

**SWELLING PROPERTIES OF SOME MONTMORILLONITE  
CLAYS IN WATER SYSTEMS**

**by**

**Dwayne Harold Fink**

**Thesis submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute  
in candidacy for the degree of  
MASTER OF SCIENCE  
in  
AGRONOMY**

**1962**

**Blacksburg, Virginia**

LD  
5655  
V855  
1962  
F564  
c. 2

## II. ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. Grant W. Thomas for his encouragement and helpful guidance which has contributed so much to the completion of this thesis.

He is indebted to Dr. Charles I. Rich for his very pertinent advice on many problems which arose. Special thanks is also extended to Dr. H. L. Dunton, Head of the Agronomy Department, and to Dr. B. W. Nelson, Professor of Geology. Thanks is extended to Dr. W. F. Bradley of the University of Texas for his personal suggestions.

Appreciation is also extended to Mr. Kent Stone for his aid in carrying out this investigation.

Finally, heartfelt thanks is offered to his wife, Edna, who undertook the difficult task of typing the rough draft and then the thesis in its final form.

III. TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
I. Title Page.....	1
II. Acknowledgements.....	2
III. Table of Contents.....	3
IV. List of Figures.....	5
V. List of Tables.....	6
VI. Introduction.....	7
VII. Literature Review.....	10
VIII. Materials and Methods.....	22
8.1 Sodium-Wyoming bentonite.....	22
8.2 Lithium-Wyoming bentonite.....	23
8.3 Calcium-Wyoming bentonite and Calcium- White Store.....	24
8.4 Sodium-Georgia kaolinite.....	24
8.5 Sodium-Soil clays.....	24
8.6 X-ray procedure.....	26
8.7 Quantitative Montmorillonite Determinations.....	30
IX. Results and Discussion.....	34
9.1 Lithium-Wyoming bentonite.....	34
9.2 Sodium-Wyoming bentonite.....	41
9.3 Calcium-Wyoming bentonite.....	47

<u>Chapter</u>	<u>Page</u>
9.4 Soil Clays.....	52
9.5 Quantitative Determination of Montmorillonite.....	63
X. General Discussion.....	70
XI. Literature Cited.....	78
XII. Vita.....	82

IV. LIST OF FIGURES

	<u>Page</u>
Fig. 1 Special apparatus used in X-ray analysis.....	33
Fig. 2 Lattice expansion of 2 to 0.08 $\mu$ , Li-Wyoming bentonite in a water system.....	39
Fig. 3 Smoothed X-ray diffraction patterns of 2 to 0.08 $\mu$ , Li-Wyoming bentonite in water systems.....	40
Fig. 4 Lattice expansion of 2 to 0.08 $\mu$ , Na-Wyoming bentonite in a water system.....	44
Fig. 5 Smoothed X-ray diffraction patterns of 2 to 0.08 $\mu$ , Na-Wyoming bentonite in water systems.....	45
Fig. 6 Lattice expansion of $< 0.08 \mu$ , Na-Wyoming bentonite in a water system.....	46
Fig. 7 Lattice expansion of $< 2 \mu$ Ca-Wyoming bentonite.....	50
Fig. 8 Smoothed X-ray diffraction patterns of $< 2 \mu$ , Ca-Wyoming bentonite.....	51
Fig. 9 Calcium-White Store; smoothed X-ray diffraction patterns for $< 2 \mu$ fraction in water systems.....	60
Fig. 10 Calcium-White Store; smoothed X-ray diffraction pattern, before and after correction for Lorentz and polarization factor.....	61
Fig. 11 Sodium-Webster; smoothed X-ray diffraction patterns for $< 0.08 \mu$ fraction in water systems.....	62
Fig. 12 Nomograph for determination of percent montmorillonite in a montmorillonite-kaolinite mixture using d-spacing (A) and percent water of the sample.....	69

V. LIST OF TABLES

	<u>Page</u>
Table 1 Soils and treatments used in expansion study of Na-soil clays.....	32
Table 2 Theoretical and actual d-spacings of the Na-Wyoming bentonite, Georgia kaolinite mixtures in water systems.....	68

## VI. INTRODUCTION

Much research has been directed towards understanding the interactions between clay and water systems. The study has been justified since soil and water represent two of our most basic resources. Swelling of certain clays in water systems represents one of the physical expressions of the complicated interaction between the two entities.

A clay must have specific mineralogic characteristics in order to absorb water interstitially. It must be of the three-layer type with an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. There also must be an interlayer charge density resulting from an unbalance of lattice charges caused by isomorphous substitution of other cations for the silica and/or aluminum ions. This charge density, normally negative, is neutralized by the presence of interlayer cations. However, if the charge density is too great, as in mica, the clay can not swell in water systems.

The extent of the swelling is likewise related to the mineralogic characteristics of the clay. Charge density is a factor; the greater the charge, the more



tightly the plates should be held together. Other factors, such as particle size, location of the substitution sites (whether octahedral or tetrahedral), homogeneity of charge distribution, etc., may affect the swelling, thereby complicating the reaction even more.

The type of saturating cation also controls the amount of interlayer water imbibed. The extent of swelling is controlled partially by the concentration of electrolyte in the solution; soluble salts suppress swelling. Under natural conditions the situation is complicated by poly-cation systems.

There are considered to be three types of clay-water associations in a three-layer clay. These are hydration of the interlayer cation, surface water (both external and internal), and osmotic water. In montmorillonite all three account for interlayer swelling. At low water vapor pressures most cations hydrate in some stable configuration which produces expansion by layers. The individual cations exhibit differences in this respect, however.

The interlayer surface water is thought to be hydrogen-bonded to the hexagonally arranged surface oxygens of the clay lattice. This water generally is considered to be at a higher energy state than the water associated

with the cations; therefore, the H-bonded water is thought to exert only a moderate force in expanding the clay lattice.

The osmotic water is associated with higher water contents and continuously expanding clay lattices. The osmotic force results from an activity gradient between the external and internal water. The causal factors responsible for this activity gradient are not entirely known. If the interlayer hydration energy is greater than the attractive forces holding the clay plates together, the clay will expand osmotically.

This study was undertaken to improve the understanding of the swelling properties of clays in water systems. In particular, the montmorillonite, Wyoming bentonite, which has been well defined mineralogically, was used to help gain an insight into the processes involved in swelling, and to clarify points of conflict reported by previous workers.

The methods employed with this montmorillonite were applied to a similar study of soil clays. Results obtained from the various clays were compared, and practical applications of swelling properties were investigated.

## VII. LITERATURE REVIEW

Hofmann, Endell and Wilm (1933) were the first to show that montmorillonite expanded interstitially in a water system. The same year Falconer and Mattson (1933) reported on the "water of osmotic imbibition", which they found was capable of swelling a clay. The amount of swelling was related to the saturating cation, and was proportional to the cation exchange capacity. They found that changing the saturating cation from Na to certain other cations, while the clay was dispersed, did not cause the clay to collapse; also, they found that the amount of water held by the clay was reduced in the presence of salts. The observations of these men have formed the basis for most subsequent work on swelling properties of clay.

A mechanism to describe the relation between the soil and water was needed. Hendricks and Jefferson (1938) applied Bernal and Fowler's (1933) description of a water molecule with tetrahedral distribution of charge, to postulate that the hydrating water was hydrogen-bonded to the interstitially exposed oxygens of the clay silicate groups. This resulted in a hexagonal, ice-like structure for the bound water with the oxygens spaced 3.0 Å apart.

They envisioned a layered system with additional sheets of water being H-bonded to the first layers.

Another classic paper on the hydrating mechanisms of clay was presented by Hendricks et al. (1940). They found that hydration of the interstitial cation provided a second swelling mechanism, which operated in conjunction with the previously proposed H-bonding of the water to the silicate sheets. They concluded that if the interlayer cation was Mg or one of the alkaline earths, the first water adsorbed by the system, hydrated the cation with six water molecules. Additional layers of water, if present, were H-bonded to the clay. Lithium also hydrated, but not as extensively as the previously listed cations; Na, K and Cs were not found to hydrate.

The water molecules which hydrate the cation are normally pictured with their dipoles radially arranged around the cation. Conceivably several hydration shells could exist, but Tan (1957) opposed the concept of large numbers of adsorbed water molecules on the basis that the heat of wetting was too small to warrant it.

Mathieson and Walker (1954), in work with Mg-vermiculite pictured the cation in a midway position between the clay plates with one layer of water on each side of it. The structure of the water molecules is arranged so as to

conform to the distorted hexagonal arrangement of the surface oxygen network, and simultaneously conform to the tendency for the  $Mg^{++}$  to form an octahedral hydration shell. This arrangement requires that the Mg ions be regularly spaced laterally; also electrostatic forces must be effectively uniform throughout the interlamellar region.

Norrish (1954a) considered H-bonding to be of only minor importance; his opinion is based on the fact that the free energy of H-bonded water is similar to that of free water. He pointed out in defense of his opinion that pyrophyllite and talc, with no interlayer cations, do not swell. Hemwall and Low (1956) suppressed the H-bonding mechanism in montmorillonite with a coating of dioxane, yet found no reduction in the swelling properties of the clay.

Density measurements also indicate that the initial adsorbed water hydrates the cation and not the clay surface. Mackenzie (1958) stated that the hexagonal net structure should have a density of about 0.9, while that of a close-packed, octahedrally coordinated water structure surrounding a cation would have a density  $\gg 1$ . He found that the density of adsorbed water ranges from 1.38 at 9 percent to 1.06 at 20 percent water. A reduction in density to

$< 1$  at the higher moistures ( $\sim 30\%$   $H_2O$ ) suggests that this water has an open structure which may or may not be the hexagonal H-bonded structure.

Mering (1946), in partial defense of the H-bonding theory, postulated that in a Na-system, the first layer of water is adsorbed on the surface, and possesses hexagonal structure. However, since the H-bonding force involved is weak, he believes that there is little influence exerted toward formation of additional water layers. There is disagreement, however, on the hydrating properties of Na-montmorillonite. For example, Hendricks et al. (1940), feel that the cation does not hydrate at all, while Mooney et al. (1952), and White (1955) believe that it does, but only after several layers of water have formed on the internal clay surfaces. Norrish (1954a) states "that for the monovalent cations the degree of swelling is directly related to the hydration energy of the cation".

Low (1961), in his extensive review on clay-water interactions, strongly supports the relative importance of H-bonding. He cites supporting literature in the areas of density, viscosity, infra-red, X-ray and others.

Cownie and Palmer (1952), for example, noted a reduction of the dielectric constant for water near the clay surface, an indication of the presence of an ordered

water structure. Further evidence was provided by Anderson and Low (1957) who found a decrease in density of the water near the clay surface when using Li-, Na-, and K-clays. The density of the initial adsorbed water was not determined, however. Increasing viscosity of this surface water was interpreted by Low (1961) as further proof of the H-bonding theory.

The initial interlayer swelling in a water system, as already stated, is characterized by the formation of distinct layers as the clay is progressively hydrated; these layers are approximately 3 Å thick. The exact spacing however, depends on the saturating cation, charge density, and other factors. Various workers have studied this phenomena and generally agree quite well on the layered spacings formed at low water contents. Morrish (1954a) has summarized much of the current work on several of the saturating cations in tabular form: (p.146).

A certain amount of disagreement with the above table does exist however. For example, various workers have reported quite different allowed spacings for Ca-montmorillonite.

Mering (1946) reports an initial expansion to 14 Å, followed by a jump to 15.5 Å at a slightly higher water content. This is followed by formation of a third and

Interlayer Spacings,  $d_{001}$  A, Formed  
During Water Uptake by Montmorillonite

Interlayer cation

$H_3O^+$	$Li^+$	$Na^+$	$K^+$	$NH_4^+$	$Cs^+$	$Mg^{2+}$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$
10.0	9.5	9.5	10.0	10	12	9.5	9.5	9.5	9.8
12.4	12.4	12.4	12.4	?				12.0	12.0
15.4	15.4	15	15.0	15		15.4	15.4	15.5	15.5
19.0	19.0	19.0				19.2	18.9	?	18.9
22.4	22.5								

Data from Norrish (1954a)



fourth complete molecular layer, each increasing the d-spacing  $\sim 3$  A.

Blackmore and Warkentin (1960) found the highest spacing for the Ca-system to be 18.8 A, as did Blackmore and Miller (1961). Norrish (1954b), and Foster et al. (1955) report a maximum spacing of 19 A. Brindley (1951) obtained a 19.2 A spacing, and Barshad (1950) found two Ca-bentonites which, when immersed in water, expanded to 19.6 and 17.9 A respectively.

Interlayer swelling changes to an osmotic imbibition when the clay plates begin to swell in a continuous and linear manner with increasing water content. Thus far the only clays to exhibit this type expansion are montmorillonites saturated with the monovalent cations, and an isolated case or two of Li-vermiculite (Walker and Milne, 1950, and Brown, 1961).

Norrish (1954b), and Foster et al. (1955) presented papers showing the nature of this expansion as detected by X-ray diffraction. Foster and coworkers found Li-montmorillonite of the Belle Fourche variety expanded in a continuous manner at moistures greater than 35 percent, and was only slightly irregular at moistures less than this. In an electrolyte system they found the (001)

spacings decreased in a regular manner at increasing concentrations of LiCl until a minimum spacing of 20.5 Å was reached.

Norrish (1954b), also using a controlled electrolyte system, found that Li-Wyoming bentonite gave a rational series of (001) spacings at 15.4, 19 and 22.5 Å, with decreasing concentration of electrolyte. At 0.5 M the spacing jumped from 22.5 to 36 Å. Beyond this the d-spacing increased linearly as a function of the square root of the normality. Perhaps the differences noted are a result of somewhat different methods used by these workers.

In a similar study, using salt-free Na-montmorillonite, Foster et al. (1955) found a discontinuity in the d-spacing between 19.2 and 31 Å. Between 50 and 120 percent water the intensities of these two peaks shifted - the 19.2 Å line became weaker while the 31 Å peak became stronger. When the 19.2 Å peak had disappeared the lattice expansion proceeded in a continuous manner. Norrish (1954a) in a similar study, reported the d-spacing jumped from a crystalline 19 Å to a diffuse 40 Å. He reported that the double peak was detectable between 37 and 119 percent water. He also showed a continuous expansion of the lattice after the 19.2 Å spacing has disappeared.

In the presence of electrolyte, Norrish found the discontinuity in the Na-system extended from 19 to 40 Å, while Foster et al. report the discontinuity extended from 19.2 to 50 Å. The differences in the results of the two papers may be due to differences in the clays used.

Foster and coworkers were able to expand K-montmorillonite into the osmotic region by neutralizing a hydrogen-clay with KOH. Apparently the sample was kept quite wet during preparation; then was allowed to dry to the desired moisture for X-ray analysis. A discontinuity extended from 15.6 Å to 88 Å over the moisture range 120 to 200 percent water.

Norrish (1954a) was also able to expand K-montmorillonite into the osmotic region by first expanding the clay with Na, and then passing a dilute solution of KCl through it. Addition of 0.2 N salt solution caused the clay to partially collapse, producing a discontinuity which was similar in appearance to the previously noted one for Na-montmorillonite in a water system. He found  $\text{NH}_4^+$ - and  $\text{Ca}^+$ -montmorillonites could also be expanded this way. A similar attempt was made with  $\text{Ca}^{++}$ , but it was not successful. He found H-montmorillonite expanded in about the same way as the Li-clay.

It is generally agreed that for osmotic expansion to occur, the osmotic forces must be greater than the electrostatic Coulomb attraction between the interlayer cations and the clay plates. Except for  $\text{H}_3\text{O}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$ -montmorillonites, osmotic expansion of clay in a water system normally does not occur. Norrish (1954b), as already stated, applied the principle of Coulomb's law ( $F \propto \frac{1}{R^2}$ ) to also expand  $\text{NH}_4^+$  and  $\text{Cs}^+$ -montmorillonite. The difference in attractive force between these two groups of cations is obviously not related to their valence (all are monovalent). Norrish (1954a) believes it is a function of the hydration of the cation. This in turn is thought to be related to the cation's size - the bigger the cation, the less it hydrates.

Coulomb's law also implies that the electrostatic force should be proportional to the charge density of the clay. The fact that vermiculite, a high charge density clay, ordinarily does not exhibit osmotic expansion, while montmorillonite with a lower charge does, provides verification. Jonas and Roberson (1960), however, discount the importance of charge density. They point out that neither talc nor biotite (two extremes with respect to charge density) exhibit expansion properties. They believe that expansion properties are a function of the

areal extent of the particle. Theoretically then, even mica should expand if the particles become small enough.

Osmotic expansion at the higher interlayer spacings is generally considered to follow that predicted by the Gouy diffuse double layer theory (Bolt and Miller, 1955 and Warkentin et al., 1957). Norrish (1954a) found it applied for expansion  $> 35$  A, and was independent of the cation for monovalent cations. Thomas and Moody (1962), working with Na-Wyoming bentonite, and using pressure membrane apparatus, showed that the  $\text{Cl}^-$  concentration in the adsorbed water decreased at decreasing distances from the clay surface according to that predicted by the diffuse double layer.

Lutz and Kemper (1959) postulated a diffuse double layer in which the stable state represented equilibrium between outward forces of diffusion of the cations and the inward forces of electrostatic attraction. A high concentration of electrolyte would decrease the diffusion gradient and suppress the double layer. They believe that in a calcium system the double layer extends to only 10 A. Similar results were obtained by Thomas and Moody (1962). Others, e.g. Aylmore and Quirk (1959), and Blackmore and Miller (1961), believe the double layer theory does not apply to a calcium system.

Wiklander (1955) attributed the osmotic pressure to the ion concentration gradient in the double layer. Low (1961) believes the semipermeable membrane in interlayer osmotic expansion is provided by the electric field of the clay particles. He points out, however, that the field is not rigid as with an ordinary membrane, and is affected by such things as the H-bonding of the water to the clay plates, ion-water interactions, and the relation of the cation to the clay.

A considerable amount of the work on swelling properties of three-layer clays has been done using organic compounds in the interlayer positions. An example of this type expansion is the work by Barshad (1950) in which he expanded montmorillonite and vermiculite with glycerol. He found the spacing to be dependent on the interlayer cation and on the charge density of the clay. Mac Ewan (1948) states that organic molecules are used in identification work because the spacings are highly repeatable and give sharp reflections.

Use of organic compounds permits the study of the effects of variation in dielectric constant and dipole moment on swelling. Barshad (1952) used various organic compounds to study the relative importance of the dielectric constant and the dipole moment of the interstitial

fluid on swelling properties. He concluded that the dielectric constant has a greater effect on expansion than does the dipole moment. He also concluded that if the dielectric constant were greater than 150, Mg-vermiculite could be made to expand osmotically.

The present state of knowledge on the expanding properties of three-layer-clays suggests a multi-interaction between the clay and the interlayer medium. Several specific mechanisms have been proposed. Considerable research has been directed at evaluating the relative merit of these mechanisms under a variety of conditions. While the results are generally in accord, the interpretations in certain cases are not.

## VIII. MATERIALS AND METHODS

Preliminary investigations of the swelling properties of clays in water systems were carried out with various cation saturations of Wyoming bentonite. The techniques employed were extended to a study of swelling properties of soil clays. Since individual clay preparation procedures varied, each clay used is listed separately along with the methods used in its preparation.

### 8.1 Na-Wyoming bentonite:

The unprocessed material was dispersed with NaOH (approximately 20 me per 100 ga). The  $< 2 \mu$  clay was removed by centrifuging at the prescribed rate and time (Jackson, 1956) in a No. 2 International centrifuge. Sodium saturation was accomplished by running one percent water suspensions of the  $< 2 \mu$  clay through a Dowex 50W-X8, Na-saturated resin at a rate of 3 to 5 ml per minute. Excess salt and water were removed by running the sodium-clay through a Sharples Supercentrifuge at 212 ml per minute, and at 50,000 RPM. The collected sample was resuspended in distilled water using a Waring blender, and again run through the Sharples. This process was repeated until the sample was essentially salt free. The clay sample (2 to 0.08  $\mu$ ) was air-dried and ground to pass a 40



mesh screen. All the clays used were air dried, and all except the first-named sample, were ground to pass an 80 mesh screen.

The remaining  $< 0.08 \mu$  fraction was flocculated by lowering the pH of the suspension to 3.5 with HCl. It later was resaturated with sodium by repeated (4 x) washings with  $N$  NaCl. Excess salt was removed by washing twice with water, followed by methanol washes until the sample was free of  $Cl^-$  as determined by the  $AgNO_3$  test. After two methanol washes the sample dispersed so badly it could not be settled in the International centrifuge. Therefore, it was transferred to a Servall angle-head centrifuge to complete the removal of salts.

### 8.2 Li-Wyoming bentonite:

This clay was prepared by passing a one percent suspension of the 2 to  $0.08 \mu$  Na-clay through a column of Li-saturated Dowex 50W-X12 resin, heated to near  $100^\circ C$ . A 50 symmetry concentration was used to ensure complete exchange. Excess liquid was removed by running the suspension through the supercentrifuge at a rate of 212 ml per minute, at a speed of 50,000 RPM. No attempt was made to save any of the  $< 0.08 \mu$  fraction which may have been present.

### 8.3 Ca-Wyoming bentonite and Ca-White Store:

The procedure for the initial separation of the  $< 2 \mu$  fraction was identical to that used for Na-Wyoming bentonite. Calcium saturation was accomplished by leaching the clay with  $\underline{N}$   $\text{CaCl}_2$  in a Buchner funnel, and then washing with distilled water until no  $\text{Cl}^-$  was found with the  $\text{AgNO}_3$  test.

### 8.4 Na-Georgia kaolinite:

The  $< 2 \mu$  fraction (separated by the previously described procedure) was sodium saturated by washing five times with  $\underline{N}$   $\text{NaCl}$ . Excess salt was removed by washing with water and centrifuging in the International, No. 2 centrifuge until the clay began to disperse. The entire sample then was resuspended by mixing, and run through the supercentrifuge one time at 212 ml per minute and 50,000 RPM. This was assumed to produce an essentially salt free, 2 to  $0.08 \mu$  clay.

### 8.5 Na-Soil clays:

Four soil clays, all known to be high in montmorillonite, were selected. All contained some 1:1 type clays. Three of the soils (White Store, Iredell, and Hunt) were from the Southeastern United States: the White Store came from Chatham, Virginia; the Iredell came from Mitchells, Virginia; and the Hunt came from the Black Belt Branch

Station, Brooksville, Mississippi. The fourth was a Webster soil from Conger, Minnesota. The clay fractions used in this study were taken from the B horizon of the three Southeastern soils, and from the C horizon of the Minnesota soil. The above information and the various treatments given the clay are summarized in Table 1.

Carbonates and organic matter were removed (where applicable) by the methods given in Southern Cooperative Series Bulletin 61 (1959). Carbonates were removed with  $\underline{N}$  HCl, and organic matter was treated with 30%  $\text{H}_2\text{O}_2$ . The samples then were dispersed by bringing them to pH 10 with  $\underline{N}$   $\text{Na}_2\text{CO}_3$ .

The  $< 2 \mu$  clay was removed using the method of Jackson (1956), by repeated washings with a  $\text{Na}_2\text{CO}_3$  solution (at pH 10) - each wash followed by centrifuging in an International, No. 2 centrifuge at the prescribed rate and time. The  $< 0.08 \mu$  clay was separated out in the Sharples Supercentrifuge. The dispersed clays were flocculated by lowering the pH to 3.5 with HCl. Preliminary investigations on the swelling properties of soil clays were carried out using the  $< 2 \mu$  fraction. Later work was carried out using the  $< 0.08 \mu$  fraction.

The various iron and aluminum removal treatments, summarized in Table 1, were applied after fractionation.

The iron removal treatment was the method of Jackson (1956) using sodium citrate and sodium dithionate. Aluminum was removed by a method suggested by Rich which involved the following treatments:

1. 3 washes with  $\underline{N}$  Na-citrate; each heated 1 hour at  $100^{\circ}\text{C}$ .
2. Shaking one hour in a composite solution of  
0.4  $\underline{N}$   $\text{NH}_4\text{F}$   
0.1  $\underline{N}$   $\text{HCl}$   
 $\underline{N}$   $\text{NH}_4\text{Cl}$ .
3. Washing immediately 4 times with  $\underline{N}$   $\text{NaCl}$ .
4. Warming in water bath ( $100^{\circ}\text{C}$ ) for 15 minutes.

After the iron and aluminum removal treatments (where applicable) the samples were sodium saturated by washing 5 times with  $\underline{N}$   $\text{NaCl}$ . Excess salt was removed by two water washes, followed by methanol washes until  $\text{Cl}^-$  free. If dispersion occurred during the salt removal, the samples were transferred to the Servall angle centrifuge to complete the operation.

#### 8.6 X-ray procedure:

The high water contents used in this project presented some unique problems not ordinarily encountered in mineralogical identification. The following techniques of sample preparation and X-ray procedure were devised, and were found to give excellent results.

Two methods were used in preparing the samples. In method 1, the desired amount of sample was weighed on a triple beam balance, then transferred to a 2 dram shell vial in which the desired amount of water already had been placed with a buret. The sample was thoroughly mixed with a small spatula. Samples with less than 30 percent water could not be properly mixed using this technique, and also were difficult to transfer to the X-ray slide. Samples with less than 50 percent water were stoppered; those containing greater than 50 percent water were placed in a desiccator with a free water surface. All were allowed to equilibrate for one week. The exact moisture content at the time of X-ray analysis was determined by running a standard moisture determination on part of the equilibrated sample. All moisture determinations were made on samples heated to 110° C.

In method 2, the final moisture content desired was calculated prior to mixing. This was done by first equilibrating a substantial quantity of sample several days in a desiccator. The relative humidity in the desiccator was controlled using sulfuric acid-water mixtures. Part of the sample then was used for a moisture determination. The amount of sample needed for X-ray analysis then was weighed out accurately and added to the

shell vials in which the desired amount of water had been added with a micro-buret. The sample was mixed, stoppered, and allowed to equilibrate for one week. The actual percent moisture by this method, was controllable to within two percent of the calculated value. Greater precision could have been obtained if the relative humidity of the preparation room had been controlled.

A grooved aluminum slide (Figure 1) was designed to hold the sample during X-ray analysis. The groove provides a convenient means of holding a thick, flat layer of sample. The clay sample was smeared on the slide with a flat spatula, with care being taken to assure a flat surface which was flush with the top edge of the slide. This is especially important at low angles. The smearing technique has been found by Theisen and Harward (1962) to give preferred orientation in the (001) plane, thereby increasing the intensity of the diffracted beam. The increased thickness of the sample, provided by this slide, also was considered advantageous in increasing the intensity by compensating for the presence of the water. The optimum thickness was not determined however.

The slide was made longer than ordinary in order to provide a greater surface area to the impinging X-rays.

It is also recommended<sup>1</sup> that the slide be displaced toward the Geiger tube when working with low angles because the peak intensity is also slightly displaced in that direction.

The X-ray analyses were run on a General Electric XRD-3 unit, with a recording spectrogoniometer using copper K $\alpha$  radiation (nickel filter), a current of 25 milliamperes and a voltage of 35 KV. Slit sizes found best for this low angle work were: 0.4° beam slit for two theta > 0.5°, and 1° beam slit for two theta > 1.5°; a 0.2° detector slit; and an MR soller slit. A scanning speed of 2° degrees per minute, with a chart speed of 24 inches per hour was used throughout.

Humidity during X-ray analysis was controlled by a relatively simple, yet effective apparatus (Figure 1). A slow, steady stream of air was equilibrated at approximately 100 percent relative humidity by passing it through the water in the two Erylenmyer flasks. Lower relative humidities could have been obtained by substituting other solutions for water. Air bubble size was controlled with gas dispersion tubes (Will Corp., No. 15166).

---

<sup>1</sup>Instruction Manual XRD-3, X-ray diffraction unit, Direction 11690A, SPG Spectrogoniometer, p. 20.

The moisture chamber was a cardboard ice cream box in which two slits had been cut to provide a path for the X-ray beam. The slits were covered with Saran wrap. No interference from the Saran wrap was detected, except for a very slight loss in intensity. The slides were prepared and run as quickly as possible to keep evaporation at a minimum.

Several studies were made on the ability of the moisture chamber to prevent evaporation from the clay during the analysis of a slide. It was found that no detectable reduction in d-spacing occurred in the length of time required to complete X-ray analysis of a slide.

#### 8.7 Quantitative Montmorillonite Determinations:

It was hypothesized that the degree of swelling of a three layer clay mineral, in a mixture of swelling and non-swelling clays, was related to the relative proportions of each. To test this hypothesis, mixtures of Na-saturated, 2 to 0.08 $\mu$ , Wyoming bentonite and Georgia kaolinite clays were prepared using method 2 previously described under X-ray procedures.

Several sets of these Georgia kaolinite, Wyoming bentonite mixtures were prepared, with the amount of Wyoming bentonite in each set varying from 0 to 100 percent of the dry clay mixture. The amount of water added



to the mixed samples was calculated so that each sample of a particular set would contain the same amount of water. A final check on the percent water of each sample was made at the time of X-ray analysis. It was found that the actual percent water was controlled to within two percent of the calculated value.

**Table 1—Soils and treatments used in expansion study of  
Na-soil clays.**

Soil	Horizon	Treatment*							
		CaCO <sub>3</sub>	O.M.	< 2 $\mu$			< 0.08 $\mu$		
				N T	Fe R	Fe & Al R	N T	Fe R	Fe & Al R
White Store	B	-	x	x	x	x	x	-	x
Hunt	B	-	x	-	-	-	x	-	x
Iredell	B	-	x	x	x	-	x	x	-
Minnesota	C	x	x**	x	-	-	x	-	-

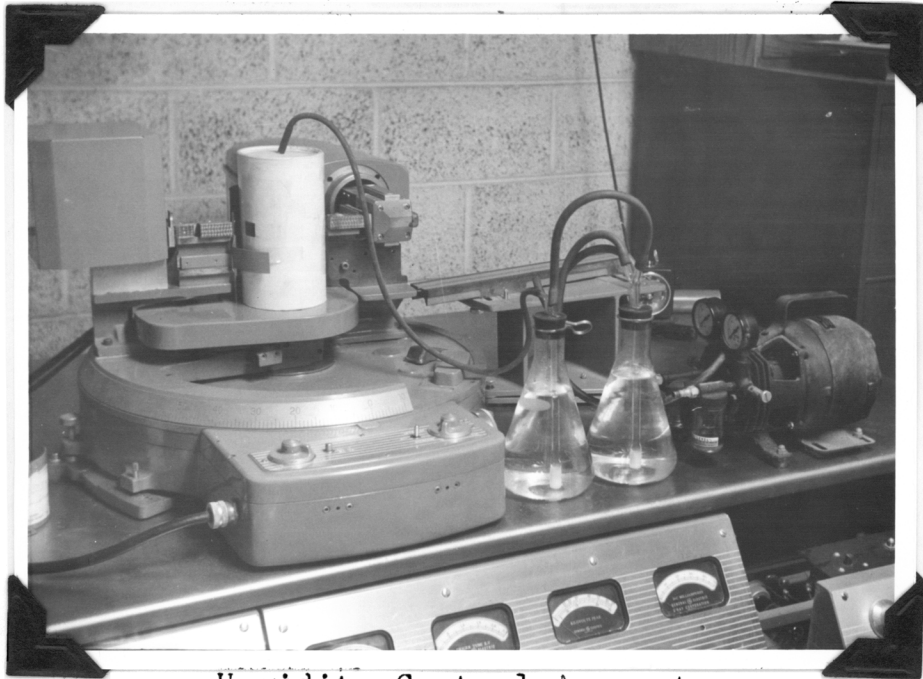
O.M. = organic matter; N T = no treatment;

Fe R = iron removed; Fe & Al R = iron and aluminum removed.

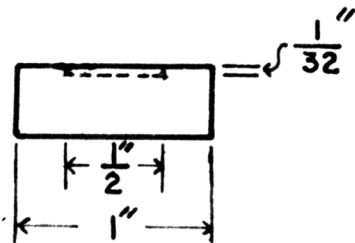
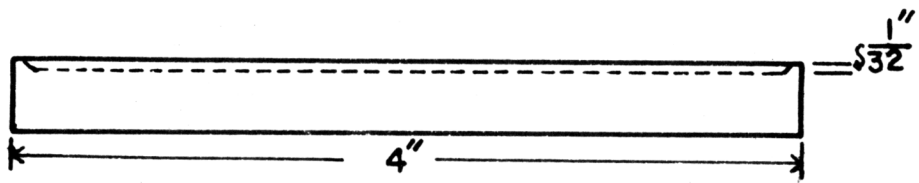
\*:All clays were sodium saturated as a final treatment.

\*\* :The sample was slightly contaminated with organic matter.

**Figure 1—Special apparatus used in X-ray analysis.**



Humidity Control Apparatus



Grooved Slide

## IX. RESULTS AND DISCUSSION

### 9.1 Lithium Wyoming bentonite:

Figure 2 shows the interlayer expansion of Li-bentonite to be continuous and linear for water contents greater than 35 percent. The X-ray diffraction peaks of the (001) d-spacings, as shown in Figure 3, were intense and clearly defined for moisture contents below 400 percent, but graded into diffuse patterns which were difficult to read at water contents greater than 400 percent. Second order peaks were evident at the lower moisture contents.

At water contents below about 40 percent evidence was found for hydration by layers. The X-ray pattern at 36.2 percent water in Figure 3 depicts this with the presence of a shoulder at  $\sim 19$  A, superimposed on the 16.7 A peak. This would represent an increase of one water layer.

The linear equation,

$$d = 10 + \frac{\% \text{ H}_2\text{O}}{4} \quad (1)$$

in Figure 2, represents the theoretical expansion curve for the clay if it expands in a continuous manner as water is added. The constant term (10 A), represents the initial, basal (001) spacing of the dehydrated clay.

The derivation of the independent variable ( $\% \text{H}_2\text{O}/4$ ), is based on three assumptions: (1), that the internal surface area is  $800 \text{ m}^2/\text{gm}$ ; (2), that the external surface water is negligible; and (3), that the density ( $\rho$ ) of the adsorbed water is equal to one. Each gram of water, spread uniformly over the entire internal surface area, then assumes a height of,

$$\frac{(2)(\text{H}_2\text{O})}{(\rho)(8 \times 10^6)} = \frac{1}{4} \times 10^{-6} \text{ cm} \quad (2)$$

$$= \frac{100}{4} \text{ \AA}$$

where ( $\text{H}_2\text{O}$ ) is in gms water per gm clay, ( $\rho$ ) represents the density of the water in  $\text{gm}/\text{cm}^3$ , and the term ( $8 \times 10^6$ ) represents the internal surface area in  $\text{cm}^2$  per gm clay. The term (2) in the numerator arises from the fact that an increment of interlayer water contributes equally to both the top and bottom clay surfaces, therefore must be counted twice. The interlayer thickness of the imbibed water then becomes:

$$\frac{\% \text{H}_2\text{O}}{4}$$

Over most of the water range studied, the experimentally determined d-spacings lay close to the theoretical line. At low moistures they were slightly below the line, while at the higher moistures they lay slightly above it.

The d-spacings at the higher moistures ( $> 400\%$ ), were difficult to read however, since the peaks were so diffuse. In addition, errors in reading  $2\theta$  at these low angles were compounded when converted to d-values using the standard Bragg equation.

At the lower moistures ( $< 100\%$ ), the actual d-spacings were found to lie along a linear curve slightly below, and parallel to the theoretical curve. The upper inset of Figure 2 shows this difference to be 2.2 Å. The original equation for expansion assumed all the water to be in interlayer position; therefore, the difference between the two curves should provide an approximate means for determining the amount of external surface water.

Using the equation

$$d = \frac{\% \text{ H}_2\text{O}}{4} \quad (3)$$

and substituting values, one finds the amount of external water to be,

$$\% \text{ H}_2\text{O} = (2.2)(4)$$

$$\% \text{ H}_2\text{O} = 8.8\%$$

If this water were uniformly distributed over the entire external surface, and if the surface area were  $50 \text{ m}^2$  (Dyal and Hendricks, 1950), then the water would be



17.6 A thick:

$$\frac{(0.08 \text{ gm H}_2\text{O/gm clay})(10^8 \text{ A/cm})}{(\rho \text{ gm/cm}^3)(0.5 \times 10^6 \text{ cm}^2/\text{gm clay})} = 17.6 \text{ A}$$

The term (2) was omitted from the numerator in this case, since the surfaces were assumed not to share water layers. The above derivations assumed all the water was removed at 110°C. It is also realized that the basal (001) spacing for Wyoming bentonite is less than the 10 A used in this derivation, but it is considered to be within the experimental error associated with the other terms.

Using Aylmore and Quirk's (1959) value for the internal surface area (648 m<sup>2</sup>/gm) in determination of the theoretical expansion curve, the above method would indicate that the external area contained 14.4 percent water, and that it was approximately 30 A thick. Obviously, the two approaches produce quite different results. The results do show, however, that the amount of external water is relatively small compared to the internal water, at least where appreciable water is present.

The problem of quantitatively determining the distribution of the water between internal and external positions could be resolved if the internal surface area could be accurately determined. One postulated approach would be to block external water adsorption sites only, e.g. using

silane (Hemwall and Low, 1956). The theoretical expansion curve would then equal the actual curve and could be used to determine the internal surface area by using the relation:

$$d' = 10 + \frac{\% \text{ H}_2\text{O}}{K}, \quad (4)$$

where  $2K \times 10^2$  equals the internal surface area in  $\text{m}^2/\text{gm}$ . The untreated clay would give a smaller (001) spacing at the same water content. The amount of external water would be equal to

$$\% \text{ H}_2\text{O}_{\text{ext}} = (K)(d' - d). \quad (5)$$

Figure 2—Lattice expansion of 2 to 0.08 $\mu$ , Li-Wyoming bentonite in a water system.

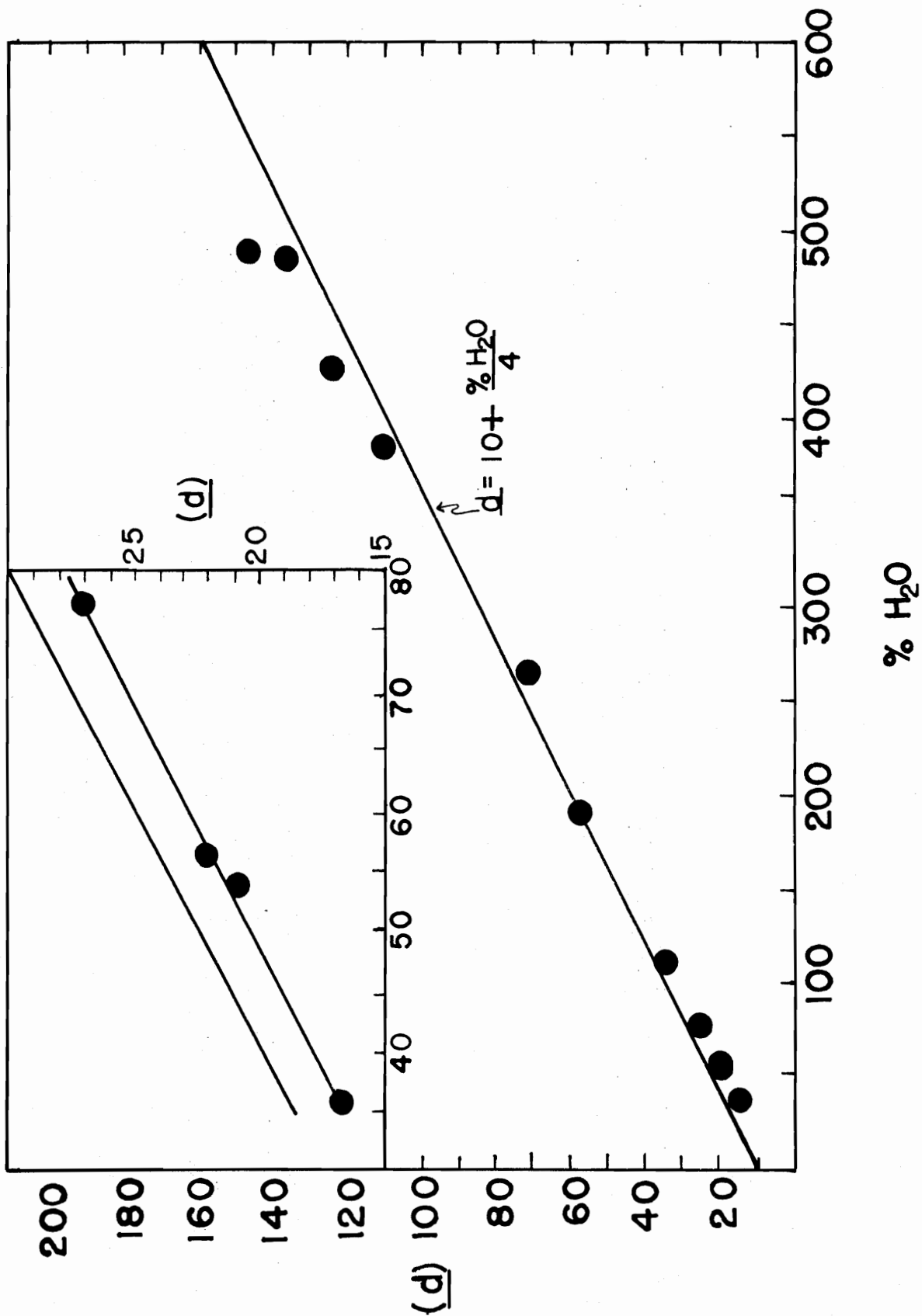
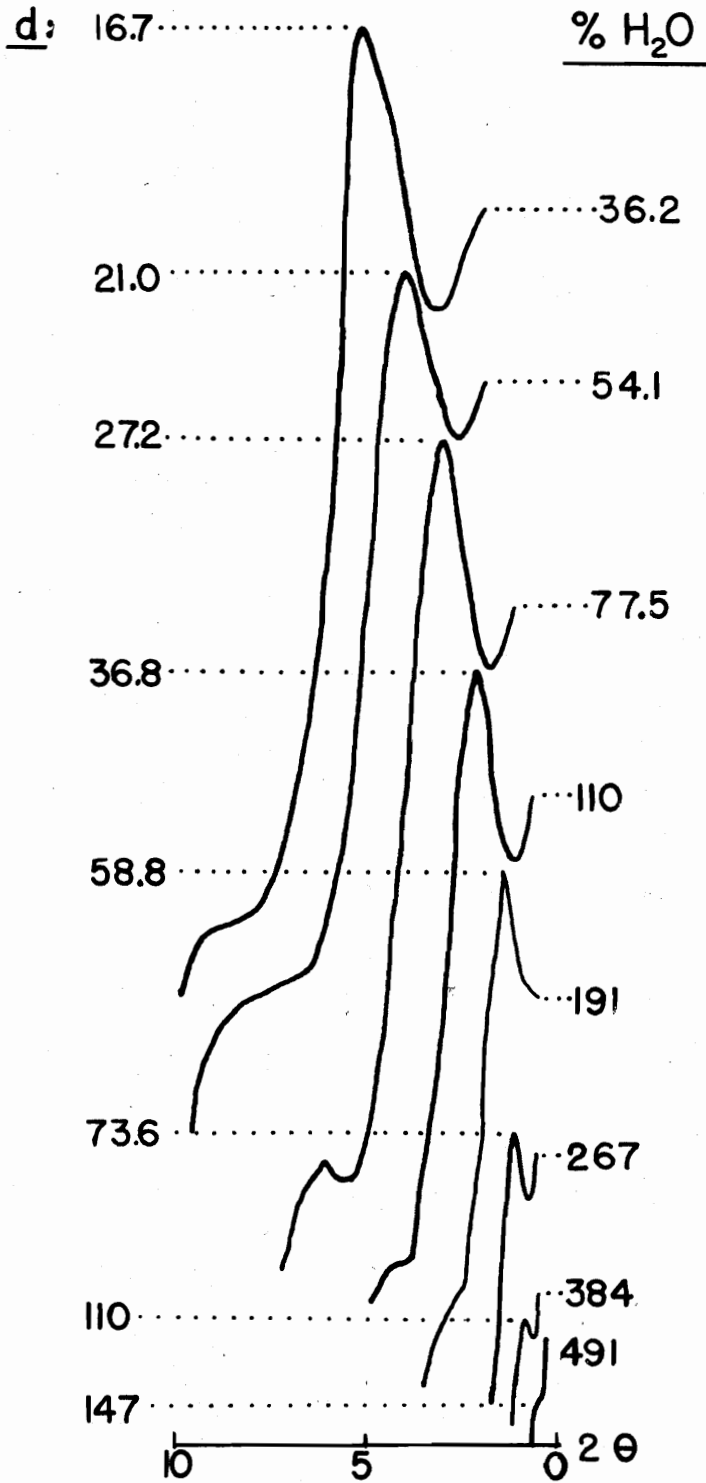


Figure 3--Smoothed X-ray diffraction patterns of 2 to 0.08  $\mu$ , Li-Wyoming bentonite in water systems.



Li-WYO. BENTONITE

## 9.2 Sodium-Wyoming bentonite:

Expansion of the 2 to 0.08  $\mu$  Na-bentonite versus water content is shown in Figure 4. The Na-clay expanded in a definite step-wise manner to about 35 A, and showed indications of step-wise expansion to considerably higher spacings.

The first stable (001) spacing detectable by this method was at 16 A, which extended over the 35 to 40 percent moisture range. The next stable spacing occurred at 19.2 A. This 19.2 A peak persisted over a large moisture range, extending from about 40 to beyond 110 percent water. As water was added over this range a second diffuse peak appeared with a d-spacing between 30 and 40 A. The peak gradually increased in intensity (Figure 5), while the 19.2 A peak diminished in intensity. The expansion from 19.2 A to the higher spacing occurred as a single step with no intermediate spacings. The clay plates apparently expanded individually as additional water was added, thereby resulting in a gradual intensity shift from one peak to the other.

Over the moisture interval 100 to 130 percent water, the d-spacing gradually increased with increasing water content until it had expanded to about 40 A. The second order of this higher spacing then became superimposed on the

weakened 19.2 Å (001) peak, making differentiation between the two difficult.

A fourth plateau appeared at 50 Å, which extended from 150 to 190 percent water. An example of one of the X-ray patterns in this moisture range appears in Figure 5. The first order peak is fairly intense, sharp and symmetrical. Another stable interlayer spacing was indicated at about 73 Å, extending from 240 to 310 percent water. Figure 5 also shows a typical pattern in this range. Beyond 350 percent water the diffraction peaks became too diffuse to determine the presence of additional plateaus in the expansion pattern.

The data suggests that the expansion of Na-Wyoming bentonite occurs in a step-wise, manner, even at high water contents. This conflicts with the previous reports of Norrish (1954), and Foster *et al.* (1955) which state that the expansion pattern is continuous beyond  $\sim 120$  percent water. However, to provide conclusive proof of this step-wise expansion at the high moisture levels, additional points will need to be run, and all curves will need to be corrected for polarization and Lorentz effects to determine their exact d-spacings.

A similar series was run using the  $<0.08\mu$  fraction of Na-bentonite. The discontinuity between 19 and 35 Å



was similar to that found with the larger clay fraction, but Figure 6 shows that the 19 Å peak of the <0.08 μ material extended over a much shorter moisture range than with the 2 to 0.08 μ fraction (45 to 90 percent H<sub>2</sub>O and 40 to 130 percent H<sub>2</sub>O respectively). This is not unreasonable since the <0.08 μ fraction should contain a much smaller internal surface area in proportion to its external surface area, than does the 2 to 0.08 μ fraction.

The X-ray diffraction peaks of the <0.08 μ fraction were broader and more diffuse than those of the larger fraction; e.g., the characteristic 19.2 Å peak of the 2 to 0.08 μ clay was no longer so clearly defined (upper insets of Figures 4 and 6). Several factors may be responsible for this broadening and loss of intensity: (1) the smaller particles contain fewer diffracting layers per particle; (2) the smaller particles may be bent, resulting in strain broadening; (3) small particles would not orient very well; (4) exchangeable aluminum which was not removed by the four sodium washes may be present. Item (4) is probable since the <0.08 μ clay was stored as a slurry at about pH 4 for several months prior to its resaturation with sodium. This would have allowed ample time for the dissolution of substantial quantities of clay.

Figure 4--Lattice expansion of 2 to 6.08  $\mu$ , Na-Wyoming  
bentonite in a water system.

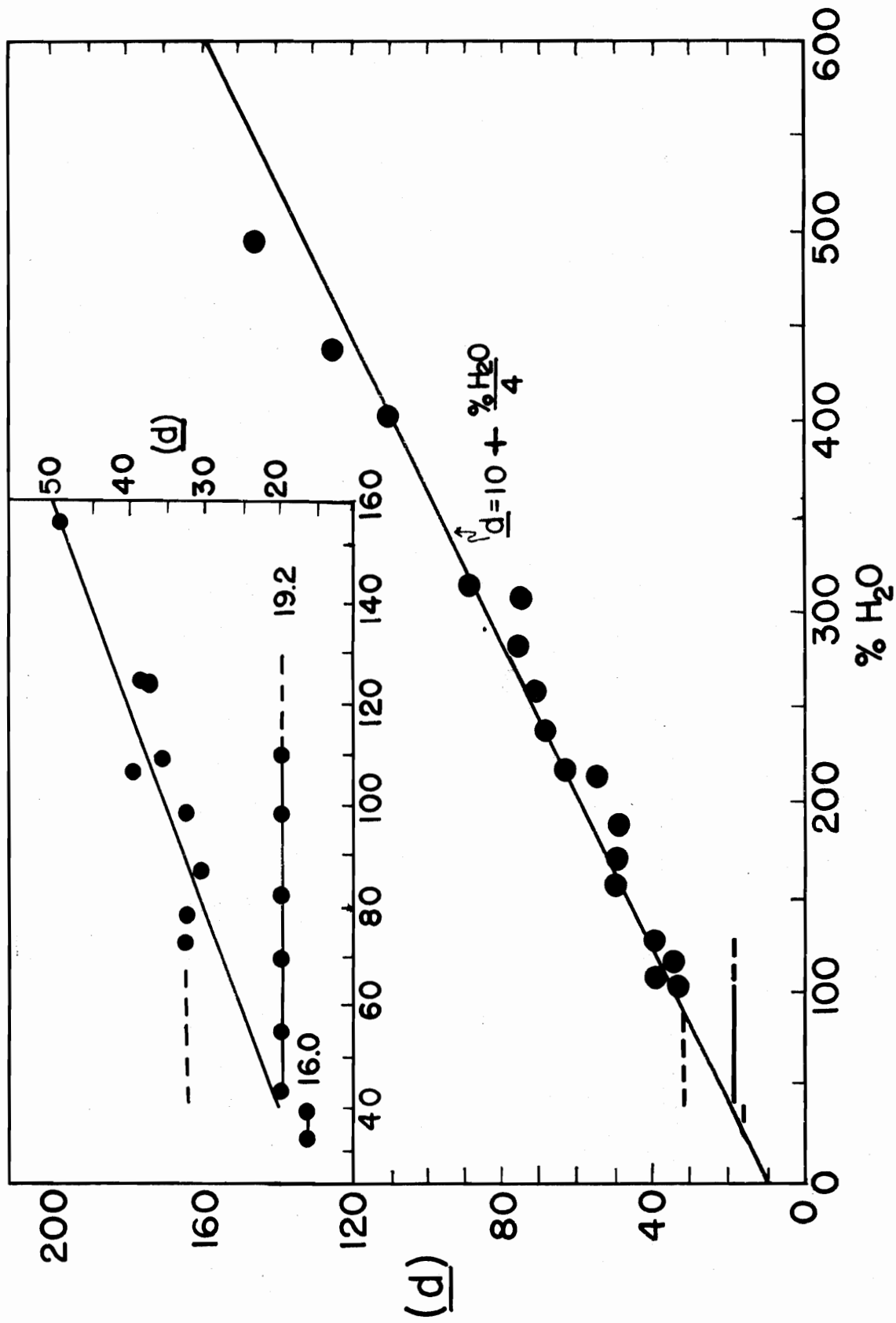
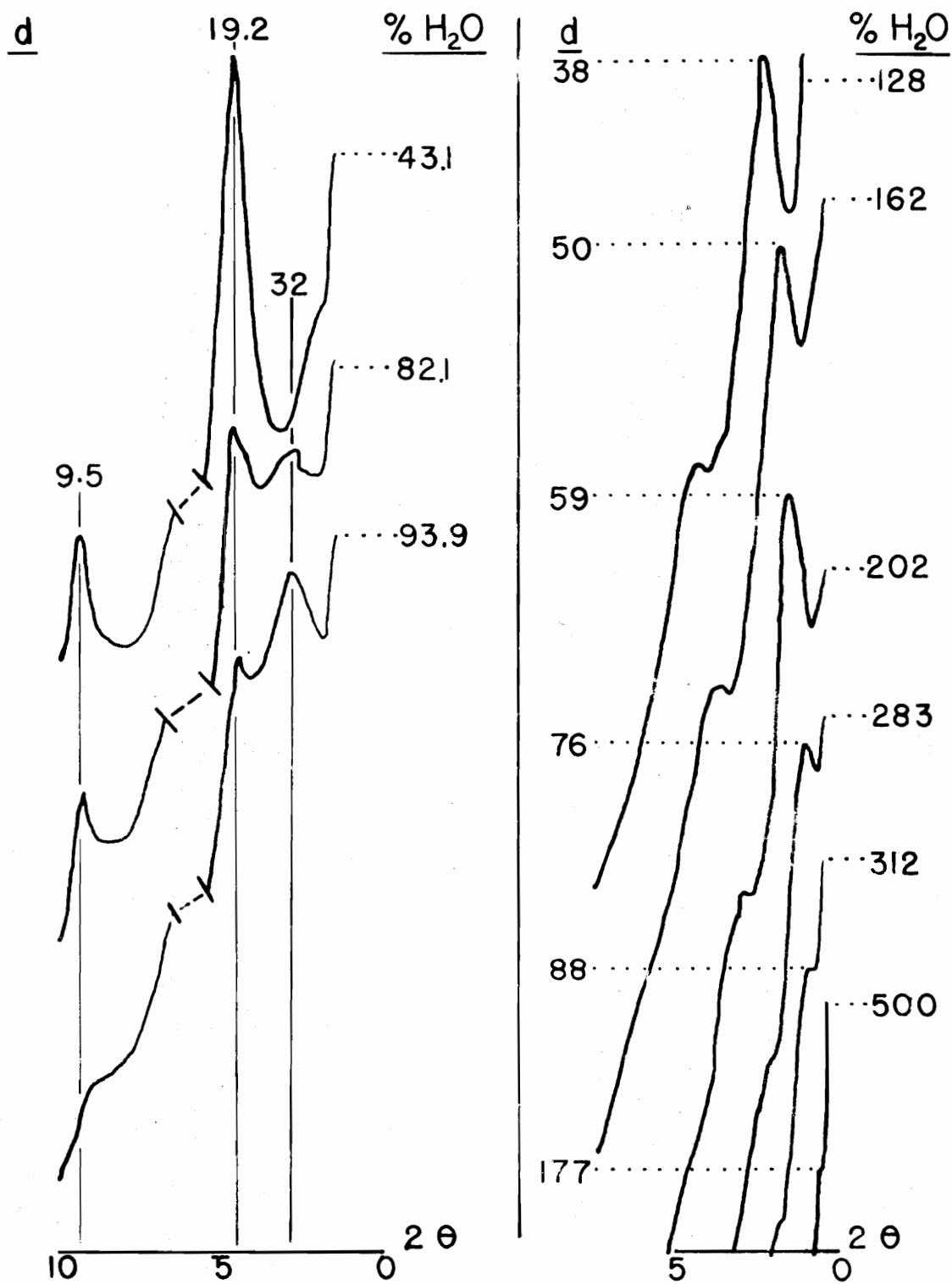
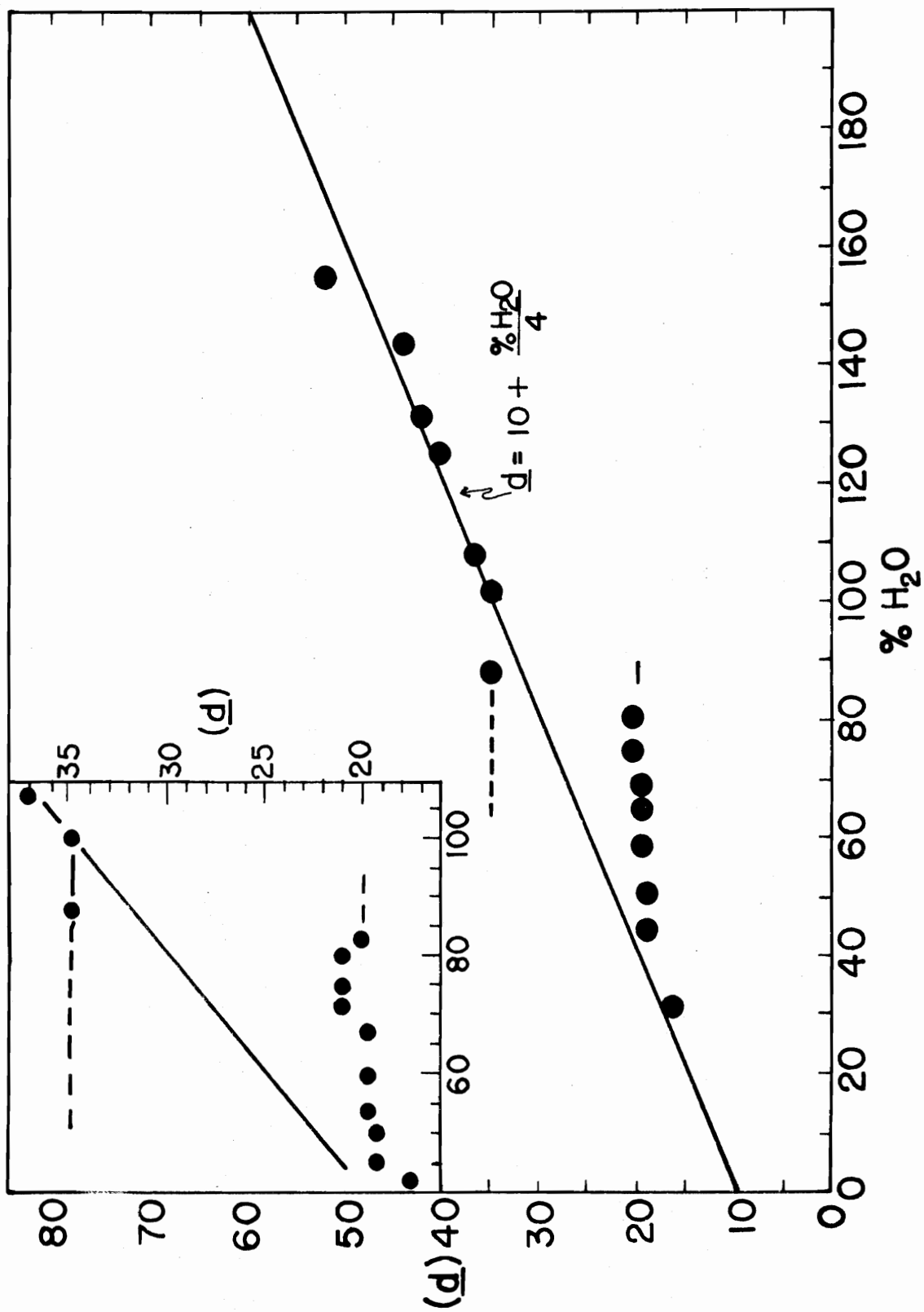


Figure 5—Smoothed X-ray diffraction patterns of 2 to  
0.05 $\mu$ , Na-Wyoming bentonite in water systems.



Na. WYO. BENTONITE

Figure 6—Lattice expansion of  $< 0.08\mu$ , Na-Wyoming  
bentonite in a water system.



### 9.3 Calcium Wyoming bentonite:

Ca-bentonite expanded to 19.2 Å (001) at 35 percent water (Figure 7); at 45 percent water the lattice expanded another 0.4 Å to 19.6 Å. No explanation other than in terms of general thermodynamic principles could be found to explain this small, 0.4 Å increase. Over the 45 to 50 percent moisture range both peaks were found, but beyond 50 percent water only the 19.6 Å spacing was detected. Even though the various workers (Chapter VII, p. 14) do not agree completely on the maximum spacing, all reported work shows no expansion beyond 20 Å.

Obviously, the forces of attraction holding the clay plates together are greater than the forces which would allow the water to enter and expand the plates into the osmotic region. The dominant force is attributed to the electrostatic attraction between the calcium cations and the net negative interlayer surfaces. However, an equation describing this attraction in terms of Coulombic forces would be difficult to attain since the variables are generally indeterminate. For example, the dielectric constant of the water is variable, depending upon whether it is associated with the cation or the clay surface, and on its distance from either.



Coulomb's law is based on the charges existing as point charges. An unhydrated cation approaches this, but once the cation is hydrated the positive charge becomes distributed over the periphery of the water shell.

Also, it is difficult to ascertain the areal extent of the net negative charges associated with the clay surfaces. Hendricks (1945) envisioned each charge as being associated with a limited area, the size of which depended upon whether the isomorphous substitution occurred in tetrahedral or octahedral position.

Mathieson and Walker (1954) presupposed a uniform charge distribution to explain their concept of a uniform internal electrostatic field.

All the water added after the final lattice expansion to 19.6 Å is associated with the external surfaces of the individual packets (Blackmore and Miller, 1961). This external surface water is thought to have a free energy very close to that of free water. At 250 percent water the sample became so fluid it ran on the slide, thus imposing an upper limit for X-ray diffraction by this technique.

Figure 8, shows the X-ray peaks to be fairly sharp and symmetrical, even at the highest moisture studied.

There was some loss of intensity, however, at the higher water contents, especially in the higher orders.

Figure 7--Lattice expansion of  $\langle 2^{\mu}$  Ca-Wyoming bentonite.

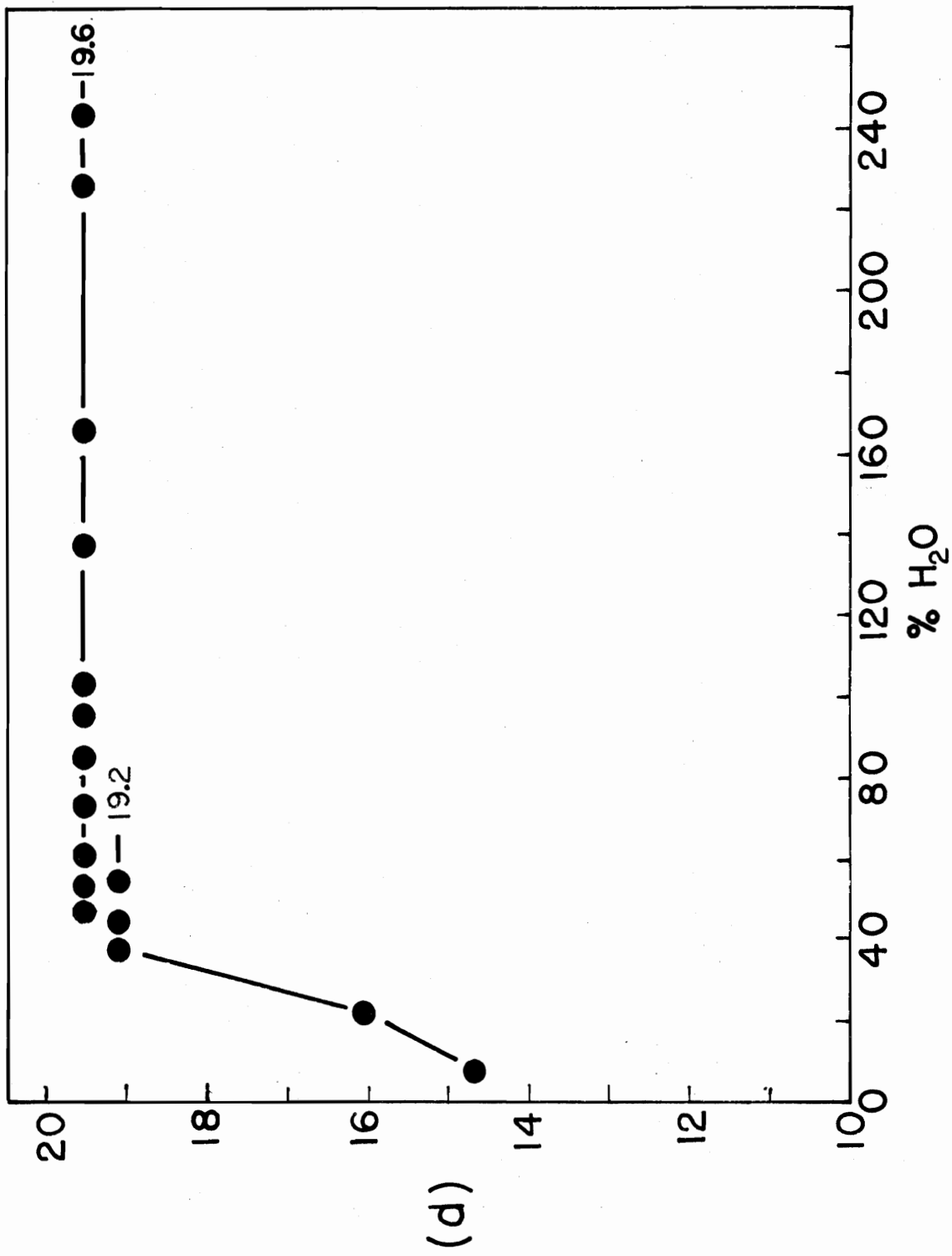
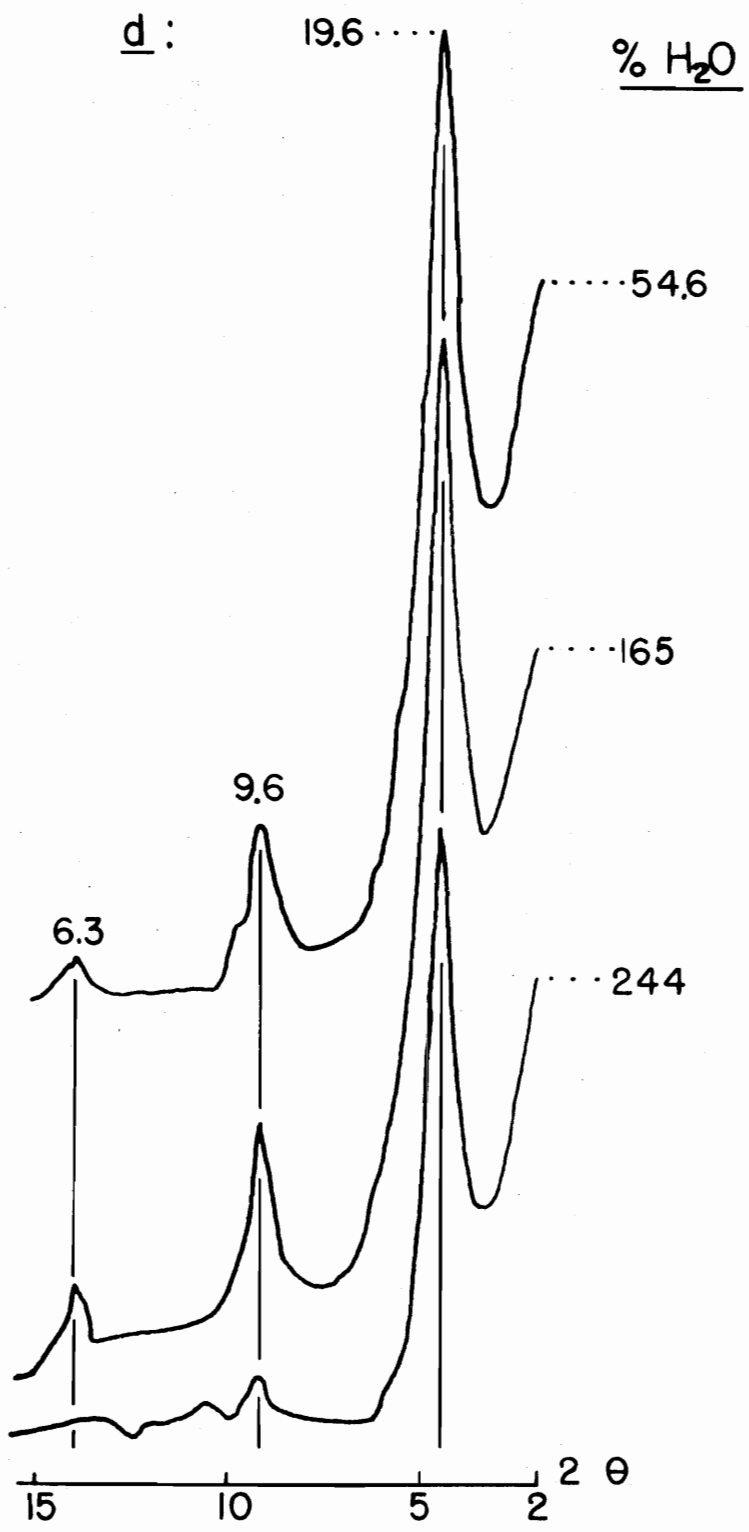


Figure 6--Smoothed X-ray diffraction patterns of  $< 2 \mu$ ,  
Ca-Wyoming bentonite.



Ca. WYO. BENTONITE

#### 9.4 Soil Clays:

The techniques developed to study the expansion of Wyoming bentonite were applied to Ca- and Na-soil clays.

Calcium-White Store (Figure 9), the only Ca-saturated soil clay studied, showed expansion characteristics similar to those of Ca-Wyoming bentonite. The White Store already had expanded to about 20 Å at 30 percent water content and maintained this spacing through the upper limit of adsorbed water studied by this technique ( $\sim 130\% \text{ H}_2\text{O}$ ).

The predominant force which restricts expansion again is attributed to the electrostatic attraction between the cation and the interlayer clay surfaces. The interlayer swelling up to 15 Å is attributed mainly to hydration of the  $\text{Ca}^{++}$  ion. Two layers of water apparently are then hydrogen bonded to the interlayer clay surfaces, resulting in the 20 Å spacing. The swelling, therefore, occurs in layers, as with Ca-Wyoming bentonite.

The diffraction peaks for the expanded Ca-White Store were broader and more diffuse than were those of Ca-Wyoming bentonite. A number of factors produce broadening. Brindley (1951) groups these under instrument broadening, lattice strain, lattice mistakes and small crystal size.

Instrument broadening arises from such factors as slit widths defining the X-ray beam, size and form of the

specimen, and the presence of the  $K\alpha$  doublet. Since this type of broadening is nearly equal for both clays at the same diffraction angle, it may be disregarded in a comparison.

Crystal size is a factor in line broadening (Klug and Alexander, 1954); the number of layers per packet in White Store may be less than for Wyoming bentonite. Lattice strain broadening results from irregularities in the crystal structure, such as the presence of the end groups of the crystal plates, bending of the crystals, and irregular isomorphous substitution. Lattice mistakes are due to such things as lattice displacement, and interstratification.

Probably the main reason, however, for the line broadening and diffuseness in this case is an irregular expansion of the clay plates, caused by slight differences in the amount of interlayer water between the clay plates. These irregularities in the amount of interlayer water are thought to be caused by heterogeneous inter-lattice forces which result from an irregular arrangement of charge sites in the lattice.

It is conceivable that if the isomorphous substitution were completely random, as Grim and Kulbicki (1961) have proposed for Wyoming bentonite, the irregular expansion



effects due to heterogeneous inter-lattice forces would cancel in X-ray diffraction. The diffraction peak then merely would represent the most probable spacing of a bell shaped expansion curve of lattice spacings versus the number of plates with this spacing.

The sharpness of the diffraction peaks in the osmotic swelling region then should be a good indicator of the degree of randomness of the isomorphous substitution.

Another factor which may cause irregular expansion of the clay plates is the presence of interlayer hydroxy aluminum polymers (Rich and Obenshain, 1955). These polymers in addition to affecting interlayer swelling, will increase the background radiation, thus masking diffraction peaks. The presence of other clay minerals, e.g., vermiculite and chlorite, also has a masking effect.

The presence of these non-expanding materials also caused the Ca-White Store clay to exceed the liquid limit at a fairly low water content. The clay flowed on the slide at  $\sim$  130 percent water, considerably less than the comparable value of 250 percent water for Ca-Wyoming bentonite. The fact that non-expanding clays adsorb less water than montmorillonite has been utilized (section 9.5) to provide a quantitative identification method for montmorillonite in soil clays.

The method of analyzing a Ca-clay-H<sub>2</sub>O slurry may have value in qualitative identification of soil clays. The diffraction peaks for the Ca-White Store at 50 percent water were as sharp and intense as those found in the standard identification method using Mg-glycerol.

The exact (001) d-spacing of this soil montmorillonite, however, was very difficult to determine from the X-ray diffraction pattern, due to the aforementioned broadening effect and the weak intensity of the peak over background. This latter effect is especially troublesome at low angles due to the geometry of X-ray diffraction, which tends to increase the background as the central beam is approached, giving the characteristic logarithmic curve of intensity versus decreasing  $2\theta$ .

The background due to geometric effects may be eliminated (Klug and Alexander, 1954) by dividing the linear intensity (I) of the trace by the combined Lorentz and Polarization Factor:

$$I / \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) = F^2$$

where F equals the structure factor.

A corrected curve of  $F^2$  versus  $2\theta$  is plotted in Figure 10, along with the original uncorrected trace. These differences show: the (001) peak of the montmorillonite on the corrected curve is clearly defined and has shifted

to a higher  $2\theta$  angle; the orders also have become integral; the higher order peaks do not shift extensively upon correction.

Previous general practice in X-ray diffraction studies of clays has been to ascribe the d-spacing as that attributable to the uncorrected (001) peak. Bradley has suggested<sup>1</sup> that a more correct procedure would be to either correct the lower order peaks with the combined Lorentz and Polarization Factor, or to use the d-spacing obtained from the higher orders.

The next project undertaken was to determine whether or not sodium saturated soil montmorillonites, at high water contents, could be made to expand in a regular, crystalline manner so that the expansion could be detected by X-ray diffraction. The problem proved considerably more difficult than the previous experiments.

No diffraction peaks attributable to expanded montmorillonite were found by this method for the Na-White Store and Iredell clays, regardless of the pretreatment used. Only when a smear of the sample was allowed to air-dry on a glass slide could any semblance of a peak be detected, a broad one at about 12 Å.

---

<sup>1</sup> Personal consultation.

The Na-Hunt clay did not expand as freely as the other montmorillonites studied. A broad peak at 18 Å persisted to 85 percent water. At 118 percent water this had disappeared and no diffraction peak attributable to montmorillonite was found; apparently the plates had expanded, but in an irregular manner. Standard identification methods showed that the clay was high in montmorillonite, but it is thought that since the clay was slow to expand in the Na, water-system, it might be a vermiculite-montmorillonite intergrade. If a Li-system had been used the clay might have expanded more readily.

The Na-saturated, Webster clay, however, did produce diffraction peaks attributable to highly expanded montmorillonite. The two representative patterns in Figure 11 show that the d-spacing expanded from 50 to 63 Å as the water content increased from 121 to 164 percent, respectively, indicating that the expansion of this clay is a direct function of increasing water content.

All the Na-clays apparently adsorbed water into interlamellar positions, as evidenced by the fact that the samples did not flow on the slide as the Ca-clays did, even at water contents above 300 percent.

The difficulty is to explain why only one of the four Na-soil clays produced an X-ray diffraction peak in the

osmotic expansion region. When the predominant interlayer force is due to the hydration of the cation or the hydrogen-bonding between the clay and the interstitial water, the clay will hydrate in discrete layers. However, as more water enters between the plates, and the swelling becomes osmotic, as with the Na-saturated soil clays, the amount of interstitial water between any two plates becomes dependent on the electrostatic field for that set of plates. Since the forces controlling osmotic expansion are weak, it seems logical to assume that heterogeneity in the interlayer electrostatic fields will result in differences in water imbibition from one interlayer to another.

This method of studying soil clays promises to be a valuable tool for the agronomist. Section 9.5 describes a method using these techniques for the quantitative determination of three-layer clays in soils. The method possibly could be used to study exchange and diffusion properties in di- or multi-cation systems, e.g. going from a monovalent to a divalent cation system.

Other possible uses include a means of studying the way interlayer spacing is related to water holding capacity, or to water removal by plants. As already implied, the method could serve as an aid to determining crystallinity and morphology in clays. This technique holds promise of

being applicable for studying soil clays. In the past, most of these studies have been carried out with well-defined, crystalline clays such as Wyoming bentonite, the swelling properties of which may be quite different from soil clays. The immediate future plan is to continue the X-ray diffraction study of expanded soil montmorillonites, especially in the osmotic swelling region.

Figure 9--Calcium-White Stone; smoothed X-ray diffraction patterns for  $< 2 \mu$  fraction in water systems.

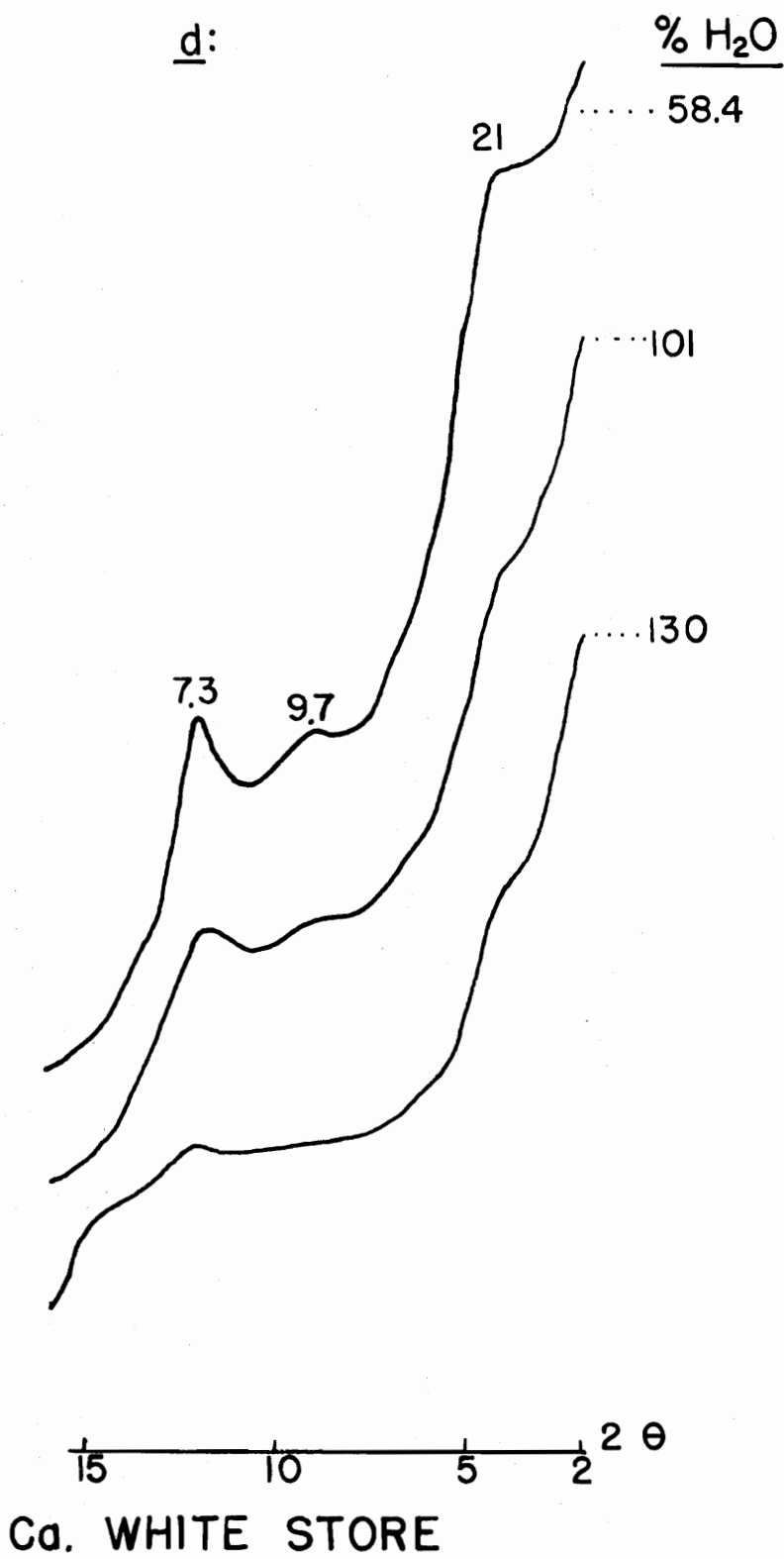
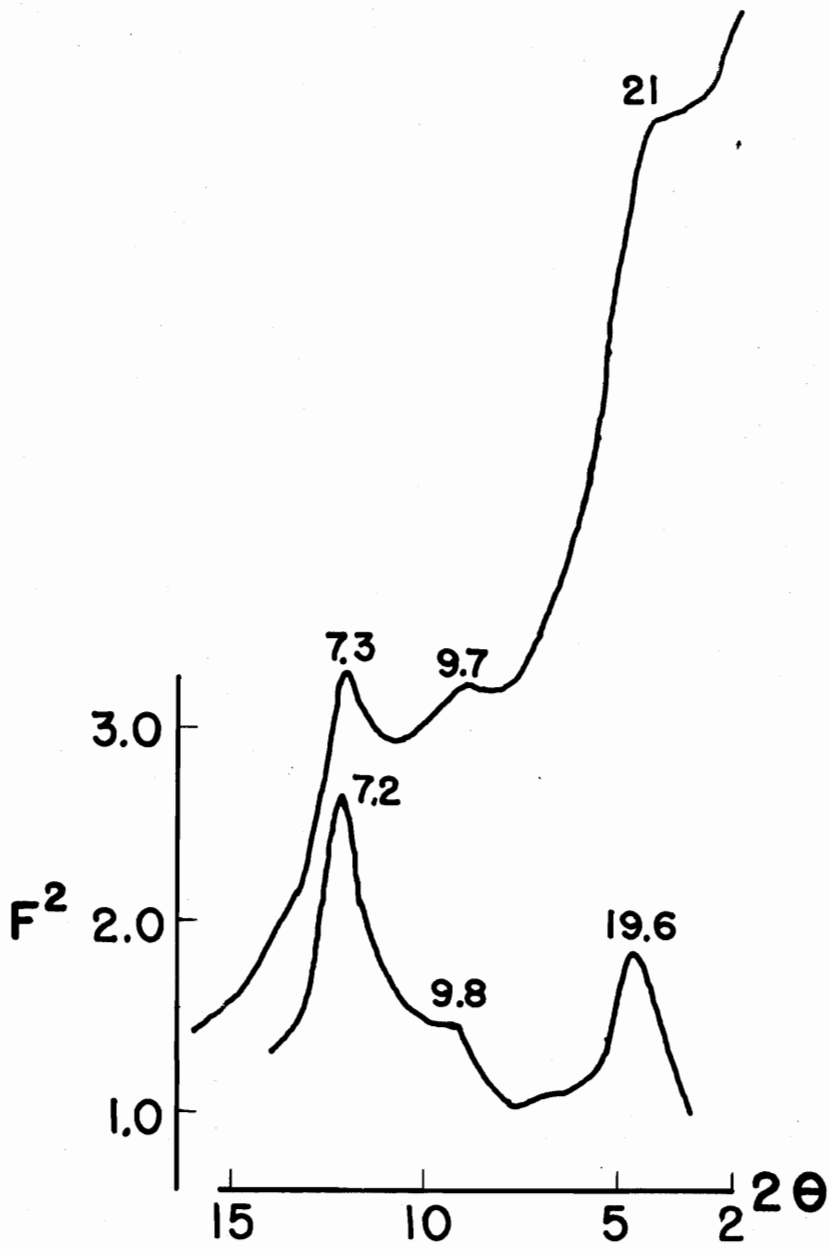


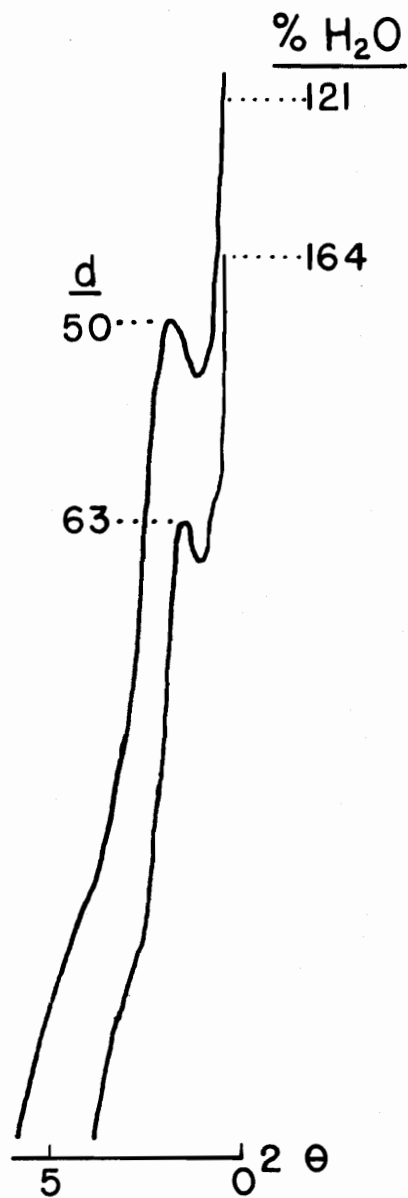


Figure 10--Calcium-White Store; smoothed X-ray diffraction pattern, before and after correction for Lorentz and polarization factor.



Ca-White Store - 58.4% H<sub>2</sub>O

Figure 11—Sodium-Webster; smoothed X-ray diffraction patterns for  $< 0.08 \mu$  fraction in water systems.



Na. WEBSTER

### 9.5 Quantitative Determination of Montmorillonite:

Since expansion of Na-Wyoming bentonite was approximately a linear function of water content, it seemed logical that the mixture of a material with the bentonite, which adsorbed water at a different rate would change the rate of expansion of the bentonite.

Several series of mixtures of Na-Wyoming bentonite and Georgia kaolinite were prepared, as outlined in the methods section, with each individual series having a fixed water content.

It was found that as the ratio of Wyoming bentonite to Georgia kaolinite decreased (moisture held constant), the measured d-spacing of the montmorillonite increased. The increase, however, was not linear, but rather appeared to be a hyperbolic function, with the individual curves being related, but not parallel.

Since the curve was hyperbolic in nature, the d-spacing quickly became quite large as the percent kaolinite was increased. It therefore appeared advantageous to use lower moisture levels to reduce the d-spacing. However, the previous study with pure Na-Wyoming bentonite showed that approximately linear expansion could only be expected at moistures greater than

150 percent. The initial series of mixtures were therefore run at moisture levels slightly above this (150 to 170 % H<sub>2</sub>O).

Excellent low angle peaks were obtained when the montmorillonite content was greater than 70 percent. As the montmorillonite content decreased below this the d-spacing increased quite rapidly with subsequent loss of intensity and resolution. Due to the masking effect of the kaolinite no peak greater than 75 Å (60 percent montmorillonite) was recorded for these series.

This restriction was partially overcome by substantially reducing the water content of those mixtures high in kaolinite. This was considered permissible since kaolinite imbibes much less water than montmorillonite, the excess water then being taken up by the montmorillonite, allowing it to expand in its near linear fashion. This technique permitted measurements to be taken for montmorillonite contents as low as 40 percent. No montmorillonite contents less than this were detected due to the complete masking of the montmorillonite by the kaolinite.

The regular expansion of the mixtures suggested the possibility of a mathematical expression to describe the family of curves. A theoretical approach was attempted

using the previously derived relation,

$$d = 10 + \frac{\% \text{ H}_2\text{O}}{4} . \quad (1)$$

By assuming that the kaolinite was constantly at liquid limit in the moisture ranges used, the following equation for the expansion of the montmorillonite was derived:

$$d = 10 + 25 \left[ \frac{\text{gm H}_2\text{O} - (\text{L.L.})(\text{gm K})}{\text{gm M}} \right] \quad (6)$$

where (gm H<sub>2</sub>O) equals total water in the system, i.e. removable at 110° C; (L.L.) equals liquid limit in grams water per gram kaolinite; (gm K) equals total kaolinite in the system; and (gm M) equals total montmorillonite. The liquid limit for kaolinite was determined by the Atterberg test, and was found to be 0.50 gm water per gm kaolinite. The expanded d-spacing, according to equation (6), is then a linear function of the moisture content for any constant ratio of kaolinite to montmorillonite.

The validity of this theoretical expansion equation was checked by comparing statistically the actual d-values obtained in the various bentonite:kaolinite mixtures with their respective theoretical values. The values used in the analysis appear in Table 2. Using methods of Snedecor (1955), the t-test showed  $t = 0.42$ , a very low value which

indicated that the correlation between actual spacings and calculated values is not significantly different from one. The linear regression gave an intercept of 3.02 which is well within the variance of the mean, 6.47. Therefore, the intercept is not significantly different from zero.

A nomograph based on equation (6) has been prepared (Figure 12) for the quantitative determination of montmorillonite in a montmorillonite-kaolinite system. Theoretically it now becomes possible to determine the amount of montmorillonite in a sample by merely measuring the d-spacing and the percent water. The percent montmorillonite is read directly from the nomograph.

This was attempted with the Webster soil clay. Substituting the %  $H_2O$  and d-spacings of Figure 11 into the nomograph, the amount of montmorillonite was quantitatively determined at 64 and 67 percent for the 50 and 63 Å peaks respectively.

The method needs further verification and it needs to be compared with other quantitative methods for determination of montmorillonite. Another factor which needs to be evaluated is the expansion curve of the montmorillonite when mixed with clay minerals other than kaolinite. Also to be considered, is the fact that the method



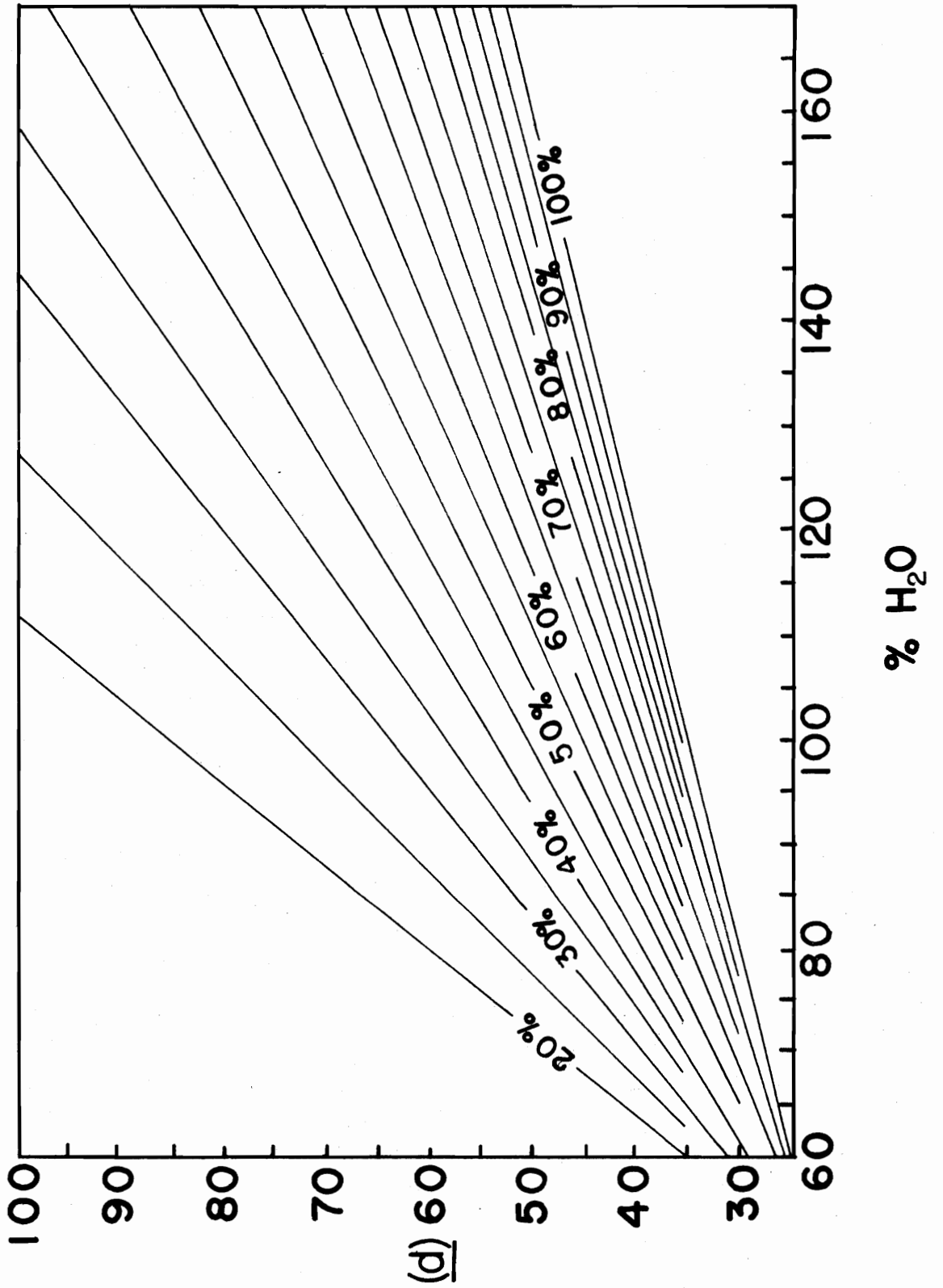
apparently will not work in all cases: first, the clay fraction must be high in montmorillonite, and second, the clay must expand regularly enough at high water contents to produce a fairly sharp X-ray diffraction peak. Only one of the four soil clays listed in section 9.4 expanded in such a regular manner.

Since Na-Wyoming bentonite expands in at least a partially discontinuous manner, it is possible that soil clays do also. Using a Li-system should eliminate this possible error. However, since certain Li-vermiculites have been shown by Brown (1961) to expand freely in a water system, these vermiculites would then be classified as montmorillonites by this method. Possibly certain organic compounds which expand either montmorillonite or vermiculite in a regular manner can be used. By proper selection of organic compounds it may be possible to quantitatively determine the separate amounts of montmorillonite and vermiculite when these two clay minerals are found mixed together.

**Table 2—Theoretical and actual d-spacings of the Na-  
Wyoming bentonite, Georgia kaolinite mixtures in  
water systems.**

% Montmorillonite	% H <sub>2</sub> O	d-spacing	
		Theoretical	Actual
50	127.2	61.1	63.0
75	160.0	59.2	59.0
81	159.3	56.1	55.0
88	160.9	54.2	50.5
90	164.5	54.1	50.5
94	150.5	49.3	49.0
97	154.1	49.4	44.0
95	171.2	54.4	51.9
90	168.7	55.5	55.2
80	168.1	59.4	58.8
70	155.0	60.0	63.0
90	132.6	45.4	46.4
80	136.9	49.7	49.0
70	134.7	52.8	55.0
60	129.8	55.8	61.0
50	132.1	63.6	68.0
40	66.7	33.7	40.1

**Figure 12—Nomograph for determination of percent montmorillonite in a montmorillonite-kaolinite mixture using d-spacing (A) and percent water of the sample.**



## X. GENERAL DISCUSSION

The swelling properties of three layer clays in water systems are strongly controlled by the particular saturating cation present. Calcium-, Lithium-, and Sodium-Wyoming bentonites, the three reference clays used in this study, reacted quite differently at similar moisture levels.

Lithium-Wyoming bentonite expanded in a linear, osmotic fashion at water contents greater than 35 percent; expansion proceeded in increments at moistures less than this. Sodium-Wyoming bentonite expanded in a definite layered manner to about 110 percent water, and showed evidence of continued step-wise expansion in the osmotic water region. A definite discontinuity in the continuous expansion pattern existed between the d-spacings of 19.2 and about 35 Å, which was similar to that reported by Norrish (1954a), and Foster *et al.* (1955). Additional and refined work will be needed to conclusively prove the existence of discontinuous expansion in the osmotic water region. Calcium-Wyoming bentonite expanded in a step-wise manner with increasing water contents to a maximum d-spacing of 19.6 Å at ~45 percent water.

Each point on the expansion curves of the three Wyoming bentonites represents the equilibrium state between the forces of attraction and expansion.

Not too much is known as yet about the attractive forces which hold these hydrated clay plates together. Work on this is needed to help explain swelling phenomena. At the present time the attractive force is generally attributed to a Coulombic interaction between the adsorbed interlayer cation and the adjacent clay surfaces.

Factors which may affect this force are: valence and size of the cation, degree of hydration of the cation, location of the exchangeable cation with respect to the interlayer surfaces in the hydrated system, amount and location of isomorphous substitution, and dielectric constant of the interlayer water.

At low moistures the forces of expansion are thought to be a combination of the hydration of the interlayer cation and the H-bonding of the interlamellar water to the exposed oxygens of the silicate layer. The relative importance of either force is dependent on the saturating cation and water content of the clay.

The calcium ion is known to have a high hydration energy, therefore the first water on Ca-Wyoming bentonite is thought to hydrate the cation. Additional water is then

H-bonded to the clay lattice. The hydration energies of  $\text{Li}^+$  and  $\text{Na}^+$  are weaker than that for  $\text{Ca}^{++}$ , therefore the hydrating forces of H-bonding are relatively more significant with Li- and Na-Wyoming bentonite than they are with Ca-Wyoming bentonite. Any difference in hydrating energy between Li and Na must be attributed to their sizes since they are similar in other properties. Lithium with its single charge concentrated over a smaller area is thought to hydrate more than sodium.

Once the  $\text{Li}^+$  has hydrated, however, the positive charge associated with the cation becomes distributed to the hydrating water molecules. The net result is that the hydrated  $\text{Li}^+$  is effectively a larger molecule than the  $\text{Na}^+$ . The effective size of the interlayer monovalent cation is thought to be the major factor controlling the initial ability of the clay to expand into the osmotic region.

The layered effect at the lower moistures is due to the physical size and arrangement of the water molecules, either as they exist in a stable configuration surrounding the interlayer cation or in the build-up of the H-bonded water layers (Hendricks and Jefferson, 1938, and Hendricks et al., 1940). Each layer represents an equilibrium point in the expansion of the clay lattice.



The interlayer hydrating force at the higher water contents is thought to be predominantly osmotic in nature (Norrish, 1954a). Osmotic forces may be present at all levels of hydration, but since these forces are weak, they are not considered to be important at the lower moistures where the forces of cation hydration and H-bonding are relatively stronger.

Two mechanisms are thought to be responsible for the osmotic force: (1) the concentration gradient of the diffuse double layer as stated by Wiklander (1955), and (2) an aligning of the water dipoles in the interlayer electrostatic field.

Wiklander states that the overall concentration of ions decreases from the charged particle surface outward. This concentration gradient results in an osmotic pressure between the internal and external solution. He believes that at equilibrium the osmotic pressure is equal to the electrostatic attraction between the clay surfaces and the counter ions.

The aligning of the water dipoles in the interlayer electrostatic field would reduce the degrees of freedom of the vibrating water molecule thereby allowing the external surface water to enter interstitially and be held.

Mathieson (1958), using X-ray procedures in studies with Mg-vermiculite concluded that the interlamellar water molecules were either arranged in a distorted hexagonal configuration or they were vibrating asymmetrically. An aligning of the water dipoles as proposed here would also result in asymmetric vibrations. Additional work is planned to further clarify and determine the relative importance of these hydrating mechanisms.

If the osmotic forces are greater than the electrostatic forces the clay will continue to expand with increasing water content. The electrostatic forces are apparently so great in the divalent Ca-Wyoming bentonite system that continuous osmotic expansion cannot occur.

With  $\text{Li}^+$  and  $\text{Na}^+$  these attractive forces are weaker and the clay layers expand into the osmotic region. The reason that the Li-Wyoming bentonite freely expanded into the osmotic region while the Na-system gave the discontinuity between 19.2 and 35 Å spacings is thought to be due to the greater Coulomb attractive forces in the Na-system. It is reasoned that the smaller  $\text{Li}^+$  cation hydrates more than the  $\text{Na}^+$ ; therefore, its charge is effectively dispersed over a greater area, resulting in a lower attractive force.

It is thought that the external plates of the packets in the Na-Wyoming bentonite system are the first to expand from 19.2 to 35 Å since these should have the lowest effective charge density. The 35 Å spacing represents a meta-stable condition, since X-ray data show that the plates do not expand beyond 35 Å until all the 19.2 Å spacings have expanded. The fact that this meta-stable 35 Å spacing exists, suggests that even at water contents and d-spacings normally attributed to osmotic swelling, certain stable spacings may be allowed.

There should be a maximum charge density for three-layer clays beyond which osmotic swelling will not occur. This, however, would also depend on the saturating cation. Alternately, with a clay of sufficiently low charge density, even  $\text{NH}_4^+$  and  $\text{K}^+$  saturations should freely expand into the osmotic region.

The principles affecting swelling in Wyoming bentonite are considered to be applicable to soil clays also. Allowances, however, must be made for the heterogeneous nature of soil clays. The Ca-White Store expanded to a d-spacing quite comparable to that of Ca-Wyoming bentonite. It is not surprising that this clay did not expand into the osmotic region, since the same strong electrostatic forces are considered to exist. One would not expect the

final d-spacing to be the same with all Ca-montmorillonites since the charge density, location of charge sites, and other factors would affect the interlayer water structure.

The study of the osmotic swelling properties of Na-soil montmorillonites proved to be a difficult task. In spite of a variety of preparatory techniques only one of the four soil types expanded regularly enough to permit intensification of the diffracted X-ray beam. The explanation for the failure of the three soil montmorillonites to expand regularly probably lies in their heterogeneous nature. Osmotic forces are quite weak, therefore any irregular variation in the electrostatic binding forces between the clay plates would materially affect their hydration. Any variation in hydration is expressed in variation in d-spacing, which in turn affects the intensification of the diffracted X-ray beam.

The main factors responsible for this heterogeneous interlayer electrostatic field are thought to be the presence of interlayer Al and Fe hydroxy compounds, and an irregular placement of isomorphous substituted lattice charge sites.

The osmotic expansion of soil montmorillonites has been utilized as a means of quantitatively determining the amount of montmorillonite present. The method is

based on the assumption that the non-swelling clays in the soil clay mixture will adsorb a predictable and relatively invariant amount of surface water, whereas the montmorillonite continues to expand in a regular and continuous manner as water content increases.

XI. LITERATURE CITED

Anderson, D. M. and Low, P. F. Density of water adsorbed on Wyoming bentonite. *Nature* 180, 1194 (1957).

Aylmore, L. A. G., and Quirk, J. P. Swelling of clay-water systems. *Nature* 183, 1752 (1959).

Barshad, I. The effect of the interlayer cations on the expansion of the mica type of crystal lattice. *Am. Miner.* 35, 225 (1950).

Barshad, I. Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances. *Soil Sci. Soc. Am. Proc.* 16, 176 (1952).

Bernal, J. D., and Fowler, R. H. A theory of water in ionic solution with particular reference to hydrogen and hydroxyl ions. *J. Chem. Phys.* 1, 515 (1933).

Blackmore, A. V., and Miller, R. D. Tactoid size and osmotic swelling in calcium montmorillonite. *Soil Sci. Soc. Am. Proc.* 25, 169 (1961).

Blackmore, A. V., and Warkentin, B. P. Swelling of calcium montmorillonite. *Nature* 186, 823 (1960).

Bolt, G. H., and Miller, R. D. Compression studies of illite suspensions. *Soil Sci. Soc. Am. Proc.* 19, 285 (1955).

Brindley, G. W. Ed. X-ray Identification and Crystal Structures of Clay Minerals. The Mineralogical Society: London, Clay Minerals Group, (1951).

Brown, G. Ed. The X-ray Identification and Crystal Structures of Clay Minerals. Chap. VII, p. 320, (1961).

Cownie, A., and Palmer, L. S. *Proc. Phys. Soc.* B65, 295 (1952).

Dyal, R. S. and Hendricks, S. B. Total surface of clays in polar liquids as a characteristic index. *Soil Sci.* 69, 421 (1950).

- Falconer, J. G., and Mattson, S. The laws of soil colloidal behavior: XIII. Osmotic imbibition. *Soil Sci.* 36, 317 (1933).
- Foster, W. R., Savins, J. G., and Waite, J. M. Lattice expansion and rheological behavior relationships in water-montmorillonite systems. *Proc. Third Natl. Conf. on Clays and Clay Min., Natl. Res. Council Publ.* 395, 296 (1955).
- Grim, R. E., and Kulbicki, G. Montmorillonite: High temperature reactions and classification. *Am. Miner.* 46, (1961).
- Hemwall, J. B., and Low, P. F. The hydrostatic repulsive force in clay swelling. *Soil Sci.* 82, 135 (1956).
- Hendricks, S. B. Base exchange of crystalline silicates. *Ind. and Eng. Chem., Ind. Ed.* 37, 625 (1945).
- Hendricks, S. B., and Jefferson, M. E. Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays. *Am. Miner.* 23, 863 (1938).
- Hendricks, S. B., Nelson, R. A., and Alexander, L. T. Hydration mechanism of the clay mineral montmorillonite saturated with various cations. *Am. Chem. Soc. J.* 62, 1457 (1940).
- Hofmann, J., Endell, K., and Wilm, O. Kristallstruktur und quellung von montmorillonit. *Z. Krist.* 86, 340 (1933).
- Jackson, M. L. Soil Chemical Analysis-Advanced Course. (1956).
- Jonas, E. C., and Roberson, H. E. Particle size as a factor influencing expansion of the three layer clay minerals. *Am. Miner.* 45, 828 (1960).
- Klug, H. P., and Alexander, L. E. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley and Sons, Inc. (1954).

- Low, P. F. Physical chemistry of clay-water interaction. *Adv. in Agron.* 13, 269 (1961).
- Lutz, J. F., and Kemper, W. D. Intrinsic permeability of clay as affected by clay-water interaction. *Soil Sci.* 88, 83 (1959).
- Mac Ewan, D. M. C. Adsorption by montmorillonite, and its relation to surface adsorption. *Nature* 162, 935 (1948).
- Mackenzie, R. G. Density of water sorbed on montmorillonite. *Nature* 181, 334 (1958).
- Mathieson, A. McL. Mg-vermiculite: a refinement and re-examination of the crystal structure of the 14.36 A phase. *Am. Miner.* 43, 216 (1958).
- Mathieson, A. McL., and Walker, G. F. Crystal structure of magnesium-vermiculite. *Am. Miner.* 39, 231 (1954).
- Mering, J. On the hydration of montmorillonite. *Tran. Faraday Soc.* 42, 205 (1946).
- Mooney, R. W., Keenan, A. G., and Wood, L. A. Adsorption of water vapor by montmorillonite II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction. *J. Am. Chem. Soc.* 74, 1371 (1952).
- Norrish, K. The swelling of montmorillonite. *Disc. Faraday Soc.* 18, 120 (1954a).
- Norrish, K. Manner of swelling of montmorillonite. *Nature* 173, 256 (1954b).
- Rich, C. I., and Obenshain, S. S. Chemical and clay mineral properties of a Red-Yellow Podzolic soil derived from muscovite schist. *Soil Sci. Soc. Am. Proc.* 19, 334 (1955).
- Snedecor, G. W. Statistical Methods. The Iowa State College Press (1955).
- Southern Cooperative Series Bull. 61, 135-146 (1959).



- Tan, T. K. Proc. Fourth Int. Conf. on Soil Mech. and Foundation Eng. London, (1957).
- Theisen, A. A., and Harward, M. E. A paste method for preparation of slides for clay mineral identification by X-ray diffraction. Soil Sci. Soc. Am. Proc. 26, 90 (1962).
- Thomas, G. W., and Moody, J. E. Chemical relationships affecting the water-holding capacities of clays. Soil Sci. Soc. Am. Proc. 26, 153 (1962).
- Walker, G. F., and Milne, A. Hydration of vermiculite saturated with various cations. Fourth Inter. Cong. Soil Sci. 2, 62 (1950).
- Warkentin, B. P., Bolt, G. H., and Miller, R. D. Swelling pressure of montmorillonite. Soil Sci. Soc. Am. Proc. 21, 495 (1957).
- White, W. A. Water sorption properties of homoionic montmorillonite. Proc. Third Natl. Conf. on Clays and Clay Min., Natl. Res. Council Publ. 395, 186 (1955).
- Wiklander, L. Cation and anion exchange phenomena. In Bear, F. E., Ed. Chemistry of the Soil, Reinhold Pub. Corp. (1955).

## XII. VITA

Dwayne Harold Fink was born in Albert Lea, Minnesota, June 15, 1932, the son of Harold and Dora Fink. His youth was mainly occupied in learning the arts of farming and in attending District 69 - a country elementary school. He attended high school at Albert Lea, Minnesota.

This was followed by two years in the army, including one year in Korea. After discharge the writer accepted a job with Consolidated Breeders Cooperative of Anoka, Minnesota and was in their employ for two years.

He enrolled at the University of Minnesota in 1955 and received his Bachelor of Science in Soils in June of 1960. While at the University of Minnesota he was a member of the Delta Theta Sigma professional fraternity.

He accepted a National Defense Fellowship from Virginia Polytechnic Institute in 1960 to continue his studies in the field of agronomy.

He is married to the former Edna Dewey of Blairstown, Iowa and has one daughter, Laura Renee Fink.

*Dwayne Fink*

## ABSTRACT

Swelling properties of montmorillonites in water systems were studied using X-ray diffraction techniques. Calcium, Lithium, and Sodium-Wyoming bentonites served as reference clays. Soil clays relatively high in montmorillonite then were examined and compared to the reference material.

Lithium-Wyoming bentonite expanded in a continuous, linear fashion at water contents greater than 35 percent; expansion was step-wise at moistures less than this. Sodium-Wyoming bentonite expanded in a definite layered manner to about 110 percent water ( $\sim 35 \text{ \AA}$ ), and showed some evidence of continued step-wise expansion to beyond 300 percent water. Calcium-Wyoming bentonite expanded in a step-wise manner with increasing water contents to a maximum d-spacing of 19.6  $\text{\AA}$ .

The montmorillonites of Ca-saturated soil clays expanded, with increasing water contents, to a maximum d-spacing comparable to that obtained with Ca-Wyoming bentonite. Only one of four Na-soil montmorillonites examined, expanded regularly enough with increasing water content to give X-ray diffraction peaks in the osmotic region.

The osmotic expansion of soil montmorillonites has been utilized as a quantitative means of determining the amount of montmorillonite present. The method is based on the assumption that the non-swelling clays in the soil-clay mixture will adsorb a predictable and relatively invariant amount of surface water, while the montmorillonite continues to adsorb water, and expand.