



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
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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-crusting 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.

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Date 9 August 1972

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by

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

of

MASTER OF SCIENCE

in

Chemistry

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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-crusting 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 impenetrable 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.

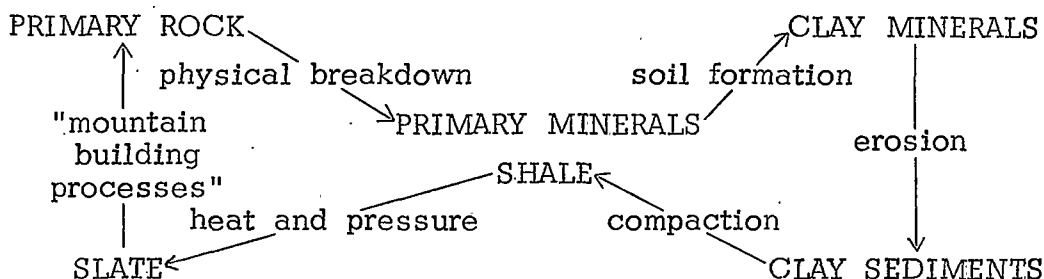


Figure I.1 - A Rock-Clay Cycle.

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).

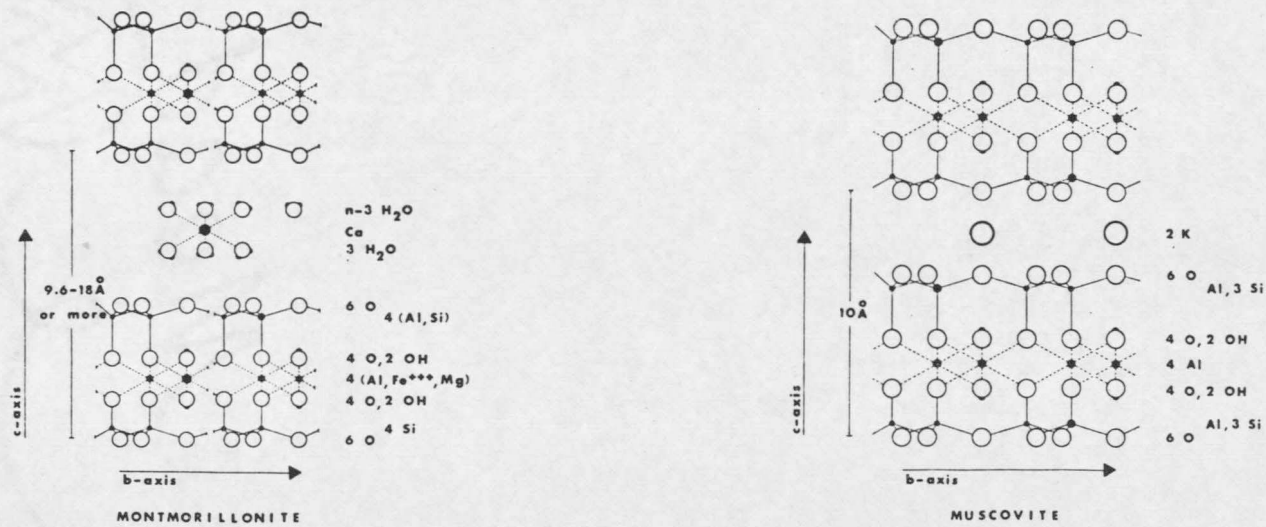


Figure I.2 - Structures of Montmorillonite and Muscovite.
(Reference: Bear's Chemistry of the Soil)

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

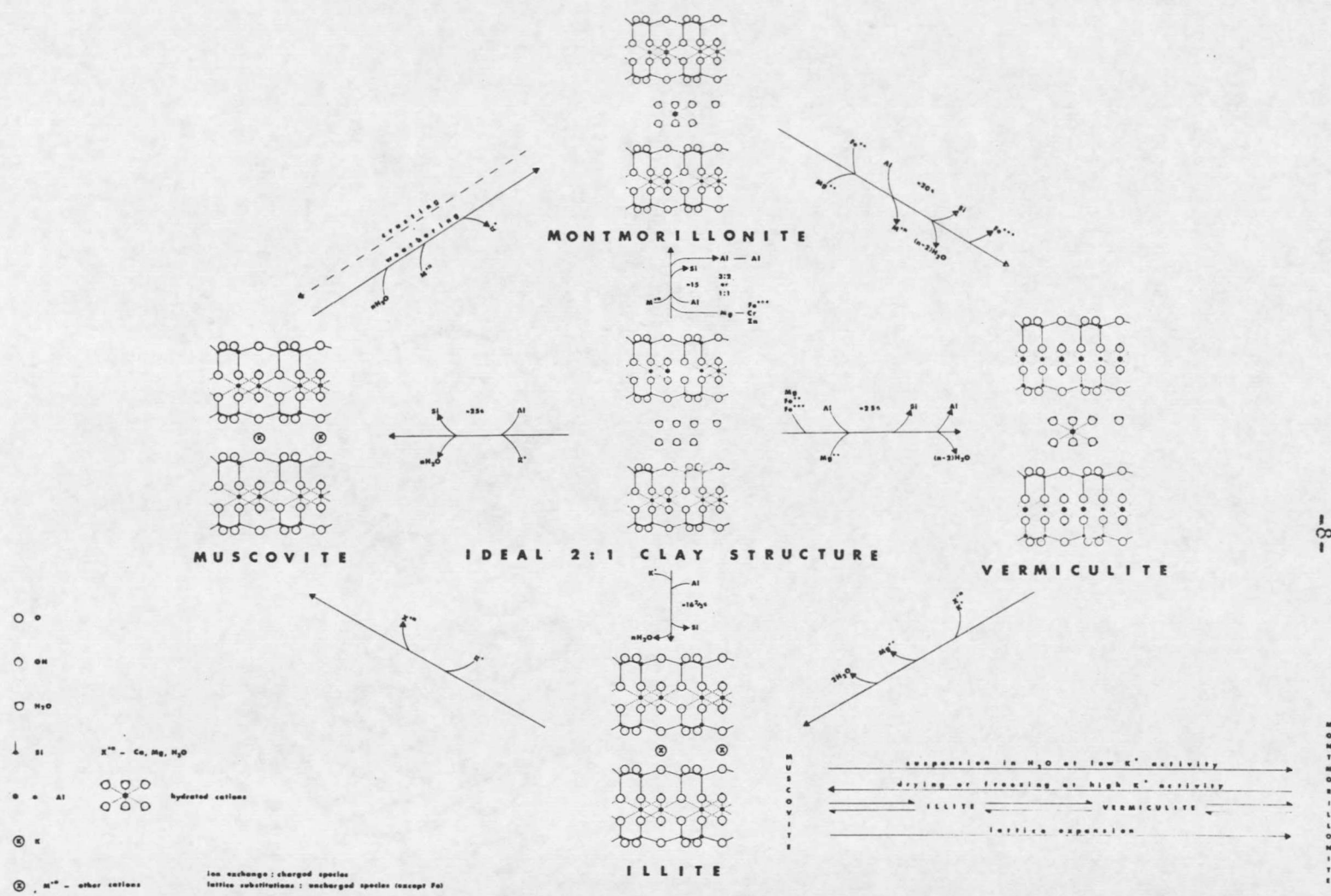


Figure I.3 - A Scheme of the Transformations in the Crystal Lattices of Minerals Occurring in Weathering and Crusting.

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.

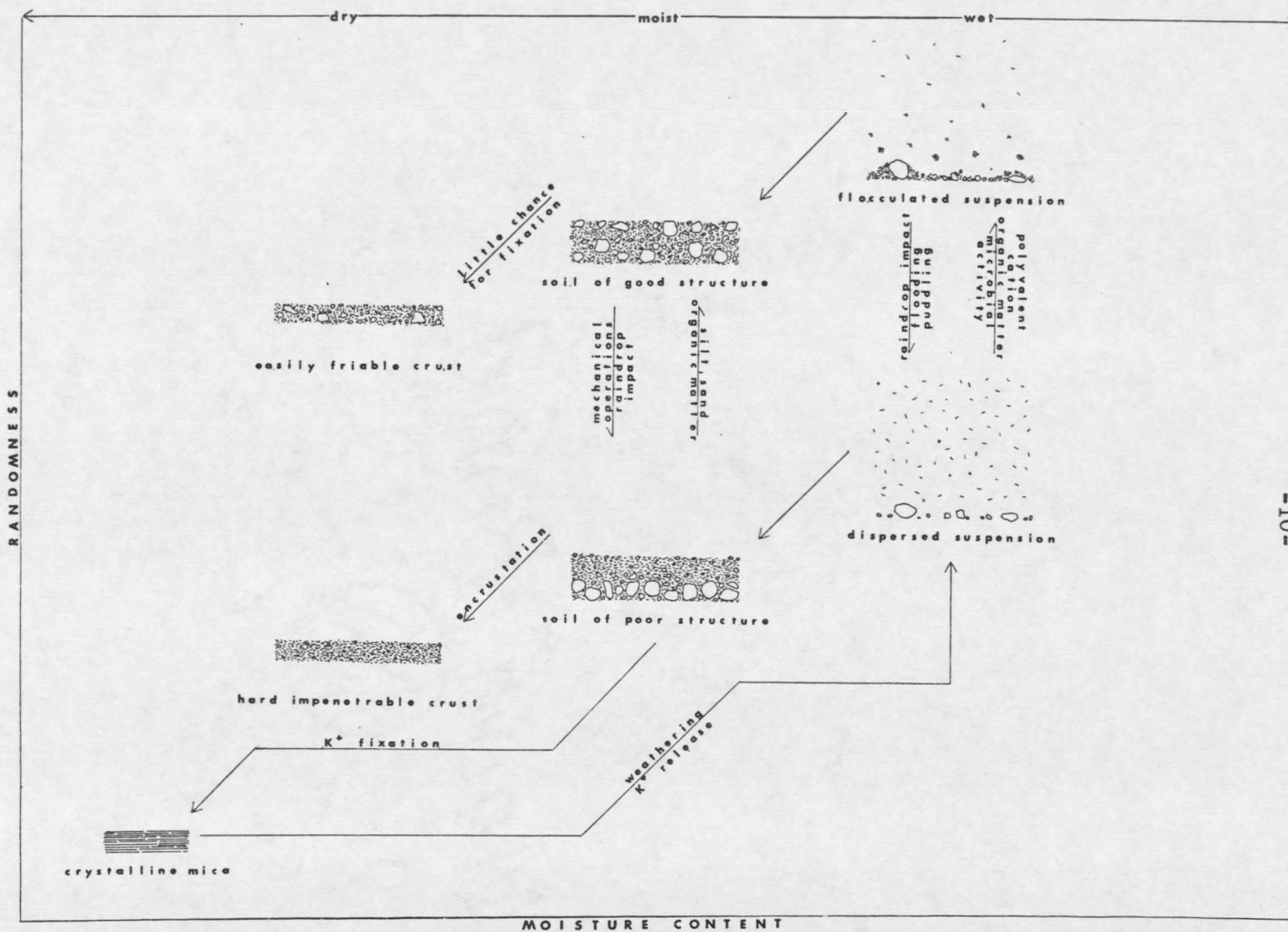


Figure I.4 - A Scheme on the Formation of Friable Crusts and Hard, Cemented Crusts.

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.

³An 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).

⁴Corresponds 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 50μ ($= 5 \times 10^{-2}$ mm). Using a $44\text{-}\mu$ sieve would not only prevent the passage of 50μ 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.

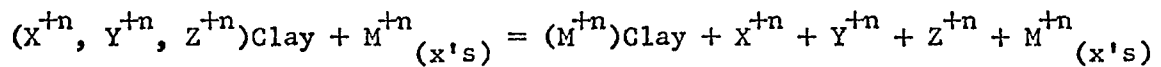
Table II - Amounts of Salts Added to the Soil⁶

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: Cs > Rb > K > Na > Li, and Ba > Sr > Ca > 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: Fe = Al > Ca = Mg > (K) > Na = 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-

⁹L. 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.

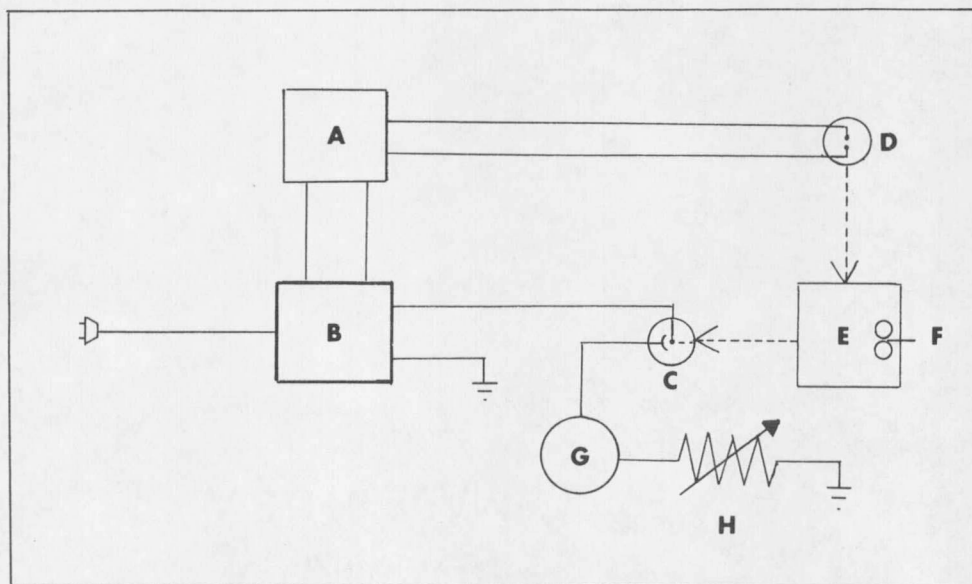


Figure III.1 - Block diagram of the turbidimetry set-up. A, voltage stabilizer; B, power supply; C, photomultiplier tube; D, mercury arc lamp; E, sample compartment; F, magnetic stirrer; G, galvanometer; H, variable resistor.

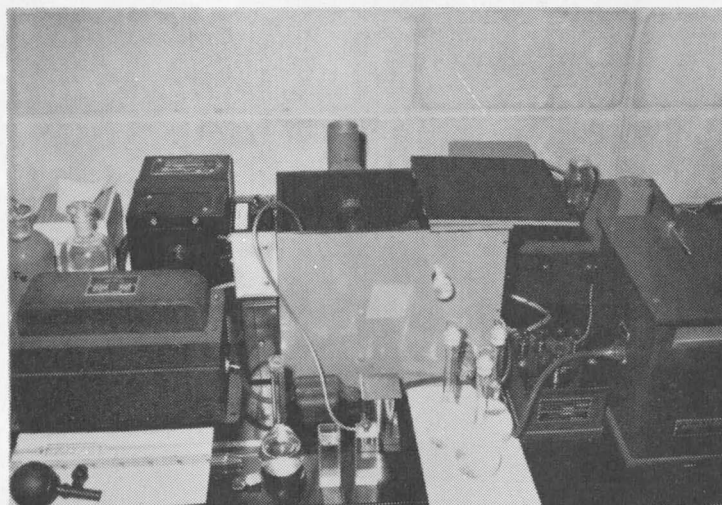


Figure III.2 - The turbidimetry set-up in full view.

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

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

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

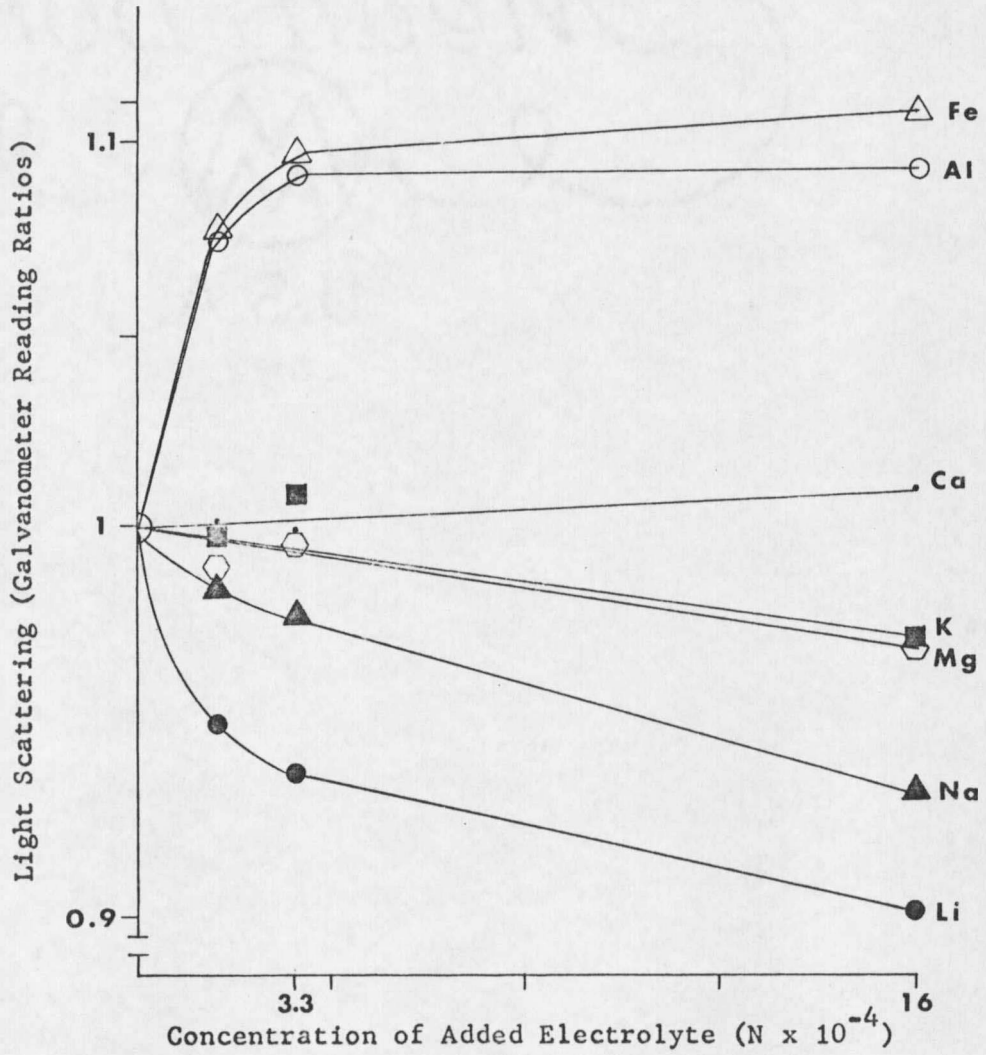


Figure III.3 - The Relationships between Light Scattering and Concentration of Added Electrolyte in Pylon Clay.

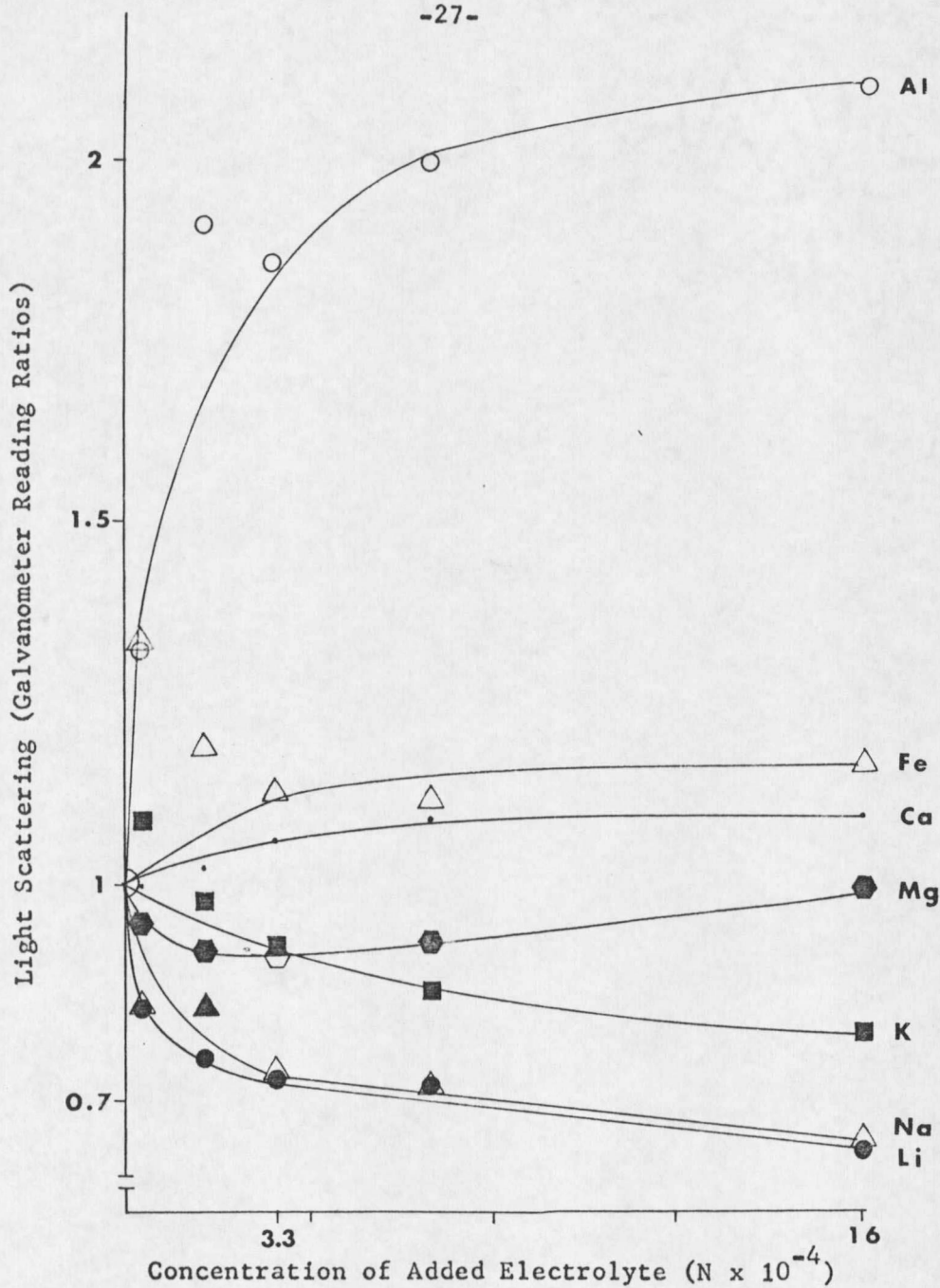


Figure III.4 - The Relationships between Light Scattering and Concentration of Added Electrolyte in Bentonite.

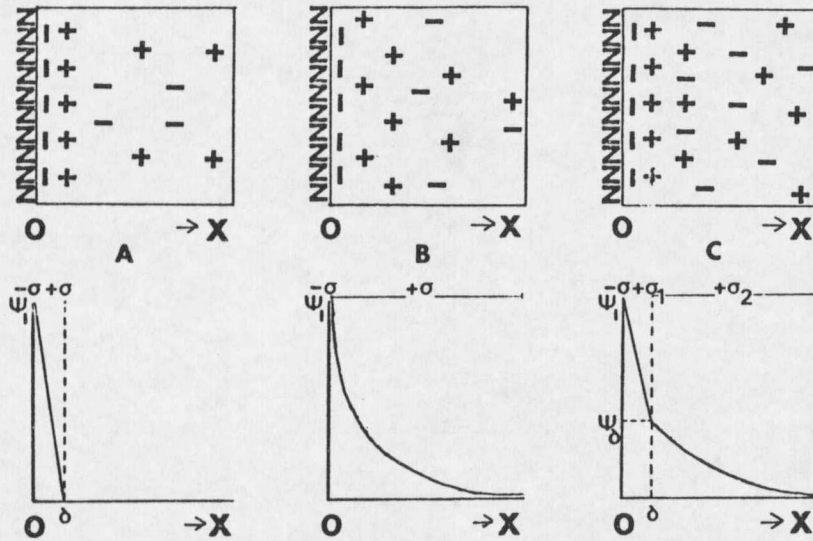


Figure III.5 - Schematic representation of ion and potential distribution in the double layer according to the theories of Helmholtz, Guoy and Stern. ψ_1 , total potential; ψ_0 , zeta potential; x , distance from particle surface; $-\sigma$, surface charge density; and δ , thickness of the Stern layer. (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.

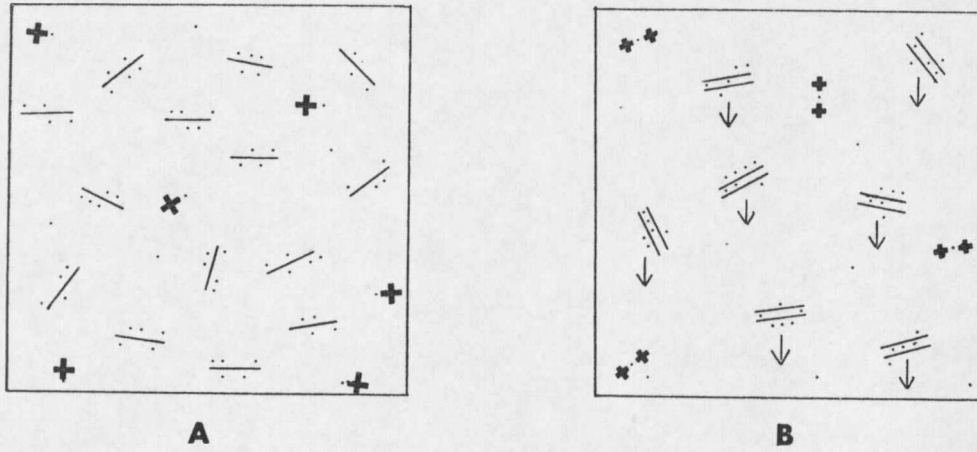


Figure III.6 - Dispersion and flocculation caused by monovalent and divalent cations respectively. Lines, clay plates; dots, cations. Arrows show that floccules tend to settle out.

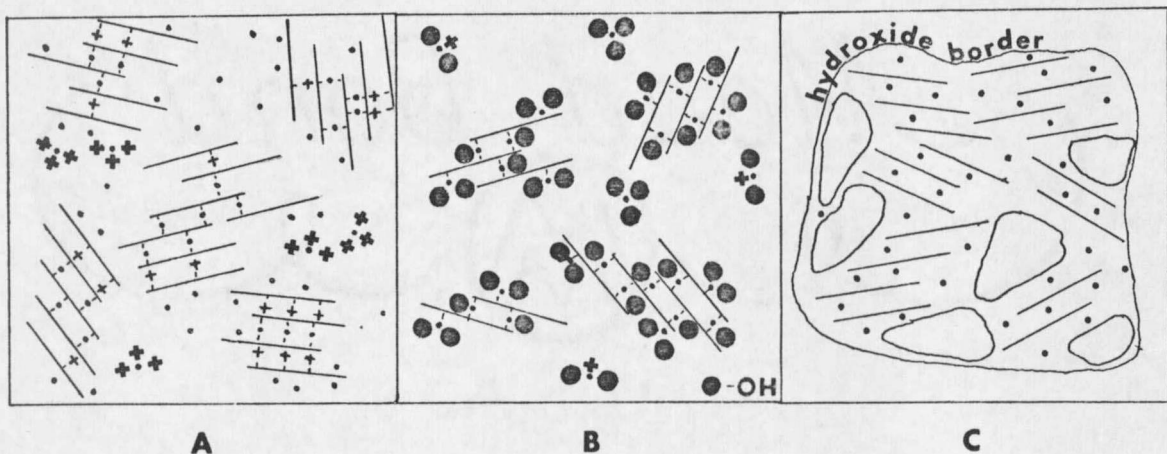
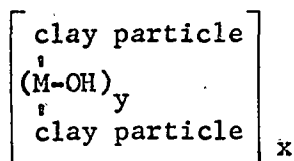


Figure III.7 - Flocculation caused by trivalent cations. A, when aggregates are imparted with a positive charge; B, when hydroxy hybrids are formed; C, when gels envelop the particles to form large aggregates.

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. Turbidimetry 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 x 3½ x 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-CaCl₂ 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; 10⁶ dynes/cm² = 1 bar); F = breaking force (in dynes; weight of water in grams x 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;

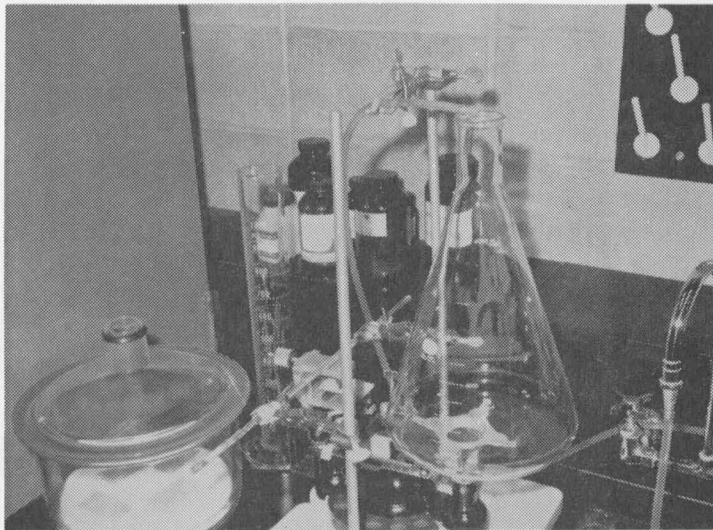


Figure IV.1 - Modulus of rupture set-up before the briquette is broken.

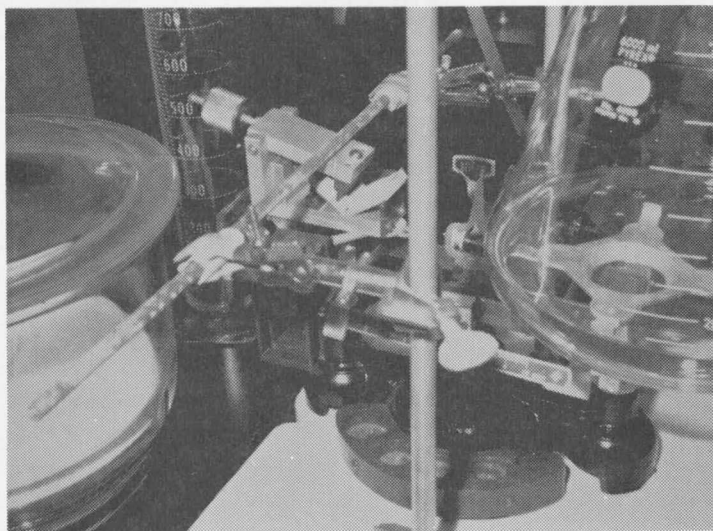


Figure IV.2 - The briquette-breaking assembly with a broken briquette.

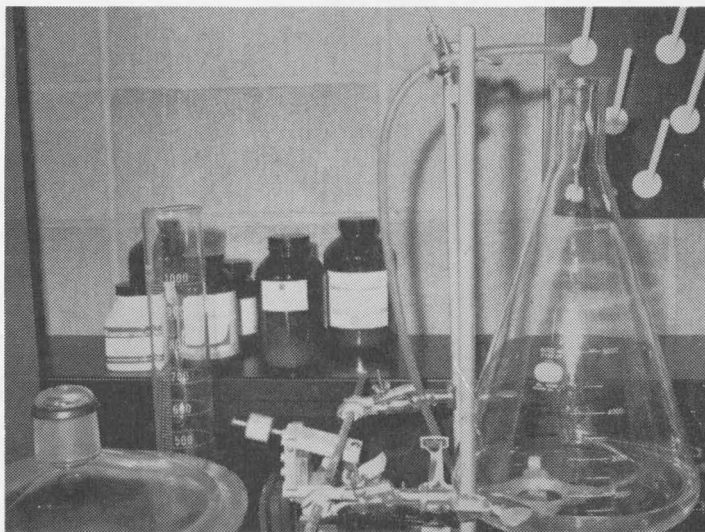


Figure IV.3 - Position of the tube delivering the jet of water after the briquette has been broken.

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

