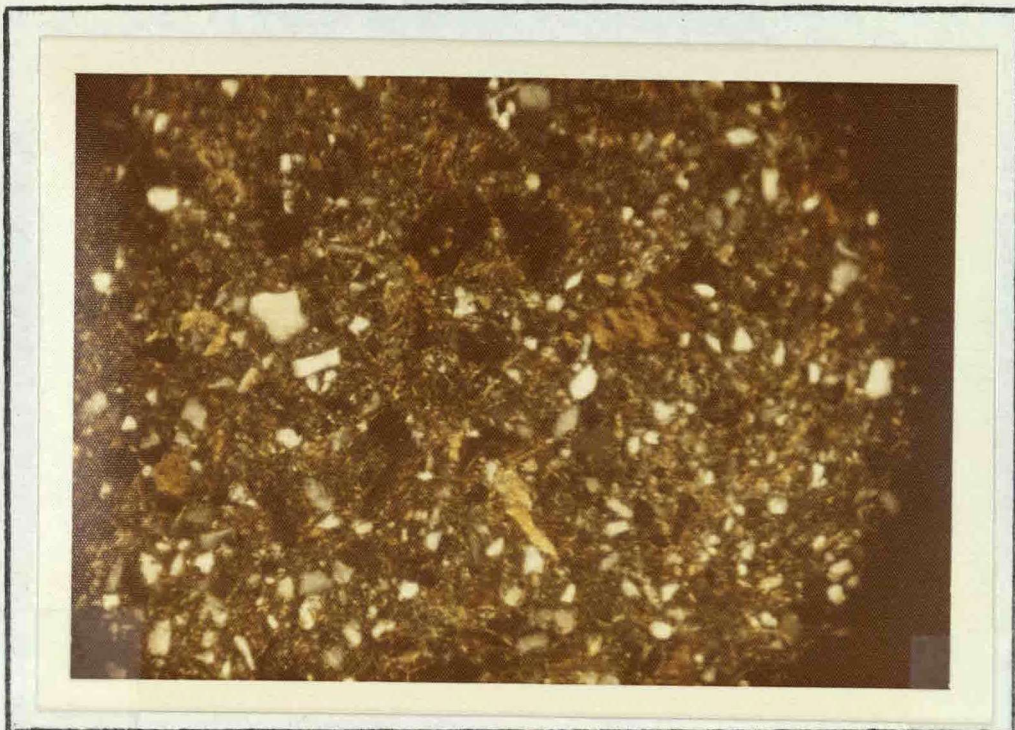




-157-

N a

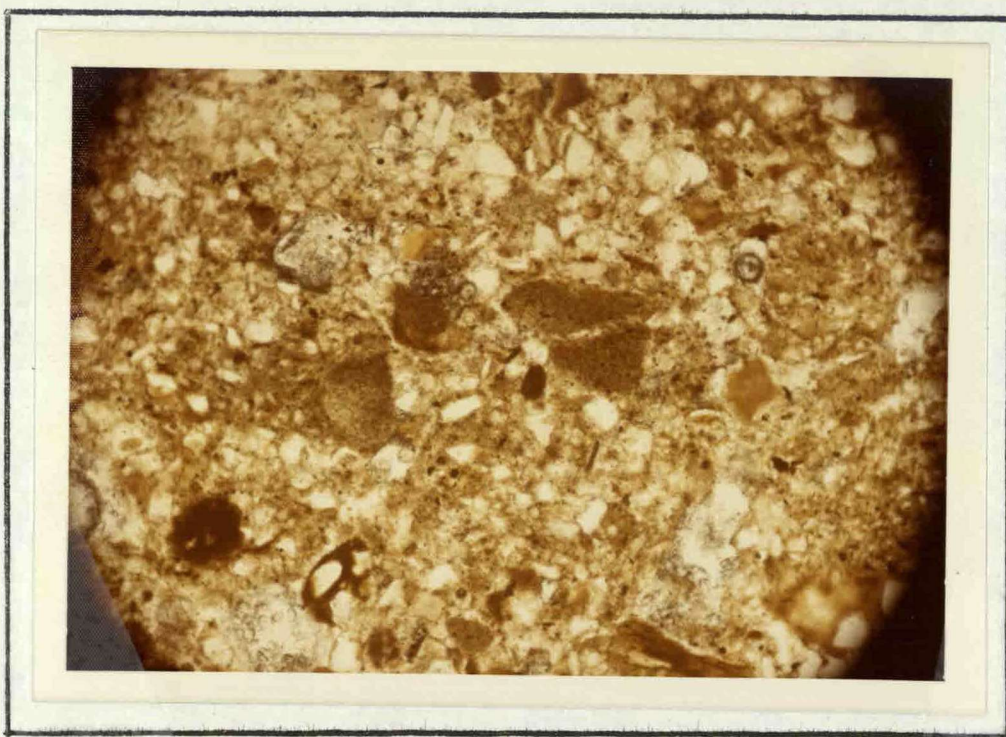


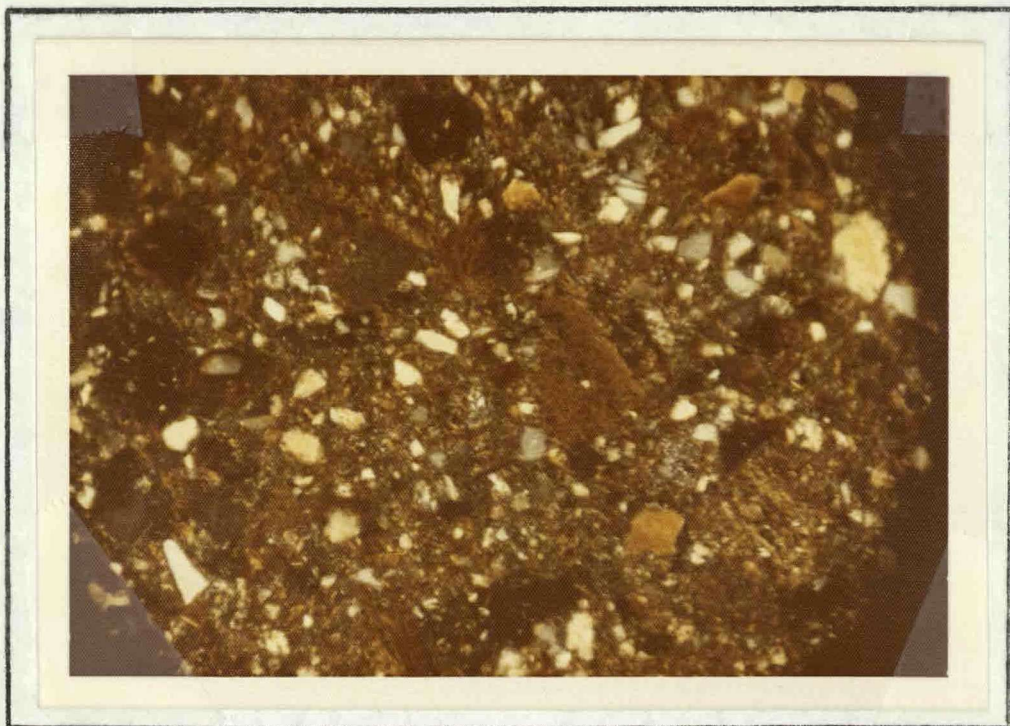
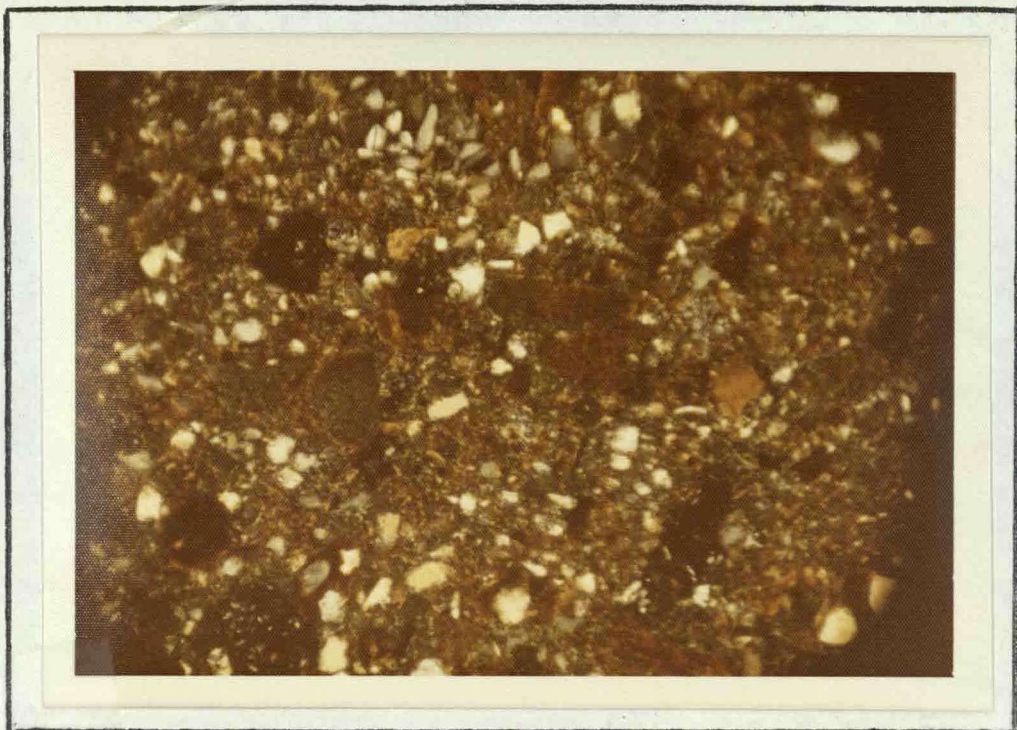


Mead Board
2500
U.S. 20

-159-

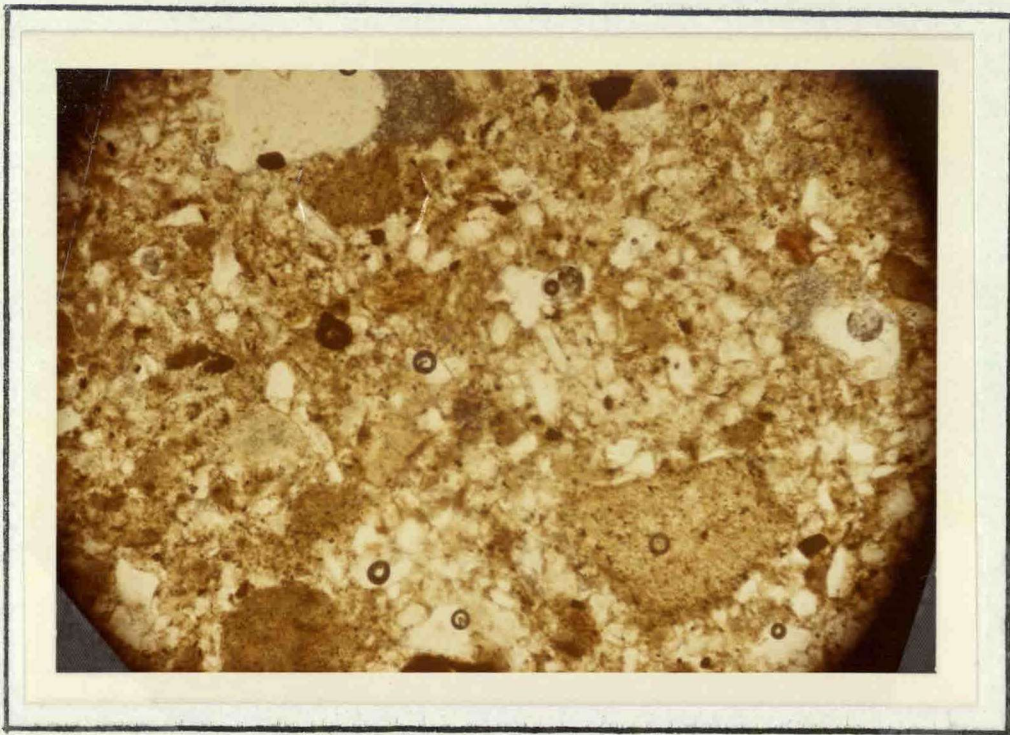
K

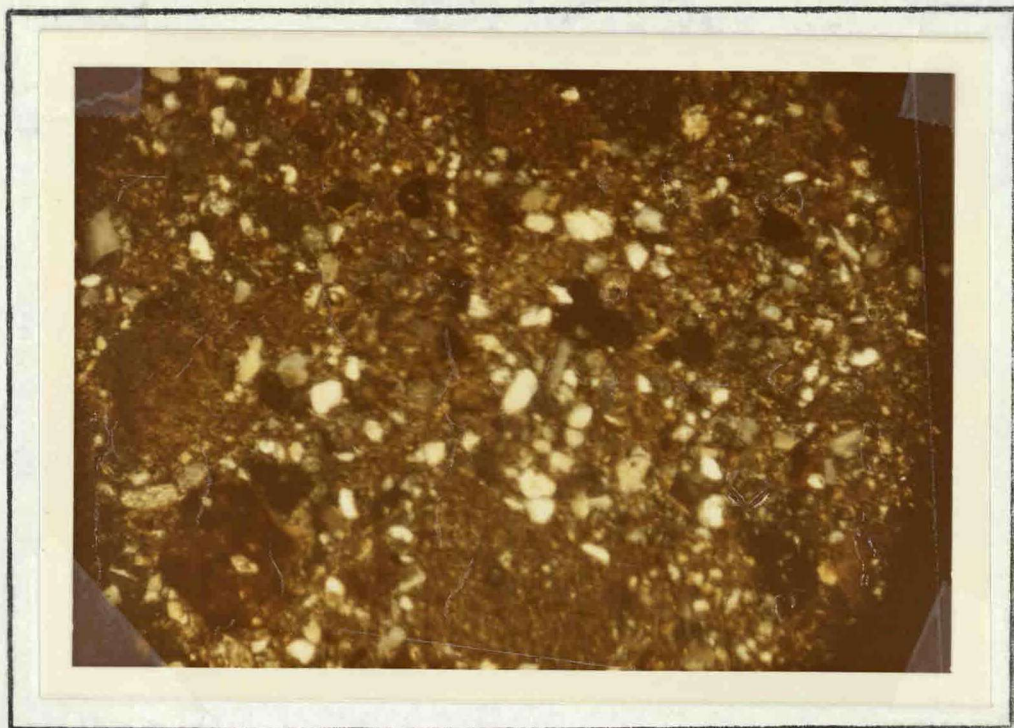
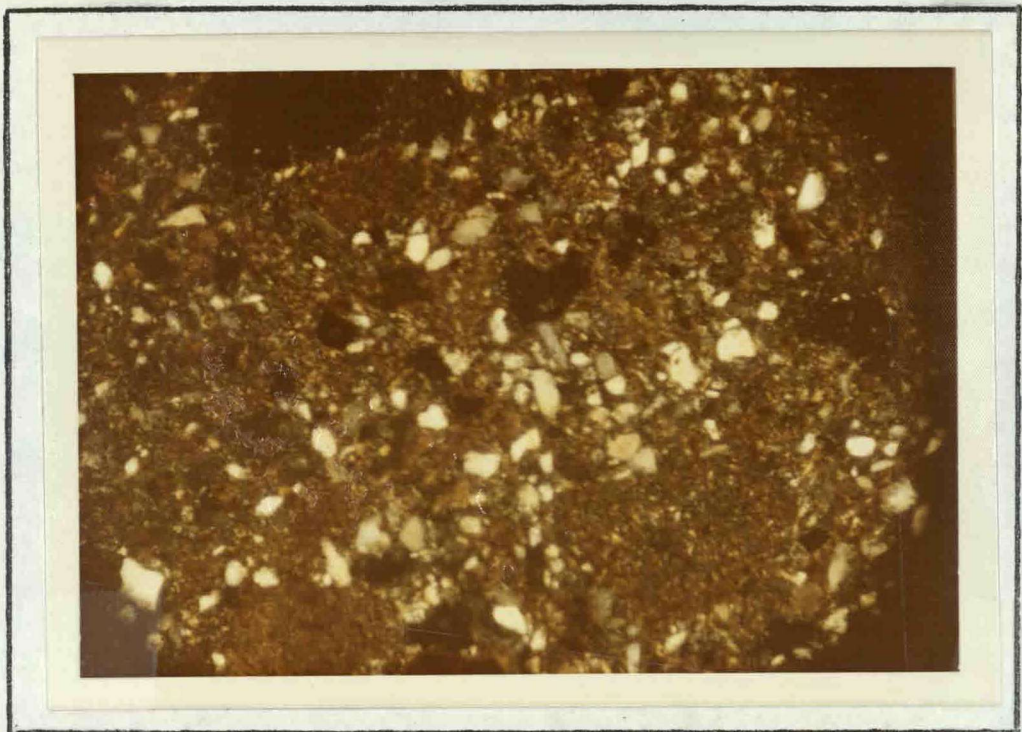




-161-

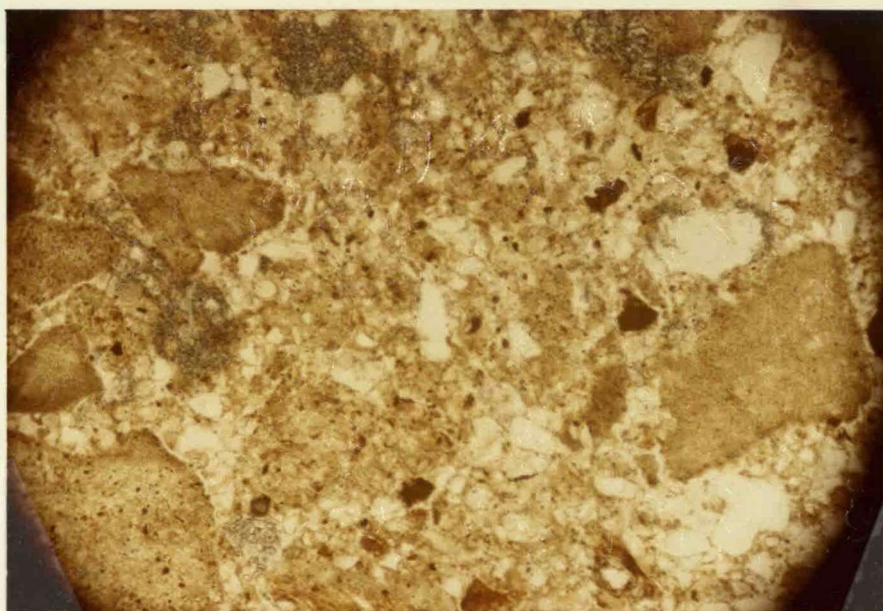
M g

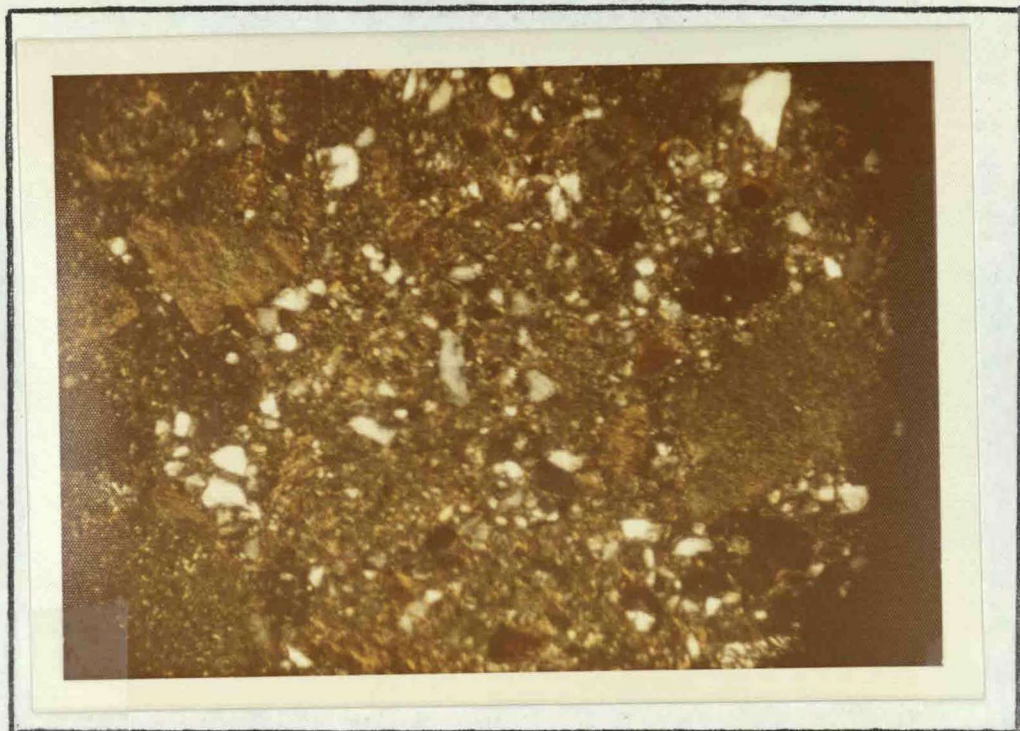




-163-

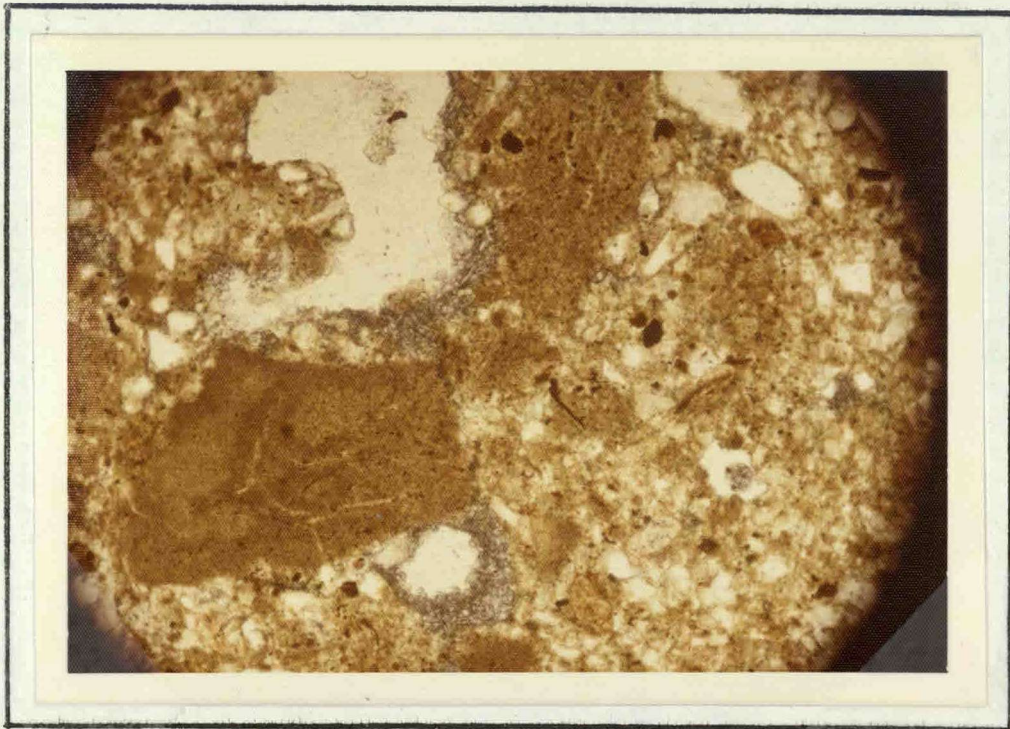
C a

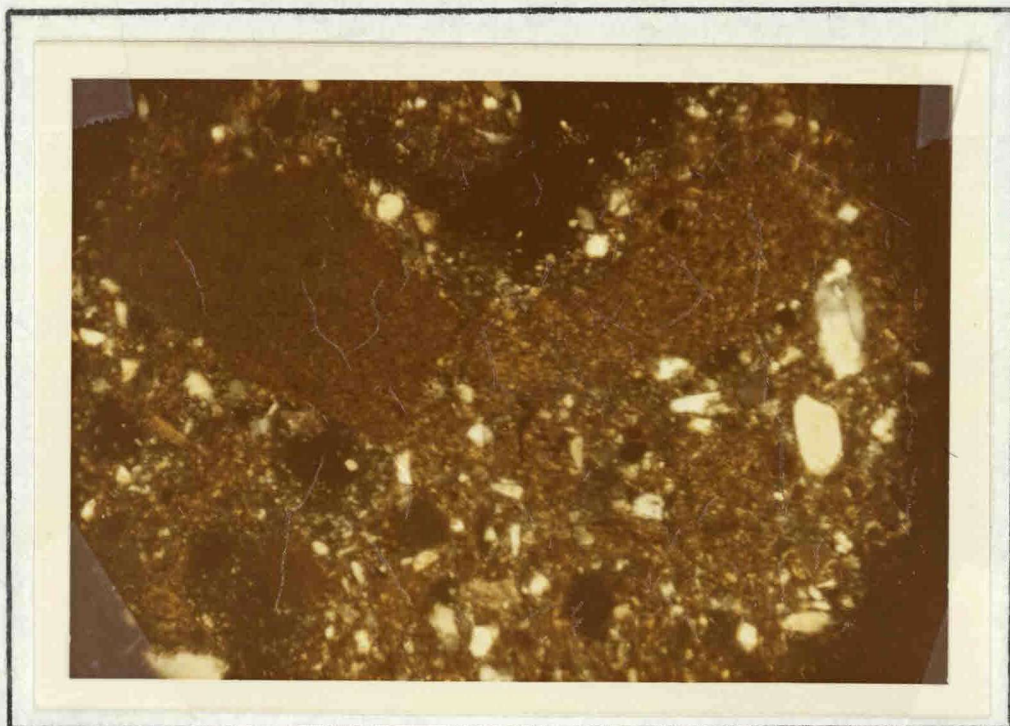
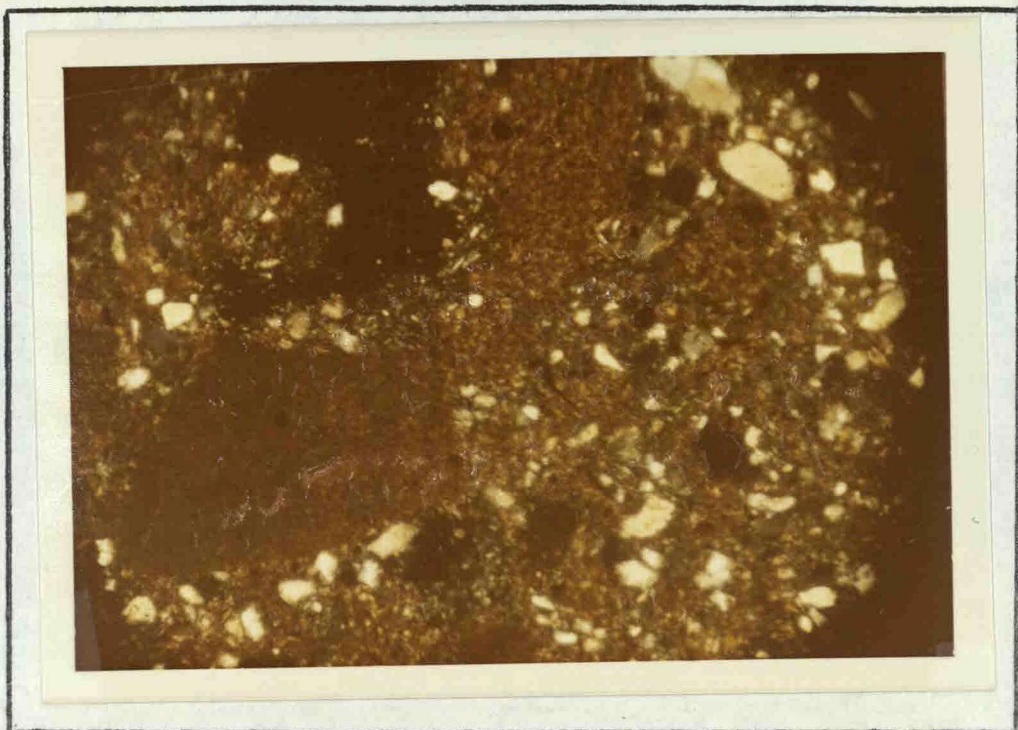




-165-

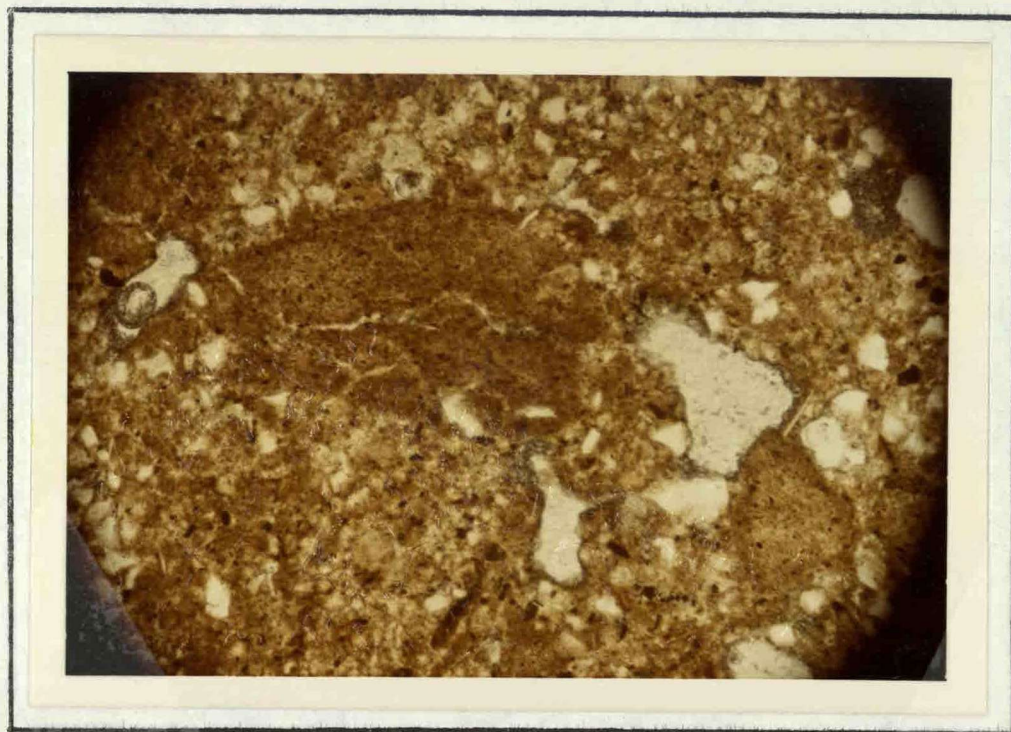
A1

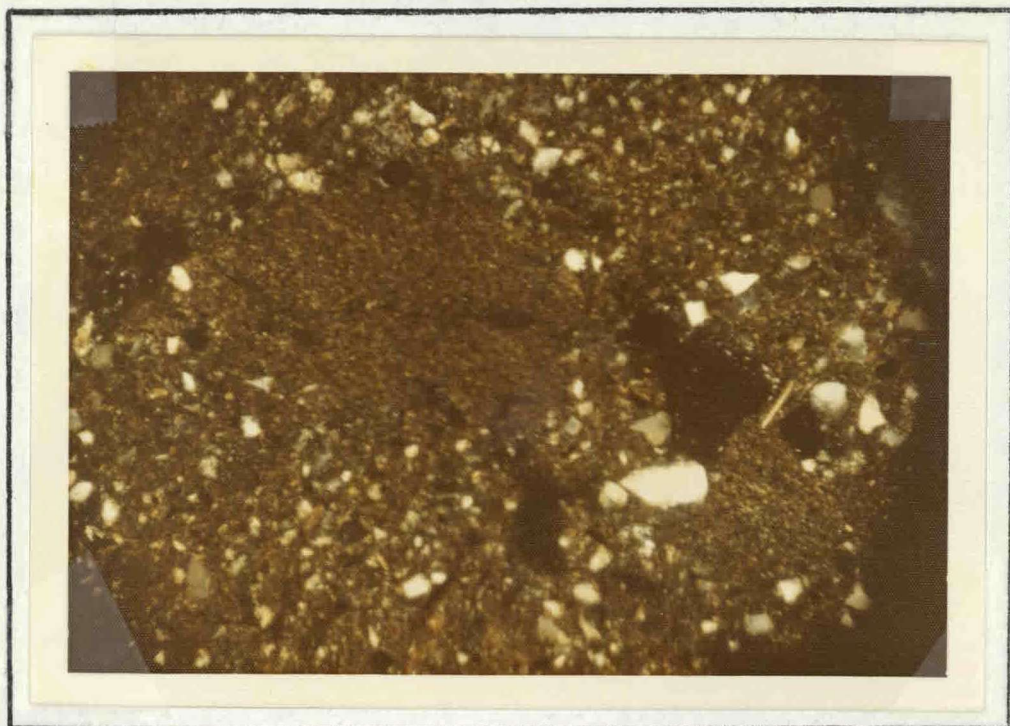
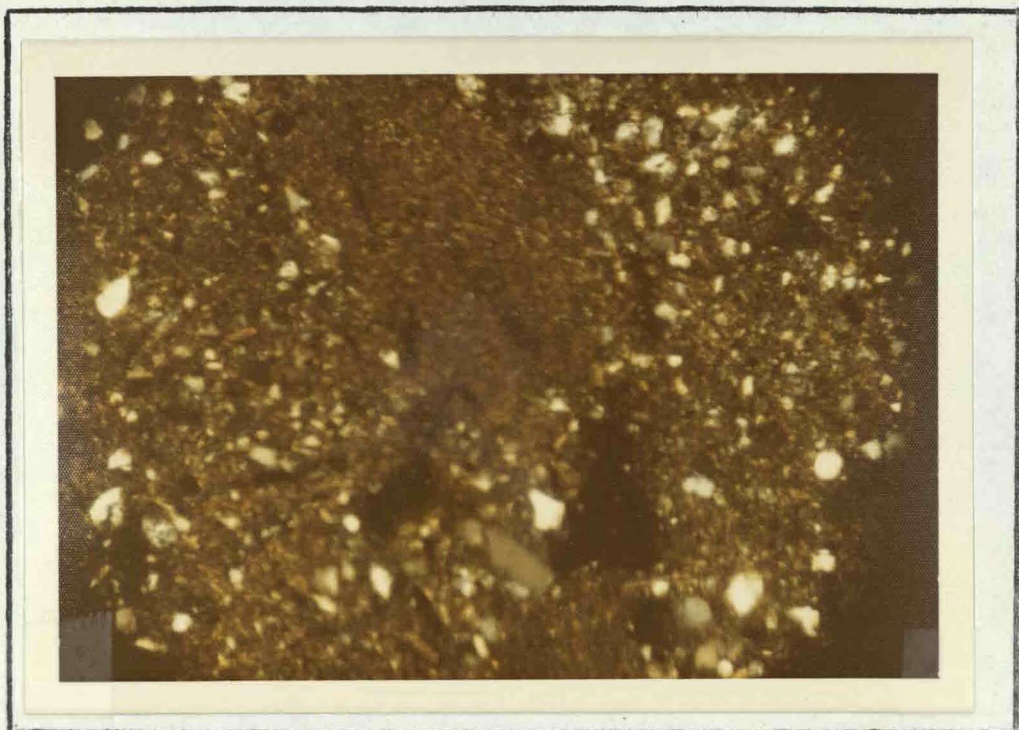




-167-

F e





3 1762 10012622

2ND PLACE, 1994