SOME MINERALOGICAL AND PHYSICAL INTERPRETATIONS OF THE FREE-SWELLING CHARACTERISTICS OF MONTMORILLONITE-WATER SYSTEMS

by

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VI Introduction

The ability of a soil to retain water against the force of gravity, and subsequently release it to plants is one of earth's most important natural processes - indeed, practically all terrestial life is dependent on it. It is only natural, therefore, that an understanding of this phenomenon has intrigued man. This thesis relates to the ability of soils to retain water. The subject has been restricted to that soil-water interaction which results in swelling of the soil complex as water is continuously imbibed interstitially, and more specifically——between the individual sheets of the expansible clay mineral, montmorillonite.

In order for a clay to imbibe water interstitially it must possess certain mineralogical properties. The clay must be of the 2:1 type, i.e. each individual sheet possesses one octahedrally coordinated layer sandwiched between two tetrahedrally coordinated layers. Normally the tetrahedral layers are composed of silicon, coordinated with oxygen, whereas the octahedral layers normally are composed of either Al or Mg coordinated with hydroxy (OH) and oxygen. Each individual sheet thus presents, externally, two planar oxygen surfaces. These sheets are stacked one on top of another to form "books or packets" of varying thickness. The interstitial or internal surface area corresponds to that planar oxygen surface which is internal to the packet, while the external area corresponds to those planar surfaces external to the packet, plus the exposed edge area.

In order for the packet to adsorb water interstitially and swell, there must be an adequate interlayer charge density. This charge density results from an imbalance of lattice charges caused by isomorphous substitution of cations in the tetrahedral or octahedral layers, e.g. Al^{3+} for Si^{4+} in the tetrahedral layers, or Mg^{2+} for Al^{3+} in the octahedral layer. This substitution results in a net negative charge on the sheet concerned. Charge neutrality, however, is maintained by the presence of sufficient interlayer cations.

Provided certain other conditions are met, this packet may then imbibe water interstitially and swell. Three types of clay-water associations have been described to account for this swelling. These are: hydration of the interlayer cations, hydration of the exposed clay surfaces, and osmosis of water.

The hydration characteristics of the various cation species differ tremendously. These differences express themselves in a variation of the energy of hydration -

thus in the amount of water associated with this hydration and finally in the physical extent of the swelling.

The hydration of the clay surfaces is thought to be mainly a hydrogen-bonding effect between the polar water molecules and the negatively charged exposed oxygen surfaces. The hydration forces of the interlayer cation and of the clay surfaces are both short range forces. Thus, these hydrating mechanisms limit the amount of adsorbed interstitial water to only several layers of water - one to three normally, depending mainly on the interlayer cation and the charge density of the clay.

The third type of water associated with clay swelling is osmotic water; it is this water which is responsible for continuously expanding ("free-swelling") clay lattices. The osmotic force results from an activity gradient between the external and internal water, which is thought to be caused by the presence and distribution of the interlayer cations with respect to the planar surfaces. These phenomena seem to conform closely to the double layer theory of ion distribution next to a charged surface. The experimentation in this study has been limited to this "free-swelling" phenomena in pure montmorillonites and in soil montmorillonites, of mixed systems.

The study consists of two separate phases. In phase I, differential swelling properties of several montmorillonites in water systems were compared, and related first to the type of cation on the exchange complex and second to certain specific mineralogical factors of the individual clays. In phase II, the theory of expansion of the swelling 2:1 type clay was developed in detail. The theory, with certain assumptions, indicated that swelling data could be used to determine quantitatively the internal surface areas of the expansible clays, the amount of externally associated water, and the amount of expansible clay present in both pure and mixed systems. The theory was then tested, using several well defined montmorillonites, as well as several soil clays known to be high in montmorillonite.

VII Literature review

A. Swelling of clay-water systems

The phenomenon of swelling and shrinking of soils has probably been observed by man ever since he first tilled the soil. Knowledge of the causal factors, however, is relatively recent. Hofmann et al. (1933) were the first to show that montmorillonite expanded in the c-dimension by adsorbing water interstitially. That same year Falconer and Mattson (1933) studied the osmotic imbibition of water by clays, along with some of the moderating factors. The intriguing and practical aspects of swelling phenomena have served to stimulate much work on the subject.

One facet of this research has been an attempt to establish the hydration mechanisms. Hendricks and Jefferson (1938) postulated that the water was hydrogen-bonded to the planar oxygens of the layer silicate minerals. Conformation of the water molecules to the hexagonally arranged planar oxygens of the silicate sheets resulted in a similar hexagonal, ice-like structure for the bound water. They envisioned that additional layers of water could then be hydrogen-bonded to the first water layers.

Hendricks et al. (1940) found that hydration of the interstitial cations of clays provided a second hydrating mechanism. They concluded that if the interlayer cations were Mg^{2+} ions or ions of one of the other alkaline earths, the first water adsorbed by the system, hydrated the cations with up to six water molecules each. Additional layers of water, if present, were thought to be H-bonded to the clay. The alkali metals, Na^+, K^+ and Cs^+ were not observed to hydrate: Li^+, however, did hydrate, but not as extensively as the alkaline earths.

Thus, the hydrating forces attributable to the surface oxygens and to the interlayer cations appear to complement each other. Additional evidence for this assumption was provided by Mathieson and Walker (1954). In work with Mg-vermiculite, they pictured the hydrated cation to be in a midway position between the clay plates with one layer of water on each side of it. The distorted hexagonal arrangement of the surface oxygen network was found to exert a distorting effect on the octahedrally coordinated hydration shell of the Mg^{2+}.

This swelling of the clay plates was observed to occur in distinct steps with characteristic d-spacings, which were dependent on the saturating cation and degree of hydration. Merling (1946), for example, found that Ca-montmorillonite expanded step-wise, with increasing vapor pressure, one water layer at a time, up to a maximum of four complete water layers; each layer increased the d-spacing about 3A. Mooney et al. (1952) also noted this step-wise expansion with mono- and di-valent homoionic montmorillonites. They also noted, in a companion experiment, that inflections in the heats of desorption curves of these clays corresponded to the transitions of adsorption of additional water layers. When polyvalent cations saturate montmorillonite clay, spacings of about 20A are the maximum obtainable (Blackmore and Warkentin, 1960). Foster and coworkers (1955) found Li-montmorillonite expanded step-wise up to about 20A, but then continued to expand, linearly, with increasing water contents. Na-bentonite reacted similarly up to 19.2A, but then exhibited a jump in spacing to about 30A. Norrish (1954) reported similar results.

Interlayer swelling changes to an osmotic imbibition when the clay plates begin to swell in a continuous or "free-swelling" manner with increasing water uptake. Both Norrish (1954) and Foster et al. (1955) studied the nature of this expansion by means of X-ray diffraction. They found that, at the higher water contents, montmorillonite saturated with the monovalent cations Li^+, Na^+, H^+, and in certain situations K^+, NH_4^+ and Cs^+, expanded continuously and linearly with increasing water content. The restriction placed on the K-, NH_4- and Cs-montmorillonite systems is that the clay must first be expanded into the osmotic region with Na- or Li-saturated montmorillonite, then be converted to a K-, NH_4^- or Cs-system by washing with dilute solutions of the appropriate salts. If the montmorillonite plates, in the process, are allowed to contract into the region of layered expansion, then they can not be reexpanded into the free-swelling region.

Free-swelling in a clay-water system closely follows that predicted by the Gouy diffuse double layer theory (Bolt and Miller, 1955 and Warkentin et al., 1957). Norrish (1954) found that the double layer theory applied to that expansion beyond about 35A, and was independent of the cation, for the monovalent cations. Lutz and Kemper (1959) postulated the existence of a diffuse double layer in which the stable state represented an equilibrium state between outward diffusion forces of the cations and inward forces of electrostatic attraction.

The swelling characteristics of an expansible clay are influenced by such factors as: charge density, location of charge site, particle size, interlayer cation, concentration of salt present in system, and other factors.

MacEwan (1955), in relating expansion to charge, pointed out that pyrophylite with zero interlattice charge does not expand at all. He also pointed out that expansion appears to decrease with increase in charge in going from montmorillonite, with 2/3 charge units per unit cell, to brittle mica, with 4 charges per unit cell. He suggests, therefore, the possibility that maximum expansion occurs between zero and 2/3 charge units per unit cell.

Walker (1958) in a study of the interlayer adsorption of glycerol and ethylene glycol by montmorillonite and vermiculite found that the degree of adsorption was related to surface charge density, to the cation present and to the crystal size. Mg-vermiculites in glycerol solutions would not expand beyond 14.5A, while Mg-montmorillonites expanded to 17.7A. This technique has been used extensively to differentiate qualitatively between vermiculite and montmorillonite in mixed clay systems.

Micas with a charge density of 2 to 4 negative cites per unit cell normally would not be expected to swell interstitially. However, White (1956) found that after treating a muscovite with molten $LiNO_3$, he was able to expand it with glycerol to 17.8A. It was postulated that the small Li^+ ions diffused into the vacant octahedral positions of the muscovite, thus lowering the charge density, and consequently permitting expansion with glycerol. Weiss et al. (1956) found that it was even possible to get limited innercrystalline swelling of micas by treating them with certain alkyl-ammonium ions. The alkyl-ammonium ions exchanged quantitatively with the interlayer potassium ions, expanding the lattices in the process.

Another measure of the restrictive nature of increasing charge density on swelling is the differential free-swelling properties of Na^+ and Li^+ saturated montmorillonites and vermiculites. Na- and Li-montmorillonites have been shown (Norrish, 1954 and Foster et al. 1955) to expand freely in water. Na-vermiculite, however, does not expand freely in water, whereas certain Li-vermiculites do (Walker and Milne, 1950), (Norrish and Rausell-Colom, 1963, Garrett and Walker, 1962).

The magnitude of the "jump-spacing" or discontinuity which separates the swelling due to hydration of the cations and surfaces from the osmotic swelling, has been found to be dependent on charge density. Norrish and Rausell-Colom (1963) for example, found that in dilute salt solutions the discontinuity for Li-montmorillonite was from 20 to 40A, whereas for Li-vermiculite it was 15 to 82A - much larger.

The location of the charge in the clay lattice affects swelling. Marshall (1936) stated that the degree of cation dissociation, which directly relates to swelling, should be greater for a montmorillonite (octahedral charge) than for a beidellite (tetrahedral charge). Foster (1954), however, reported an inverse relationship between swelling and octahedral substitution. She also found an inverse relationship between extent of swelling and the polarizability of the lattice cations.

Particle size is thought to influence swelling. Jonas and Roberson (1960) postulated that decreasing the particle size should facilitate expansion. Garrett and Walker (1962) found this to be true for Li-vermiculite, but also found the reverse relationship for butylammonium-vermiculite.

Increasing the salt concentration of the ambient solution has been shown to decrease swelling. Norrish (1954) and Foster et al. (1955) found that the decrease in d-spacing in the osmotic swelling region was inversely proportional to the square root of the salt concentration.

The dielectric constant and dipole moment of the liquid phase affect swelling. Barshad (1952) used various organic compounds to study the relative importance of these two properties on swelling properties. He concluded that the dielectric constant has a greater effect on expansion than does the dipole moment.

It is highly probable that there is an unequal distribution of the water over the various types of clay surfaces present in a clay-water system. This distribution is dependent on the total water in the system and on the magnitude and range of the various hydrating forces involved.

Marshall (1958) discusses the effect of the curvature of the hydrated surfaces on the vapor pressure of the water films. Theoretically, when equally hydrated, a convex surface should have a lower vapor pressure than a concave surface. Since in equilibrium a system can't have two vapor pressures, it follows that the two surface types will be unequally hydrated - the convex surfaces having a thinner water film than the concave or the flat surfaces.

The energy of hydration of the various surfaces differs. Fripiat (1964) points out that the hydration of hydroxyl surfaces is less active than the hydration of oxygen surfaces. The 1:1 type clays, with one layer of exposed hydroxyls and one of exposed oxygens would thus be expected to have a smaller hydration shell than the 2:1 type clays with two exposed oxygen layers. Jurinak (1963) expressed a similar belief that during the adsorption process an increase in the polarity of the adsorbate is manifested in an increase in the sensitivity of the adsorbate to the structure of the adsorbing surface. He found that the formation of water multilayers was influenced by the nature of the adsorbing surface. Fripiat (1964) also noted that cations, which were associated with clays without internal surfaces, dehydrated at a much lower temperature than those in internal positions.

Hemwall and Low (1956) treated the external surfaces of montmorillonite with silane to make them hydrophobic. They found that this treatment only reduced the swelling pressure at low pressures, thus indicating that interparticle swelling is of small magnitude compared to interlayer swelling. Similar results in the swelling pressure relationships between Na- versus Th-treated montmorillonite led to the same conclusion.

Experimental evidence thus shows that the various types of clay surface do vary in their hydrating ability, and strongly suggests that external surfaces hydrate less than internal surfaces in a free-swelling system. Of course where interlameller swelling is prevented or restricted to only several layers, any additional water added to the system must of necessity hydrate external surfaces. The energy of this additional water, however, is very close to that of free water.

Strong evidence that external surfaces initially adsorb several water layers at low water contents, then remain at a relatively constant state of hydration as additional water is imbibed interstitially in a free-swelling situation, is provided if the d-spacing increases linearly with increasing water content. Both Norrish (1954) and Foster et al. (1955) found that the d-spacing in the Na- and Li-montmorillonite systems did increase linearly with increasing water contents, once the cations had hydrated and had become dissociated from the clay surfaces. Hight et al. (1962) found linear expansion of a Na-Wyoming bentonite for water contents from 1.5 to 8.0 grams of water per gram of clay. The significance of this linearity in expansion is discussed in greater detail in the theory and in the discussion of Phase II of this study.

B. Surface area determination

The following section describes a number of methods used for determination of surface area, and points out their applicability and limitations in the study of soils and clay mineralogy.

An approach, which is particularly applicable to the determination of the surface area of certain layer silicate minerals, is to calculate the theoretical specific planar surface using the cell dimensions and molecular weight. Jackson (1956, p.331) shows the typical calculation procedure:

$$\text{area/g} = \frac{2\ abN}{M}$$

where a and b are the unit cell dimensions, M is the molecular weight and N is Avagadro's number; the factor 2 denotes the two planar surfaces per unit cell. The theoretical planar areas calculated in this way are very close to the total areas of the expanding, 2:1 type clay minerals, as obtained by other methods (Table 1). Theoretically the planar surface area should be equal to the total surface area minus the edge surface area, or it should also equal the internal area plus that planar area external to the individual "packets". If the diameter of the average individual "packet" is ten times its thickness, the external planar surface area will be nearly four times as great as the edge area. Therefore, since the total external area is small compared to the total area (Table 1), very little error is introduced by assuming that the total surface area is equal to the planar surface area. Of course the method is only applicable to those layer silicates which expand normal to the ab plane, e.g. montmorillonite and vermiculite. The method is not applicable to non-expanding clay minerals, nor is it applicable to mixed clay systems.

Another method for calculating the planar surface area of expanding layer silicates makes use of the density and the $d_{(001)}$-spacing of the mineral concerned. Emerson (1962) used this approach:

$$\text{area/g} = \frac{2}{\rho_0\, d_{001}}$$

where ρ_0 equals the density of the dry clay and d_{001} is the associated d-spacing. He obtained a value of 710 m^2/g for a Ca-Wyoming bentonite (Table 1) using $\rho_0 = 2.76$ and $d_{001} = 10.2A$. The method is dependent on the density of the water which was assumed to be 1.000. This may not be the case. Mackenzie (1958) has shown for example that the density of the water associated with the inter-planar cations may be much greater than one. This would give a "too-high" value to the density of the clay, and in turn, a "too-low" surface area. The value of 710 m^2/g, however, is relatively close to the theoretical planar area. Again, the method is only applicable to those layer silicates which expand interstitially.

Surface areas of clays may also be calculated from measurements of the negative adsorption of anions adjacent to the clay surfaces. Schofield (1947) derived the relation between this negative adsorption and surface area, using the basic assumptions of the Gouy diffuse double layer theory. He showed that a plot of a function of the negative adsorption versus a function of the concentration of the external, bulk solution was a straight line with slope equal to the surface area. De Haan and Bolt (1963) attempted this for a $<2\mu$, Na-Wyoming bentonite in a dilute NaCl solution, and obtained a value for the surface of 700 m^2/g. This approach for determination of surface areas has not attained general acceptance. The method lacks sensitivity, and therefore, is probably only applicable to the high surface, expanding type clays.

Harkins (1945) presents what he calls the "absolute" method for determination of surface area. The method is based on the loss of energy of a finely divided water mist as it combines into bulk water, losing surface area in the process. Theoretically one needs only to measure the heat evolved in the process, with the use of a calorimeter; then divide this by the known surface energy of water (118.5 ergs per cm^2 at 25C) to get the surface area of the mist. Harkins was not able to do this for a pure water system, but was able to coat titanium dioxide particles with thin films of water, then drop the suspended particles into a bulk water phase, all within a calorimeter. By dividing the amount of energy released by the value 118.5 ergs per cm^2, and correcting for the thickness of the water films on the particles, he arrived at a surface area for the titanium dioxide of 13.8 m^2/g. Using the BET method with nitrogen gas, the area for the same material was found to be 13.9 m^2/g, assuming an area per nitrogen molecule of 16.2A^2 (liquid state area), or 11.6 m^2/g assuming an area per nitrogen molecule of 13.6A^2 (solid state area). The method is not applicable to porous materials in which some of the water is adsorbed internally; therefore, it is doubtful if the method could be applied to clay systems; certainly swelling clays would be excluded. The method may possibly have value as a reference technique.

The most common procedures for determination of surface areas involve the quantitative adsorption of a thin surface phase onto the surface to be measured. It is possible to calculate the surface area if the amount adsorbed and the area covered per adsorbed molecule are known.

Probably the first such approach was devised by Langmuir (1918). He reasoned that an equilibrium would exist between a solid surface, a surrounding gas phase and the gas molecules adsorbed on the surface. At equilibrium, the rate of adsorption of gas molecules on the surface would equal the rate of evaporation. The rate of adsorption, at constant temperature, is proportional to the gas pressure P; the rate of evaporation is proportional to the fraction of the total surface covered, which is expressed as the ratio of the volume of gas adsorbed to that volume needed for a monolayer. Two assumptions are requisite: (1) the interaction between neighboring admolecules is negligible, and (2) condensation of the gas phase will only occur on bare surface sites. These restrictions limit the Langmuir equation to chemisorption of a single monolayer. The final form of the Langmuir equation is:

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{bV_m}$$

where P is the gas pressure, V is the volume of gas adsorbed, V_m is that volume needed for monolayer coverage, and b is a constant term which relates to the energy of adsorption of the adsorbed molecules and their kinetic energy in the gas state.

If these assumptions are met, a plot of P/V versus P should give a straight line with slope equal to $1/V_m$ and intercept equal to $\frac{1}{bV_m}$. If the area per molecule is known, then the area at monolayer coverage can be computed.

Attempts have been made to apply Langmuir's adsorption isotherm to soils. Chao and Kroontje (1960) tried to relate ammonia adsorption on natural soils to the equation. Ammonium concentration in a water solution was substituted in the equation for pressure, and cation exchange parameters for volume. The results were inconclusive. Later, Du Plessis (1962), following the same general procedures as Chao and Kroontje, did find that homoionic Al-clays followed Langmuir's equation with respect to ammonia retention. The resulting slopes of the curves were equal to the cation exchange capacities of the clays. However, to use this approach to determine surface area, one still would need to know the surface charge density of the clay.

It was recognized, however, that adsorption from a gas phase often involved formation of multilayers, rather than a monolayer. Also, the admolecules were often found to be held only by the relatively weak van der Waals force, in contrast to the high energy, chemical bonds characteristic of Langmuir type adsorption. Brunauer, Emmett and Teller (1938) developed the now famous BET equation to describe this physical, van der Waals adsorption on surfaces.

As with the Langmuir equation, the principle of the BET equation is based on an equilibrium condition between the adsorbed and gaseous phases. The final form of the equation is:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c} \frac{P}{P_o}$$

where P is the gas pressure, V is the volume adsorbed, V_m is that volume needed for a monolayer, and c is a constant term which relates to the energy of condensation and the kinetic energy of the gas phase.

The procedure is to plot $P/V(P_o - P)$ versus P/P_o ; V_m and c may be obtained from the slope of the adsorption isotherm and its y axis intercept. The surface area may then be obtained if the area per admolecule is known.

The BET method for determination of surface areas has obtained wide acceptance. Joy (1953) describes 56 different types of adsorption apparatus in use at that time; all were static type systems. A recent innovation is the dynamic, continuous gas flow method (Nelsen and Eggertsen, 1958). The amount of gas adsorbed was measured automatically by thermal conductivity, utilizing the changes in concentration as the gas flowed continuously through the system. Ettre and Creplinski (1963) used a commercially available gas chromatograph for this purpose.

The BET method has obtained wide acceptance for determination of surface areas of soil and clays. The earliest applications were by Emmett et al. (1938) and by Makower et al. (1937). Both groups used adsorption of enert gases on soils and soil clays. It was soon realized, however, that the non-polar molecules like nitrogen would not penetrate into the interplanar position; therefore, the BET isotherm for these gases measured only the external surface areas. Table 1 shows typical external areas of some of the common clay minerals using the BET method, and also shows that the external areas are only a small part of the total surface areas in those clays with an expanding type lattice. Table 1 also points out that large variations in external surface areas exist - both within a clay mineral type and between types. Much of this variation is due simply to differences in particle sizes and shapes. However, some of the variation is more difficult to explain. Escard (1950) found that the amount of residual water on a montmorillonite affected the adsorption of low temperature nitrogen gas. Brooks (1955) also noted this effect of residual water on nitrogen adsorption by montmorillonites and illite; he also found that the nature of the exchangeable cation affected the nitrogen adsorption. Kaolinite and pyrophyllite, with negligible cation exchange capacity and large particle size, however, showed very little relationship between specific surface as determined by nitrogen adsorption and water content of the clays.

The primary fault of applying the BET to soils when nitrogen or other inert gas is used, is that only the external surfaces are measured. In a swelling 2:1 type clay, this is only a small fraction of the total surface. It was known, however, that certain polar molecules could be adsorbed interstitially. For example, Hofmann et al. (1933) found that montmorillonite expanded interstitially in a water system and both Bradley (1945) and MacEwan (1948) showed that certain polar aliphatic organic molecules were adsorbed interstitially by 2:1 type clays.

Mooney et al. (1952) used the BET equation on water vapor desorption isotherms of Wyoming bentonite (Table 1). They also determined the external area of these clays using nitrogen adsorption; the internal area is simply the difference between the two values. The major difficulty with using water vapor isotherms is that a hysteresis effect is present between the adsorption and desorption curves. Mooney et al. chose to use the desorption isotherm since it was reproducible, while the adsorption curve was not.

Puri and Murari (1964), using average values obtained from the literature, for the specific surface area of several clays, calculated the amount of water which would be necessary to cover the surfaces of these clay minerals with a monolayer. From this they determined the relative vapor pressure in equilibrium at which this much water is adsorbed. The monolayer values obtained fell within the narrow range of 0.49 to 0.55 relative vapor pressure. From this they recommended a relative vapor pressure of 0.53 to produce a monolayer on soils and clays.

The discovery by Bradley (1945) and MacEwan (1948) that certain polar organic molecules could be adsorbed interstitially in reproducible mono- or duo-layers by certain clay minerals, suggested to Dyal and Hendricks (1950) that the total surface areas of these clays could be determined by simply weighing the amount of the organic compound adsorbed. This approach requires that coverage be uniformly controlled at mono- or duo-layer coverage, and that the area covered per admolecule be known. Dyal and Hendricks used ethylene glycol as the organic molecule, and assigned a value of 3.1×10^{-4}g glycol per m^2 of surface to calculate surface areas. External area was determined by either using the BET equation with adsorption of ethane (Table 1) or by irreversibly collapsing the expanding clays by heating at 600C, followed by adsorption of ethylene glycol.

The procedure has merit in that it provides a relatively simple means for determining both the external and internal areas of clays and soils. The method, however, like all others, has its shortcomings. One of the problems is obtaining strict mono- or duo-layer coverage. This is a function of the relative vapor pressure of the organic compound. The procedure is to use buffer systems to maintain the correct vapor pressure surrounding the sample. Marin and Jacobs (1964) have very successfully used a buffer prepared by adding just enough glycol to a bulk sample of Wyoming bentonite to give it mono-layer coverage.

The method is sensitive to the type cation on the exchange site. Bower and Gschwend (1952) found that the amount of glycol adsorbed on Wyoming bentonite varied from 261 mg/g for Ca-saturation down to 117 mg/g for K-saturation. Assuming Dyal and Hendrick's value of $3.1 \times 10^{-4} g/m^2$ for glycol coverage, the areas measured wouldbe, respectively, 842 and 376 m^2/g.

McNeal (1964) also found this variation in glycol retention as a function of the exchangeable cation; Ca- and Al-clays retained considerably more glycol than did the comparable Na- and K-clays. He found that he could explain the difference between the amount adsorbed by Ca-clays over that adsorbed by Na-clays by assigning two glycol molecules per Ca^{2+} ion, irrespective of clay type or soil used. On this basis he suggested that Na^{+} is probably the best exchangeable ion to use when determining the surface area by adsorption of polar molecules. Table 1, however, shows that his value for the surface area of Na-Wyoming bentonite (622 m^2/g) is considerably lower than most other reported values, including the theoretical area.

A problem, which is sometimes encountered when using adsorption of organic molecules to determine external surface areas, is that some of the clays are not irreversibly collapsed during the heat treatment at 600C (Bower and Gschwend, 1952, and Diamond and Kinter, 1958). To overcome this difficulty, Kinter and Diamond (1960) proposed saturating the clays with triethylammonium. This treatment was found to completely prevent the entrance of glycerol between the unit layers, and confined the sorption to the external surfaces.

As previously pointed out, determination of surface areas based on quantitative surface adsorption measurements, relies on using the correct area coverage per unit molecule. This may provide an extremely large source of error. Diamond and Kinter (1958) suggested that Dyal and Hendrick's

(1950) value for area per molecule for adsorbed glycol ($33A^2$) was too high, and that a value of $23A^2$, which is based on the liquid density of glycol and 3.9A as the thickness of the mono-layer, would be a better value. The difference between $33A^2$ and $23A^2$ is very large - nearly 30 percent, in fact. Diamond and Kinter (1958) in work with glycerol adsorption, used this approach of assuming the admolecules had a density equal to that in the liquid state, and that the thickness of the monolayer was equal to the d-spacing minus the unit layer spacing. This approach is also subject to criticism: (1) the density of adsorbed molecules probably is different from that in the liquid state, (2) the authors used a value of 9.6A for the unit layer spacing - MacEwan (1948) suggests that 9.4A is the correct value.

Certainly the art of determining surface areas of clay minerals has been advanced by the unique utilizations of the various techniques available. However, in spite of this, no absolute approach can yet be accepted, since marked and unexplained differences exist in the values obtained.

Table 1—Comparison of some published values for the surface areas of several clay minerals.

Clay mineral	Ref.*	Method**		Area		
				External	Internal	Total
				m^2/g		
Li-Wyoming bentonite	1	cell parameters	a			757
Na-Wyoming bentonite	1	cell parameters	b			746
Na-Wyoming bentonite	2	BET: H_2O & N_2	b	33	814	847
H- Wyoming bentonite	2	BET: H_2O & N_2	b	40	720	760
Ca-Wyoming bentonite	3	density & d(001)	c	38	672	710
Na-Wyoming bentonite	4	anion repulsion	d			700
H- Wyoming bentonite	5	glycol adsorption	e	44	772	816
H- Wyoming bentonite	6	glycol adsorp.	f	72	732	804
natural W. bentonite	7	glycol adsorp.	g			806
Na-Wyoming bentonite	8	glycol adsorp.	h			622
Ca-Wyoming bentonite	8	glycol adsorp.	h			861
Wyoming bentonite	9	glycerol adsorp.	i	50	570	620
S. Dakota bentonite	10	BET: N_2	j	19		
Na-Wyoming bentonite	11	BET: N_2	k	9 & 33		
Ca-Wyoming bentonite	11	BET: N_2	k	122 & 47		

Table 1, continued

Clay mineral	Ref.*	Method**		Area External	Area Internal	Area Total
				m²/g		
Li-Otay bentonite	1	cell parameters	a			762
Na-Otay bentonite	12	glycerol adsorp.	m	35	714	749
Li-nontronite	1	cell parameters	a			687
H- nontronite	13	glycol adsorp.	n			655
Na-nontronite	13	glycol adsorp.	n			619
Na-nontronite	12	glycerol adsorp.	m	25	452	477
kaolinite(Georgia)	11	BET: N_2	k			7.2 & 6.8
kaolinite	14	glycol & N_2 ads.	o			22.5 & 28.2
kaolinite(no.s 1 & 2)	9	glycerol adsorp.	i	39 & 15	10 & 0	49 & 15
kaolinite	5	glycol & ethane adsorp.	p			61 & 28
halloysite	10	BET: N_2	j,q			76 & 18
halloysite	11	BET: N_2	k			39 & 69
halloysite(no.s 1 & 2)	12	glycerol adsorp.	m			76 & 102
halloysite	5	glycol & N_2 ads.	p			64 & 44

Table 1, continued

Clay mineral	Ref.*	Method**		Area		
				External	Internal	Total
				m^2/g		
endellite	12	glycerol adsorp.	m	27	403	430
illite	11	BET: N_2	k			67 & 82
illite	5	glycol & N_2 ads.	p			236 & 90
illite	14	glycol & N_2 ads.	o			186 & 90
illite (hydrated)	14	glycol & N_2 ads.	o			174 & 53
illite	12	glycerol adsorp.	m			91 & 76
illite	9	glycerol adsorp.	i	79	56	135
pyrophillite	11	BET: N_2	k			1.7 & 2.3
allophane	9	glycerol adsorp.	i	293		293

Table 1, continued
*: Reference

1. Planar calculations based on cell dimensions and molecular weight.
2. Mooney, R.W., Keenan, A.G. and Wood, L.A. 1952. J. Am. Chem. Soc. 74:1367-71.
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14. Quirk, J.P. 1955. Soil Sci. 80:423-430.

Table 1, continued
**: Method

a. Planar calculations based on parameters of cell dimensions and molecular weight; method gives total planar surface, but not edge surface.

b. Used BET method to determine areas: (1) low temperature nitrogen gas for external and (2) water vapor desorption for an equivalent area from which total area was calculated.

c. Based on clay density times d-spacing; method gives total planar surface, but not edge surface.

d. Used double layer theory to calculate surface area from measurements of negative adsorption.

e. Total area is based on duo-layer adsorption of ethylene glycol (EG), using value of 3.10×10^{-4} g EG per m^2; external area was obtained by BET plot of adsorption of ethane at -78C.

f. Surface area based on monolayer coverage values for EG given in article, times Dyal and Hendrick's value of 3.10×10^{-4} g EG per m^2; external area based on monolayer adsorption of EG after heating clay at 600C.

g. Surface area based on monolayer point of 260mg EG per g, clay, and Dyal and Hendricks value of 3.10×10^{-4}g EG per m^2.

h. Total surface area based on monolayer coverage values for EG given in report times Dyal and Hendricks value of 3.10×10^{-4}g EG per m^2.

i. Total area based on glycerol adsorption, assuming adsorbed density of glycerol equals liquid density; external area based on glycerol adsorption after treatment of clay with triethylammonium solutions.

j. External surface areas based on BET plots of nitrogen adsorption.

k. Values obtained after degassing at 25C and 300C respectively.

m. Areas based on glycerol adsorption; external area based on glycerol adsorption on sample, which had been irreversibly collapsed at 600C.

n. Total surface area as determined by monolayer formation of ethylene glycol.

o. Values based on ethylene glycol retention and nitrogen adsorption (BET) respectively.

p. Values based on ethylene glycol and BET plot of ethane adsorption respectively.

q. Size fractions: 2mm and $<1\mu$ respectively.

C. Quantitative evaluation of mixed clay systems

Quantitative evaluation of the components in mixed clay systems has received considerable attention, and justification of this interest is readily apparent. Most of the physical and chemical properties of soils relate directly to the proportion and kind of clay present. At any given percentage of clay, soil properties frequently can be related to the relative proportion of a particular mineral in the clay fraction. Weathering and genesis studies rely on quantitative evaluations. Product quality in commercial usage of clays is dependent on quantitative knowledge.

Fortunately the increasing awareness of the need for research in quantitative differentiation of clay mixtures has been paralleled by rapid advances in instrumentation. These advances have permitted a continuously improving confidence in the individual analysis, and, in many cases, have substantially reduced the time required for each analysis.

Unfortunately, in spite of these advances, problems in quantitative analysis of clay minerals still exist - to plague the analyst on one hand, but also to stimulate a search for still better methods.

All the quantitative methods involving X-ray diffraction, thermal (differential and thermogravimetric) analysis, and infra-red absorption spectroscopy rely on comparisons of unknowns to standards. Sources of error are many: the chemical composition of many clay mineral species varies to a marked degree; the crystallinity and particle size of these species also varies. The presence of amorphous material also adds to the difficulty of accurate quantitative analyses.

Physical separation of the particles should provide the ultimate quantitative method. Attempts have been made, but, unfortunately, this procedure has not been completely successful. McEuen (1964) separated clay particles using di-electrophoresis; the clay particles were separated according to their ability to store electrical energy. Separation was accomplished by opposing an electrical dielectrophoretic force by a mechanical centrifugal force. He found that the individual minerals separated into zones, but unfortunately there was some overlap. Kittrick (1961) attempted a density separation using thallous formate solutions. He had some success with artificially prepared mixtures, but could not adapt the method to naturally occurring mixtures.

The visual count methods might also be considered as a physical separation. The normal size range of clay particles may be covered by using both the petrographic and electron microscopes. The method, however, is extremely tedious, and is limited to certain of the more crystalline clay minerals.

Surface area, or ramifications thereof, have been shown by several workers to be useful in quantitative analysis. Dyal and Hendricks (1950) found perfect additivety for ethylene glycol sorption from 5 to 100 percent montmorillonite for unheated mixtures of H-montmorillonite and H-kaolinite. They also noted the difference in sorption between montmorillonite before and after heating to 600C. By comparing this difference to a standard montmorillonite, it was possible to obtain a measure of the montmorillonite in the sample. The major difficulties here are that (1) not all montmorillonites collapse irreversibly at 600C, and (2) vermiculite also adsorbs glycol in interlamellar position. Mehra and Jackson (1959) utilized the duo- and mono-interlayer adsorption of glycerol by montmorillonite and vermiculite respectively, to differentiate the two quantitatively.

Others have related water vapor adsorption to montmorillonite content. Johansen and Dunning (1957) suggest that a comparison of the surfade area, as obtained by water vapor adsorption to that obtained by nitrogen adsorption may serve as a means for quantitatively estimating the amount of montmorillonite in a mixed clay sample. They prepared artificial mixtures of montmorillonite and ground quartz, and found that the decrease in water adsorption was directly proportional to the amount of quartz. Keeling (1958) established a ratio of moisture adsorption (at 0.75 R.H., 25C) to ignition loss, and found the clay mineral types separated into the following distribution: kaolinites = 7 to 2, illite = 0.8, montmorillonite = 0.4. Vermiculite was not included, but undoubtedly would have confounded the results for montmorillonite.

Another common means for estimating the amount of montmorillonite in a sample is to use the cation exbhange capacity (CEC). By assuming some standard value, e.g. 1.00 me/g for pure montmorillonite, and also assigning all the CEC to montmorillonite, one can roughly estimate the montmorillonite present in a mixed sample. The errors are obvious: while kaolinite may have a negligible CEC, the CEC of vermiculite and illite is quite large - in fact that of vermiculite is greater than that of montmorillonite.

Fink and Thomas (1965) devised an X-ray technique for the quantitative determination of montmorillonite in clay mixtures. This method relies on the relative spacings of the (001) peak of montmorillonite as it "freely" expands, interstitially, in water systems. They found that the d-spacings of the montmorillonite in a sample increased hyperbolically as the proportion of non-swelling component in the mixture was increased - water held constant. They were not able to apply the technique satisfactorily to natural mixtures, but this problem has been largely overcome in this dissertation. The method, however, does not appear to be applicable to low ($<20\%$) contents of montmorillonite.

Briefly, in summary, no method yet devised will differentiate quantitatively all the common clay minerals in a single mixture. One must normally be content, at best, to obtain clay mineral analyses individually - one per technique. Even this is often inadequate.

VIII Materials and Methods

A. X-ray studies of crystalline swelling in montmorillonite - (Phase I)

1. Preparation of homoionic clay samples

a. Specimen type montmorillonites

The specimen type montmorillonites used in this phase of the study were Wyoming bentonite, Otay bentonite, hectorite and nontronite. The pertinent mineralogical data appears in Table 2.

Carbonates were removed with N sodium acetate, buffered at pH 5 (Jackson, 1956, pp. 31-58). The samples were dispersed by adding N sodium carbonate to raise the pH to 10, then fractionated to remove the $< 2\mu$ material, by repeated processes of centrifugation, decantation, and resuspension in water adjusted to pH 10 with sodium carbonate. Excess salt was removed by several passes of the clay suspensions through a Sharples Supercentrifuge. This procedure also removed the $< 0.08\mu$ clay fraction.

Cation systems employed were Li^+, Na^+, and Ca^{2+}. Sodium-clays were prepared by passing one percent clay suspensions of the resultant 0.08 to 2μ fractions through a Dowex 50 W-X8 Na-saturated resin. Lithium-clays were

Table 2—Mineralogical characteristics of specimen type montmorillonites used in the study.

Name Location	Source	Lattice charge[1]		
		IV	VI	
Wyoming bentonite Upton, Wyom.	commercial	-0.24	-0.40	dioctahedral
Otay bentonite Otay, Calif.	Albert Vanselow collection	-0.40	-0.28	dioctahedral
nontronite Garfield, Wash.	API Project 49	-1.00	+0.36	dioctahedral
hectorite Hector, Calif.	National Lead Company Mine Hector, Calif.	0.00	-0.66	trioctahedral

[1] Ross, C.S., and Hendricks, S.B. 1945. U.S. Geol. Survey Profess. Paper 205B:23-77.

prepared by passing one percent suspensions of the previously prepared Na-clays through a Li-resin column. Calcium-clays were saturated by washing the $<2\mu$ material five times with N $CaCl_2$, followed by water and then methanol washes until the clays were Cl^- free. The clays were air dried and ground to pass a 40 mesh screen.

b. Soil clays

The soil clays used in Phase I of the study were: Webster from Conger, Minnesota, Lufkin from College Station, Texas, Lake Charles from Victoria, Texas, and Iredell from Mitchells, Virginia. Based on X-ray diffractograms of Mg-saturated, glycerol solvated samples, all of the clays were known to contain fairly large amounts of montmorillonite. In addition, they all contained various amounts of non-swelling clays (e.g. kaolinite and mica) or limited-swelling clays (e.g. vermiculite).

Carbonates, organic matter, and free iron oxides were removed by the methods proposed by Jackson (1956, pp. 31-58). Carbonates were removed with N sodium acetate (buffered at pH 5), organic matter was removed with 30 percent hydrogen peroxide, and free iron oxides were removed using the sodium dithionite-citrate-bicarbonate method. The $< 2\mu$ fractions of each soil were then Na-saturated using the previously described Na-resin column. The $<0.1\mu$ fraction was removed and washed free of chloride ions by repeated methanol washes using a Servall anglehead centrifuge.

2. X-ray procedure

The essential features of the X-ray techniques employed here have already been published (Fink and Thomas, 1963). Briefly they consisted of thoroughly mixing the dry clay samples with the desired amount of water. Then, after equilibrating for one week, d-spacings were determined by X-ray diffraction. The clay samples were prepared for X-ray diffraction by smearing the clay samples on a grooved slide, 10 cm long, with special care being taken to produce a smooth clay surface, flush with the top edge of the groove. This procedure tended to orient the clay platelets at the surface normal to the c-dimension.

X-ray diffraction studies of Phase I were carried out on a General Electric X-RD 3 instrument, in which intensities were recorded logarithmically. Slit sizes employed throughout the study were: 0.4° beam, MR soller, and 0.1° detector. The radiation used was CuK_{α} (nickel filtered), generated at 35kV and 21 ma.

Relative humidity during X-ray analysis was controlled at approximately 100 percent by passing a continuous stream of water-saturated air into a 2 quart, cylindrical, cardboard ice cream container surrounding the sample. To maintain humidity control and yet minimize adsorption and scatter of the X-ray beam, slits were cut in the box, and covered with one layer of Saran Wrap.

Standard gravimetric moisture determinations of the equilibrated samples were made at the time of X-ray diffraction. The percentages reported are based on the weight of the sample dried at 110C.

B. Some applications of the free-swelling characteristics of montmorillonite - (Phase II)

1. Preparation of homoionic clay samples

a. Specimen type montmorillonites

The specimen type montmorillonites used in Phase II of the study were the same as those used in Phase I. Preparatory treatments, however, were different.

Dispersion and fractionation procedures were carried out according to methods proposed by Jackson (1956, pp. 31-58). Calcium carbonates were removed with N sodium acetate (buffered at pH 5); free iron oxides were removed using the sodium dithionite-citrate-bicarbonate method.

The samples were adjusted to pH 10 with N sodium carbonate, then fractionated to remove the < 2µ material by repeated processes of centrifugation, decantation, and resuspension in water adjusted to pH 10 with sodium carbonate. The < 2µ fraction was then passed once through a Sharples Supercentrifuge to remove most of the excess salts.

Since sodium systems were employed in all of the previous preparatory procedures, it was assumed that the montmorillonites were essentially sodium saturated at this point. However, as added insurance, suspensions of the 0.08 to 2µ fractions were passed through a Dowex 50 W-X8, Na-saturated resin.

The remaining excess salt and water were removed with an 11 cm pressure-membrane extractor[1], using a pressure of 15 atmospheres of nitrogen gas. The clay, remaining on the Visking membrane after each extraction, was resuspended in water, and the extraction process repeated until all chloride salts were removed, as detected by the $AgNO_3$ test. Usually, three passes were sufficient. The resulting Na-montmorillonites were air dried, and ground to pass a 60 mesh screen.

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[1] Pressure Membrane Extractor, No. 1000; Soil Moisture Equipment Co.; Santa Barbara, California

Li-montmorillonites were prepared by passing one percent suspensions of the previously prepared Na-clay through a Li-saturated resin. Excess water was removed by one pass through the pressure-membrane extractor. The clays were also air dried and ground to pass a 60 mesh screen.

b. Montmorillonite-kaolinite mixtures

The Na-Wyoming bentonite used in this phase was taken from the previously described sample. The Na-kaolinite (Georgia) was prepared by first dispersing the bulk sample with NaOH, followed by a series of centrifugations, decantations and resuspensions in water to obtain the $< 2\mu$ material. The resulting clay was sodium saturated by washing five times with N NaCl. Excess salt was removed by washing with water and centrifuging in an International, No. 2 centrifuge until the clay began to disperse. The sample then was resuspended in water, and run through the supercentrifuge one time. The resulting 2 to 0.08μ clay was considered to be essentially salt free.

The two clays were mixed, in the air-dry state to give the following proportions of montmorillonite when subsequently dried at 300C: 0.30, 0.50, 0.70, 0.90, and 1.00 (see Appendix, Sec. 2 for the procedure). The procedure for sample preparation and X-ray analysis from this point was identical to that of the specimen type montmorillonites.

c. Soil clays

The soil clays used in this phase of the study were: Webster (C-horizon) from Conger, Minnesota; Lufkin (A-horizon) from College Station, Texas; Houston Black (A-horizon) from Temple, Texas; silty and clay sediments (C-horizon) from Prince William County, Virginia (hereafter referred to as P.W. sample). All four of these soils were known to have a fairly high quantity of montmorillonite, as determined from X-ray diffractograms of their glycerol solvated, Mg-saturated samples (Fig. 18). In addition, they all contained various amounts of non-swelling or limited-swelling clays.

All soils were treated for removal of carbonates, organic matter and free iron oxides by the methods previously referenced (Jackson, 1956, pp. 31-56). Organic matter was removed with 30 percent hydrogen peroxide. Fractionation, to remove the $< 2\mu$ material, was then carried out by the method previously described for the specimen type montmorillonites.

Most of the excess salt was removed at this point by two passes through the 15-atmosphere pressure-membrane apparatus. The resulting material was resuspended and passed through the Na-saturated Dowex 50 W-X8 resin. The small amount of remaining salt was removed by repeated leachings on the pressure-membrane apparatus. This procedure prevented loss of any of the very fine clay fraction —a serious limitation of the procedure previously employed, which used the angle-head centrifuge to remove excess salt.

The cation exchange capacities of these samples were determined by a modification of the method proposed by Rich (1961). The exchangeable sodium on duplicate, air dry, 20 mg samples was displaced by the prescribed procedure of shaking for 16 hours with 5.00 ml of N magnesium acetate. The sodium concentration in the solution phase was then analyzed on a Beckman D U Flame Photometer. The resulting values for the cation exchange capacities were converted from an air dry weight basis to a 300C dry weight basis according to the procedure outlined in the Appendix, Sec. 1.

2. X-ray procedure

The procedures for slide preparation and X-ray analysis in Phase II were identical to those used in Phase I, except that the X-ray analysis for Phase II was carried out on a

General Electric X-RD 5 instrument, with intensities recorded in linear units. Also, the X-RD 5 unit had a ΔE unit to reduce the recorded intensity of white radiation.

Standard gravimetric moisture determinations were made on the samples at the time of recording the X-ray diffraction patterns. Except for the Na-Wyoming bentonite -kaolinite mixtures, all determinations were based on 110C weights, and then were converted to a 300C dry weight basis (see Appendix, Sec. 1 for procedure). The moisture contents for the Na-Wyoming bentonite-kaolinite mixtures were determined directly from samples dried at 300C. The procedure here was to weigh out certain amounts of the air-dry samples of both the bentonite and the kaolinite to give the desired ratio after the samples were heated to 300C. The amount needed was determined by back-calculations based on average water losses between the air-dry state and 300C (see Appendix, Sec. 2 for procedure).

All diffractograms in Phase II were corrected for the combined Lorentz and polarization factors (LP) by dividing intensity by the factor:

$$\frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

which is the factor for completely oriented samples (MacEwan et al. 1961 pp 406-407). It was assumed that the smear technique, used to prepare the clay mounts for X-ray analysis, oriented the clay plates normal to the c-dimension. A table of LP versus sin θ was prepared, and then converted to degrees 2 θ versus LP, and plotted to facilitate the correction procedure. The corrected intensities were then replotted versus degrees 2 θ. Typical corrected patterns appear in Fig. 19; it was noted, that at the low angles used throughout this experiment, the point of highest intensity of the (001) peak on the original diffractogram normally shifted to a slightly higher angle upon correction for LP; also, the lower the angle, the greater the shift.

IX. Theory-phase II

List of Symbols

d = d-spacing of the (001) diffraction peak of expanded montmorillonite in Angstrom units.

A = Angstrom units.

W = weight of water in system in grams.

M = weight of montmorillonite in system in grams.

K = weight of kaolinite in system.

I = weight of illite in system.

S_i = internal area of montmorillonite (normally in m^2).

$L, L', L'', ---$ = constant terms represent that water associated with the external surfaces of each clay mineral; e.g. L = external water on montmorillonite packets, L' = external water on kaolinite, etc. The units of the L's are grams water per gram clay.

u $= \dfrac{(A/10^{-8}\,cm)(10^{-4}\,m^2/cm^2)}{\frac{1}{2}\rho}$

where ρ is the density of water in g/cm^3 (assumed to have a value of 1.000). For calculation purposes:

$$u = 2 \times 10^4 \left(\frac{A \cdot m^2}{g}\right).$$

The theoretical curve for expansion of a "free-swelling" montmorillonite in a water system is:

$$d_{(001)} = 9.4\text{A} + \frac{(V/M)(\text{A}/10^{-8}\text{cm})}{\frac{1}{2}(S_i/M)} \qquad [1]$$

where $d_{(001)}$ is the d-spacing of the expanded montmorillonite in Angstroms; 9.4A is the thickness of the individual montmorillonite sheets as measured from the center of one plane of superficial oxygens to the next, plus two times the van der Waals radius of oxygen (6.6A + 2 x 1.4A), as suggested by MacEwan (1948); V is the volume of the internal or interlayer water in cm^3; S_i is the internal surface area of the montmorillonite in cm^2; and M is the mass of montmorillonite. The term ($\frac{1}{2}$) is needed to compensate for each layer of internal water being associated with the two adjacent montmorillonite surfaces.

We may substitute total weight of water in the system for the volume term if we: (1) assume that the density of water equals 1.000, and (2) if we subtract from the total water, that water associated with external surfaces and non free-swelling internal surfaces. Assumption (1) is a reasonable assumption at the higher water contents (greater than 40 percent water, Mackenzie, 1958).

Equation [1] may be simplified and extended to the general system of clay mixtures containing montmorillonite.

The general expansion equation may be written as:

$$d = 9.4 + u\left[\frac{\left(W - (LM + L\,K + L\,I + ----)\right)\,/M}{(S_i/M)}\right] \qquad [2]$$

For a one component system (montmorillonite only):

$$d = 9.4 + u\ \left[\frac{(W - LM)/M}{S_i/M}\right] \qquad [3]$$

If we assume that the amount of externally associated water is constant over the range studied we may rearrange the values in the following manner:

$$d = \left[9.4 - \frac{uLM}{S_i}\right] + \frac{uW}{S_i} \qquad [4]$$

It is reasonable to assume that the amount of externally associated water is indeed constant over the range studied. The external surface of a pure montmorillonite is only about 1/15 to 1/30 (Mooney et al., 1952) that of the internal surface; therefore, even if the rate of increase of water thickness on all the surfaces were the same, i.e. as the total water content of the system is increased, there would still be 15 to 30 times as much water going internally as externally. Also, arguments previously presented suggest that the rate of increase of water thickness is considerably less on external surfaces than on internal surfaces.

If the assumptions are correct, a plot of d versus uW should produce a straight line with:

$$\text{slope} = \frac{1}{S_i}$$

and:

$$\text{intercept} = 9.4 - \frac{uLM}{S_i}$$

For the pure montmorillonite system, M equals one; thus, we may solve for L.

The theory, therefore, predicts a means for determining the internal area S_i, and the amount of water LM associated with the external surfaces of a montmorillonite.

Fig. 1 shows the theoretical expansion curve for a pure montmorillonite.

For a two component system:

$$d = 9.4 + u\left[\frac{(W - (LM + L'K))\ /M}{(S_i/M)}\right. \qquad [5]$$

Since for a two component system: $K = 1 - M$

$$d = 9.4 + u\left\{\frac{\left[W - (LM + L'(1 - M))\right]/M}{(S_i/M)}\right\} \qquad [6]$$

Rearranging terms and cancelling:

$$d = \left[9.4 - \frac{u(LM + L'(1 - M))}{S_i}\right] + \frac{uW}{S_i} \qquad [7]$$

Thus, again, if the assumptions are correct, we will find that a plot of d versus uW will be a straight line with:

$$\text{slope} = \frac{1}{S_i}$$

and:

$$\text{intercept} = \left[9.4 - \frac{u\left(LM + L'(1 - M)\right)}{S_i}\right]$$

If $L = L'$:

$$\text{intercept} = 9.4 - \frac{uL}{S_i}$$

If $L \neq L'$, theoretically it should be possible to evaluate L and L' using a series of expansion curves with different values of M for each curve.

If, for the general case of a clay mixture containing montmorillonite, we assume, that over the water range of interest, the water associated with the composite external surfaces remains constant, we may rewrite equation [2] as follows:

$$d = 9.4 + u\left[\frac{(W - \theta)/M}{S_i/M}\right] \qquad [8]$$

Where θ represents the externally associated water. Rearranging equation [8] in the usual manner we obtain:

$$d = \left[9.4 - \frac{u\theta}{S_i}\right] + \frac{uW}{S_i} \qquad [9]$$

Equation [9] represents the general equation for determining the internal area of the freely-expanding component, and for the determination of the externally associated water - both per unit of the total clay mixture.

If we now assume some average value for the surface area per gram of montmorillonite in a clay mixture, we then have a means of determining quantitatively the amount of montmorillonite M in that sample. For example, by assigning (S_1/M) the value 800 m^2/g in equation [8], we obtain the relation:

$$d = 9.4 + u \left[\frac{(W - \theta)/M}{800}\right] \qquad [10]$$

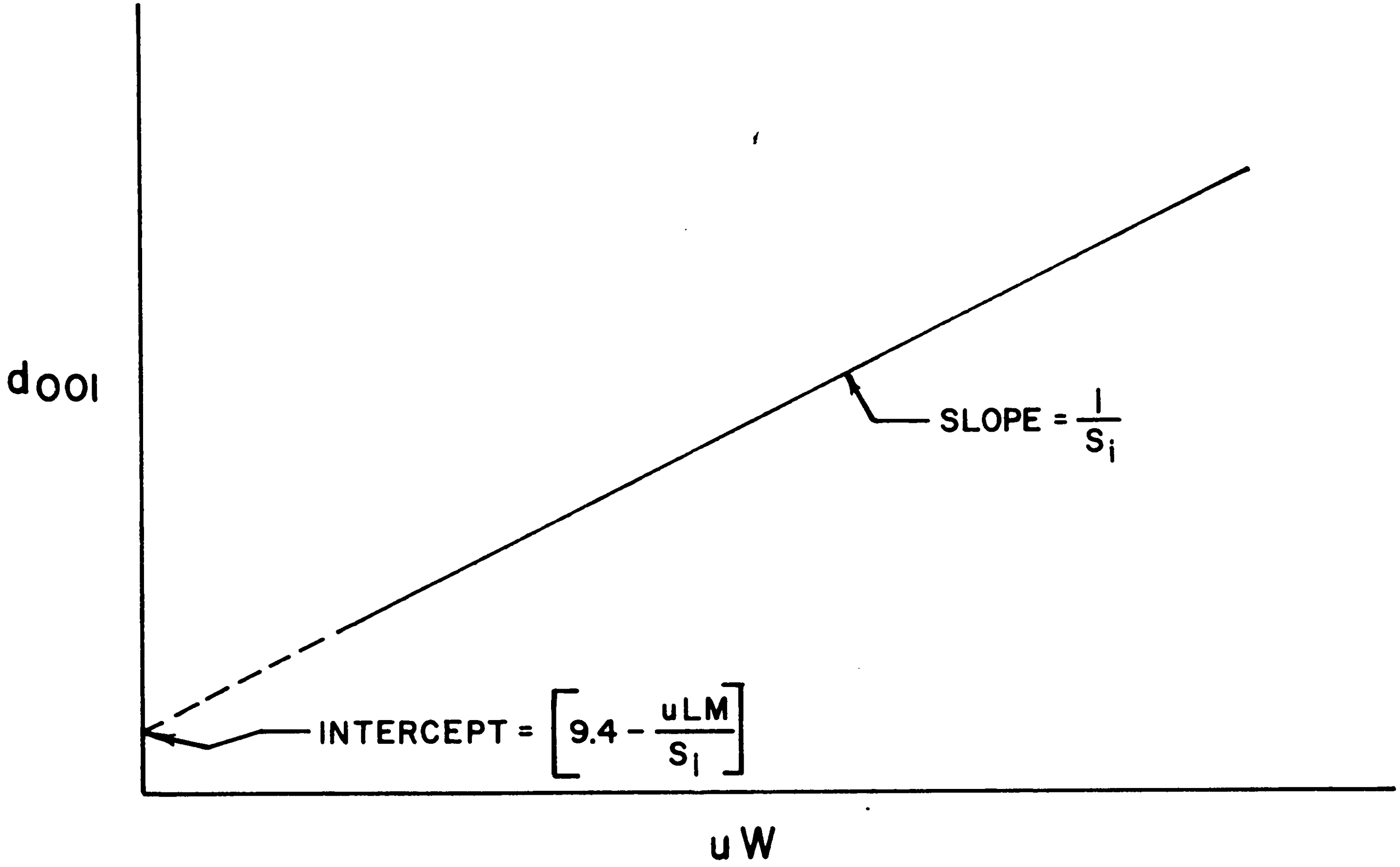
or upon rearranging terms:

$$M = 25\left[\frac{W - \theta}{d - 9.4}\right] \qquad [11]$$

The value of (θ) may be obtained, from the intercept; therefore, we can solve for M.

It may be possible to assign some average value to θ, so that M may be obtained directly from each determination. This is permissible if it can be shown that the variation in θ between samples is small, and/or if the error involved in the determination of M is small, even for reasonably large errors in the accepted value of θ.

Fig. 1—Theoretical expansion curve for a pure montmorillonite.



d_{001}
SLOPE = $\frac{1}{S_i}$
INTERCEPT = $\left[9.4 - \frac{uLM}{S_i}\right]$
uW

X Results and discussion

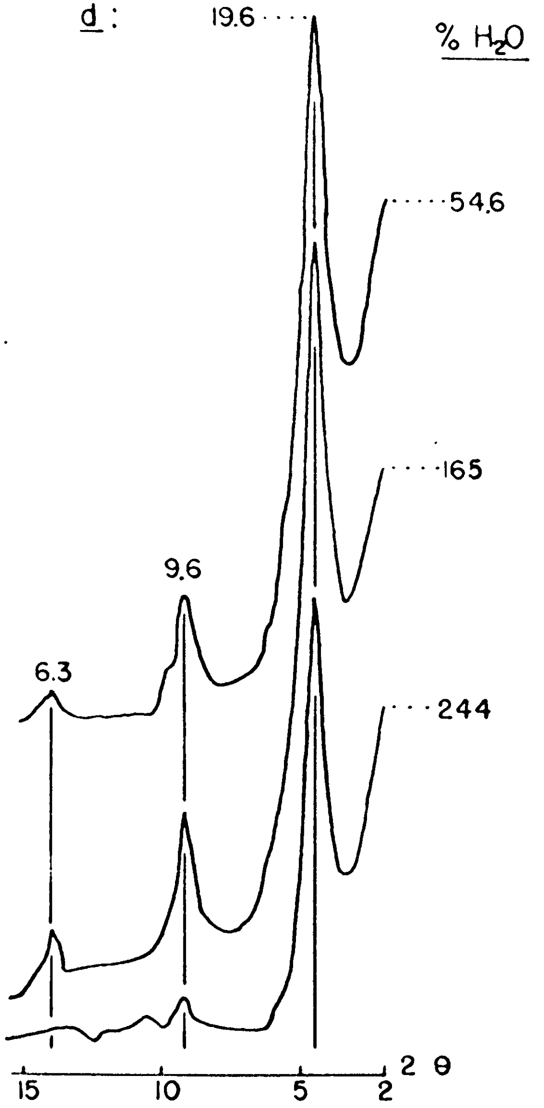
A. X-ray studies of crystalline swelling in montmorillonite - (Phase I)

Typical diffractograms for Ca-montmorillonite pastes appear in Fig. 2. The peaks were quite sharp and had high intensity, indicated on a logarithmic scale. Peak intensity,however, slowly decreased with increasing water contents. The number of orders recorded varied from two to five, the number decreasing with increasing water content.

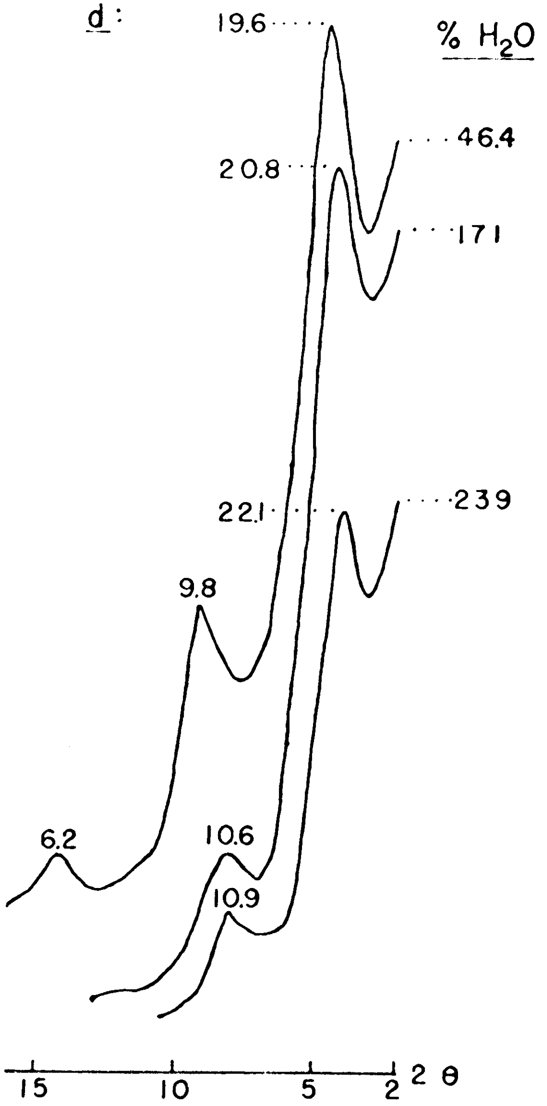
Fig. 3 shows these data plotted as d-spacings in Angstrom units versus percent water for Wyoming and Otay bentonites, and for hectorite. All three clays failed to show continuous expansion with increasing water contents. The 19.2 and 19.6A spacings for Wyoming bentonite were stable in their respective water ranges. The other two clays expanded slightly more than did Wyoming bentonite, but more variability was also obtained. Hectorite expanded to as much as 22A, showing that it has more tendency to expand than the other clays used.

Diffractograms for Li-nontronite and Li-hectorite are shown in Fig. 4. The diffractograms for Li-Wyoming and Otay bentonites were almost identical in form to these. No evidence was found for discontinuous expansion

Fig. 2—Smoothed X-ray diffraction patterns of <2µ Ca-montmorillonites.



Ca. WYO. BENTONITE



Ca. HECTORITE

Fig. 3—Lattice (001) spacings of $<2\mu$ Ca-montmorillonites vs. water percentage.

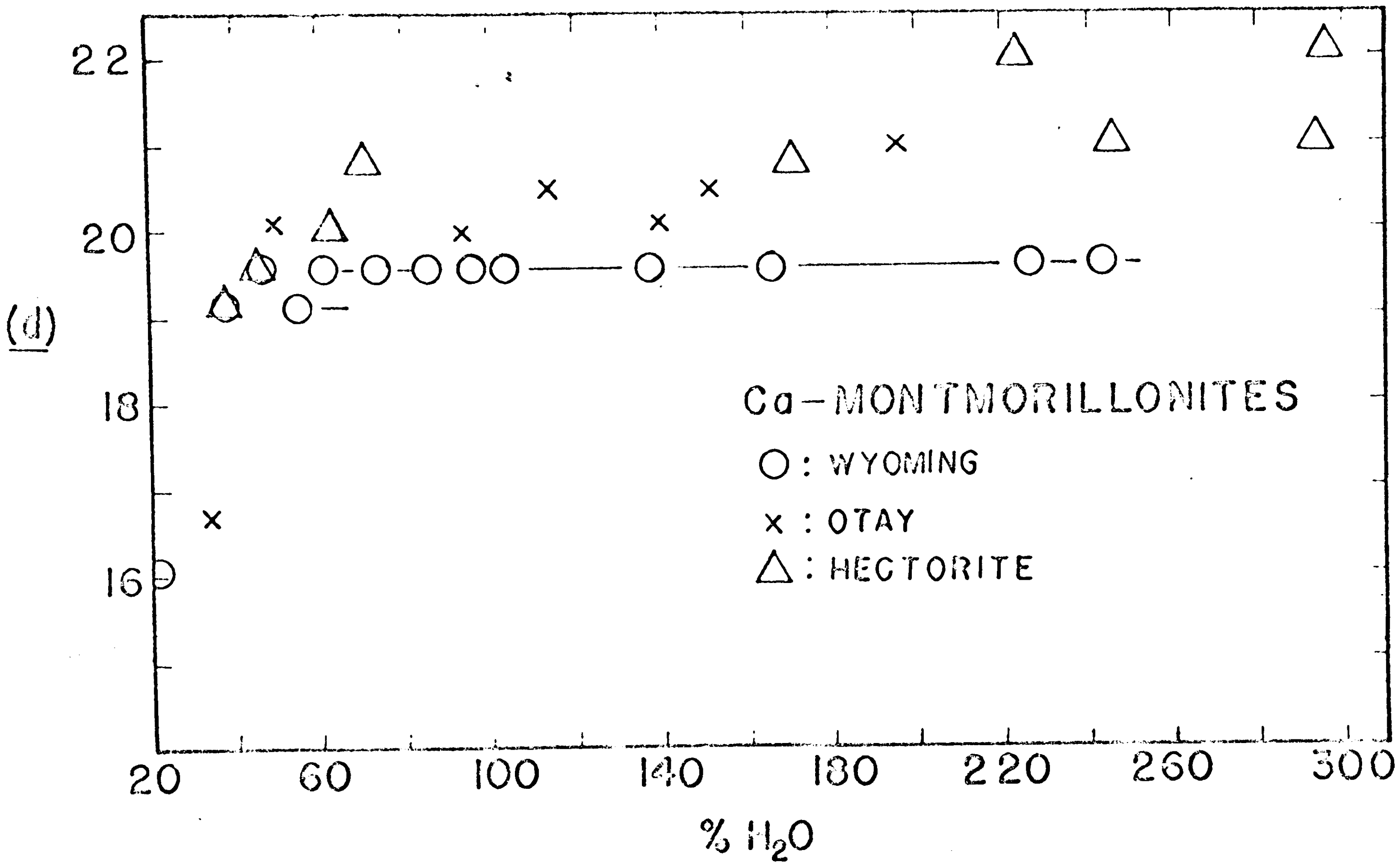
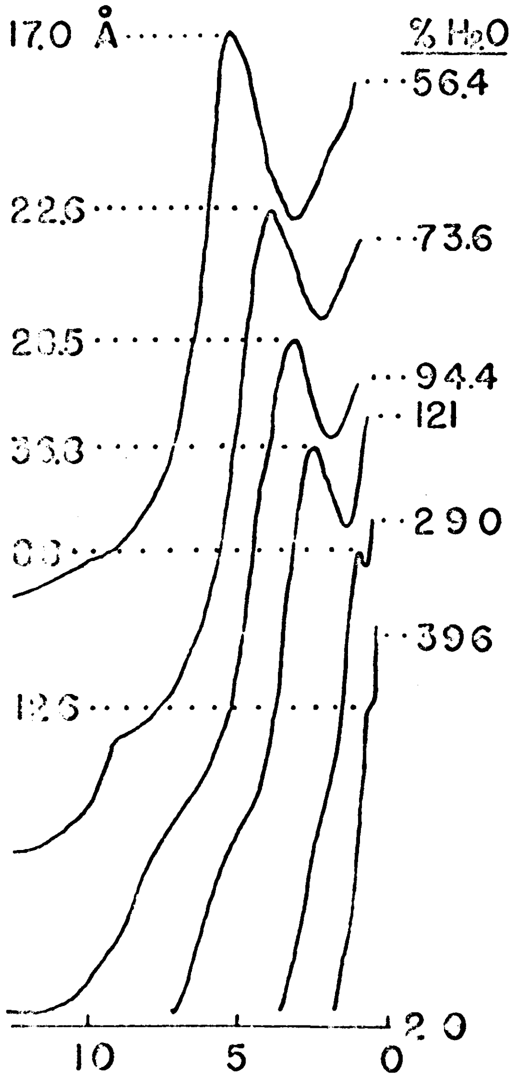
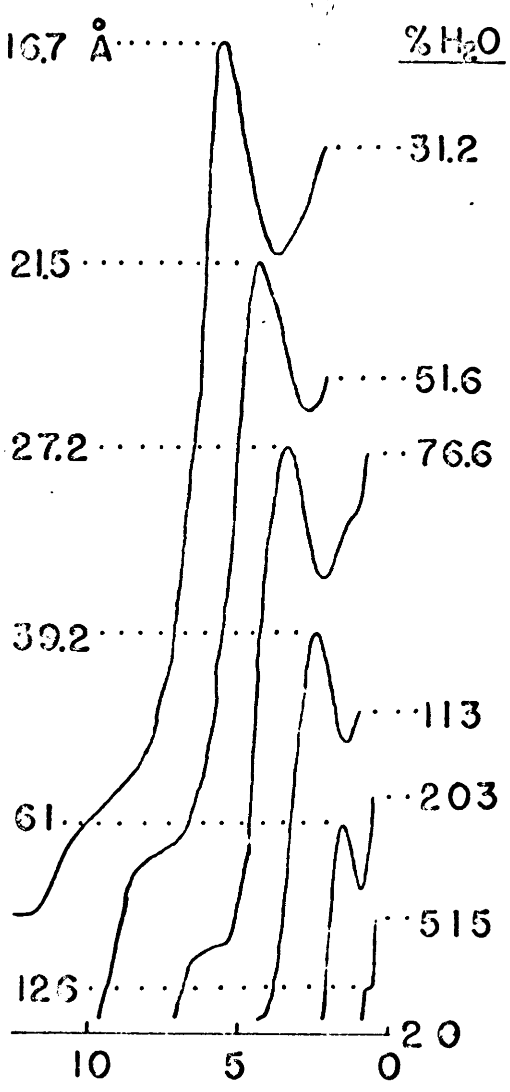

22
20
(d)
18
16
20
60
100
140
180
220
260
300
% H_2O
Ca—MONTMORILLONITES
○ : WYOMING
× : OTAY
△ : HECTORITE

Fig. 4—Smoothed X-ray diffraction patterns of 2 to 0.08μ Li-montmorillonites.



Li-NONTRONITE



Li-HECTORITE

at these water contents.

Fig. 5 shows d-spacings of the montmorillonites plotted against percentage water. The theoretical expansion curves to which the X-ray data are compared:

$$d = 10 + \frac{\% \, H_2O}{4} \qquad [12]$$

is derived from equation [1]. Equation [12] approximates the collapsed d-spacing to be 10A, assumes an internal surface area of 800 m^2/g, and neglects the small amount of externally associated water.

A series of X-ray patterns of Na-Wyoming bentonite, showing its swelling characteristics, is shown in Fig. 6. Expansion no longer was linear nor continuous as the water content was increased. There was a persistent 19.2A spacing which gradually lost intensity with increasing water contents. At the same time a second peak gradually formed at about 32A, which increased in intensity with increasing water content. At still higher moistures, the 19.2A spacing gradually faded into the 2nd order peak of the expanded 32A phase. Slightly beyond this point expansion became linear with increasing water content. These results for the expansion of Na-Wyoming bentonite are similar to those reported by Norrish (1954) and by Foster et al. (1955).

Fig. 5—Lattice (001) spacings of 2 to 0.08μ Li-montmorillonites vs. water percentage.

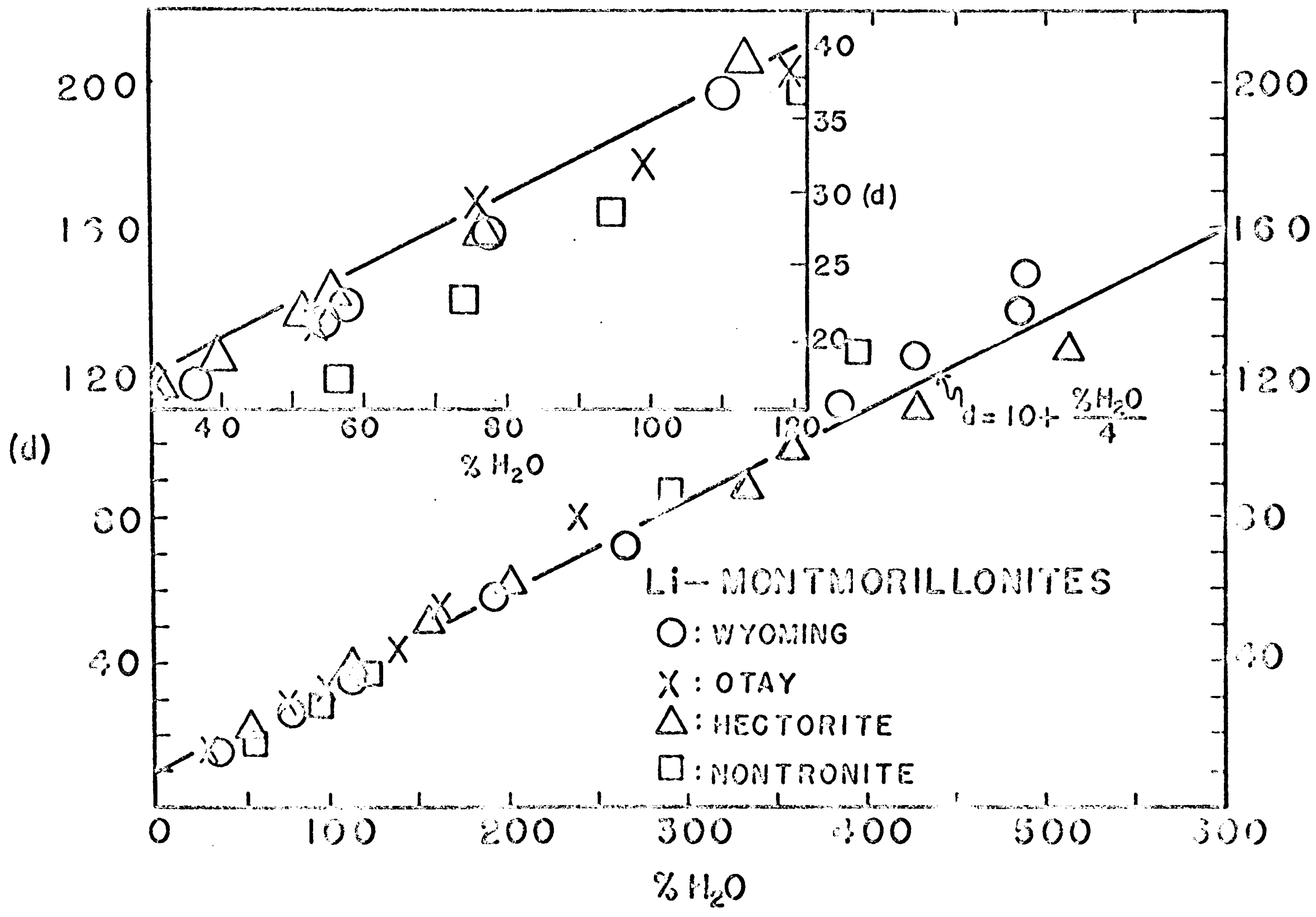
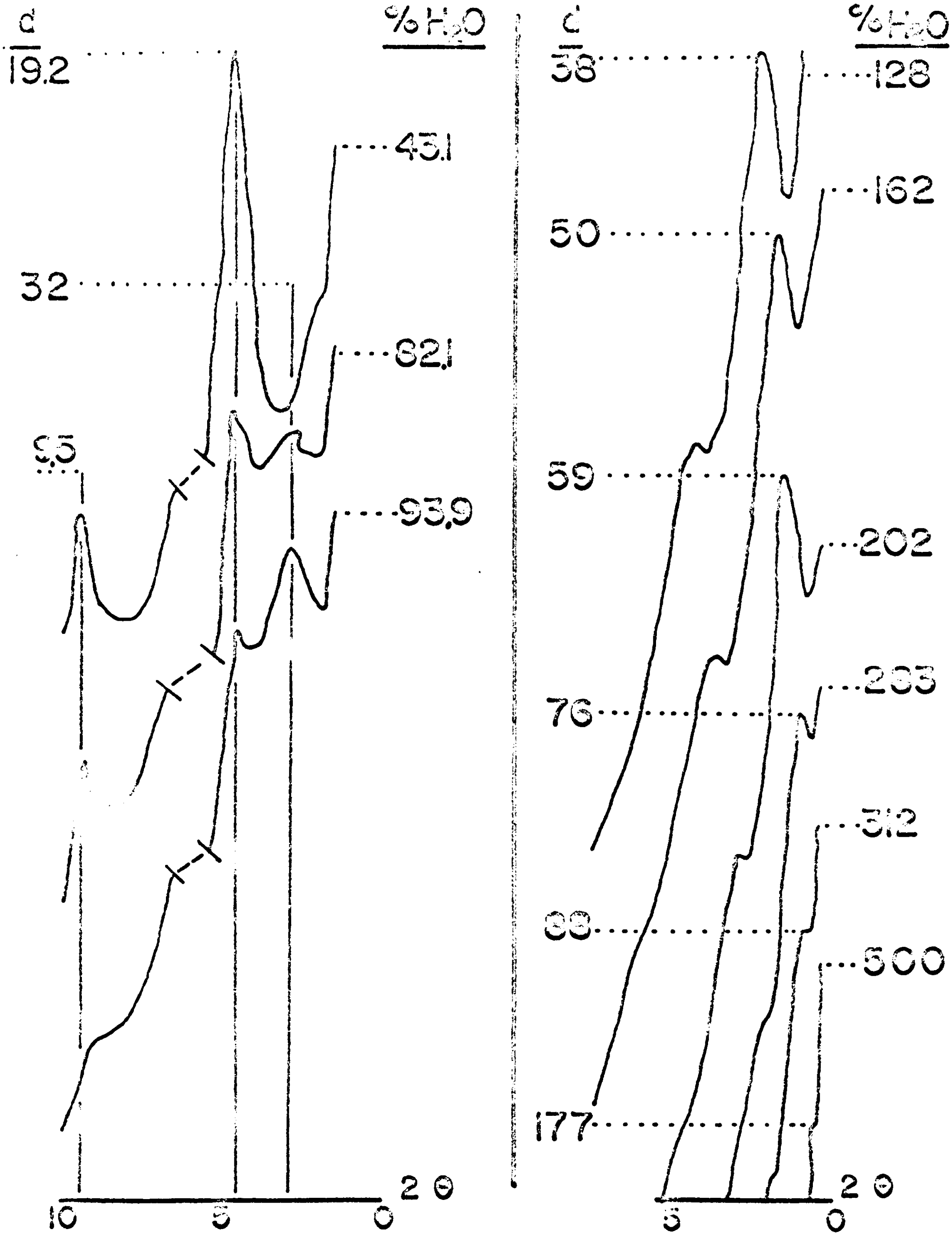

(d)
200
160
120
80
40
200
160
120
80
40
0
100
200
300
400
500
600
% H_2O
40
35
30 (d)
25
20
40
60
80
100
120
% H_2O
$d = 10 + \frac{\% H_2O}{4}$
Li– MONTMORILLONITES
○ : WYOMING
X : OTAY
△ : HECTORITE
□ : NONTRONITE

Fig. 6—Smoothed X-ray diffraction patterns of 2 to 0.08µ Na-saturated Wyoming bentonite.

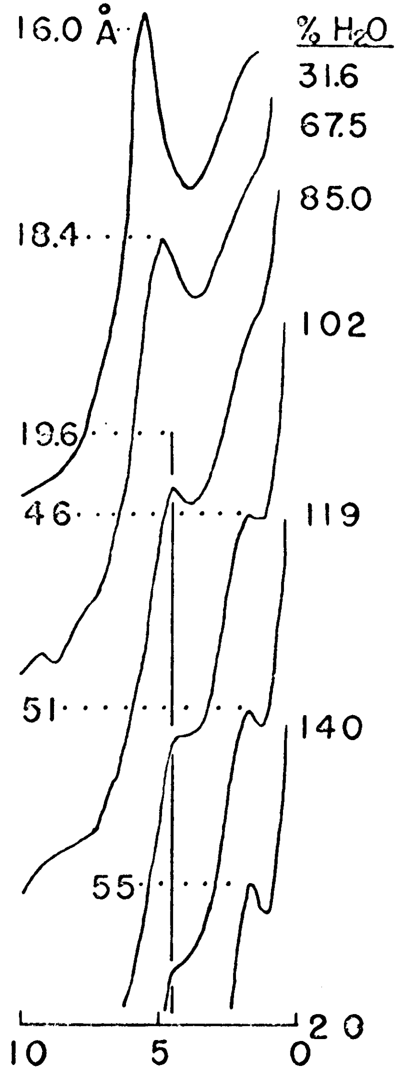


Na. WYO. BENTONITE

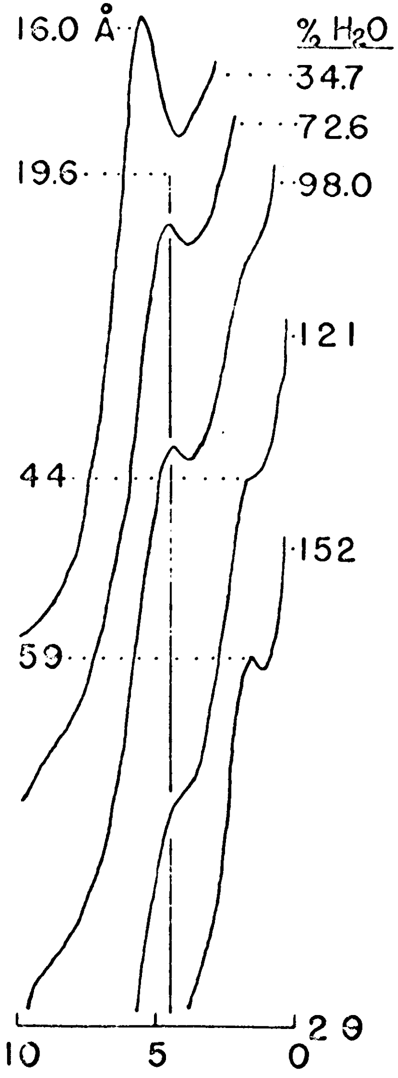
Typical diffractograms of the other three Na-montmorillonites are shown in Fig. 7. Na-nontronite and Na-Otay bentonite had expansion properties similar to those of Wyoming bentonite. Both had a stable phase at 19.6A, and an expanded second phase which gradually was expressed at about 45A. After the 19.6A phase had disappeared completely, the second phase spacing began to expand with increasing water content. Na-hectorite, however, did not show any stable, persistent spacing. Instead, expansion was continuous and very similar to the Li-montmorillonite patterns shown in Fig. 4.

These Na-montmorillonite data are plotted as d-spacing versus percent water in Fig. 8. The clay plates for these three montmorillonites appear to be expanding, one at a time, from a meta-stable phase at about 19A to a quasi-stable expanded phase. The shift involves a jump in spacing of about 14A for Wyoming bentonite, and 24A for Otay bentonite and nontronite. Hectorite, however, did not show these two separate phases, but expanded linearly over this range. The expansion pattern of Na-hectorite was nearly identical to that of its Li-analog. Expansion at higher water contents was essentially linear for all four clays, although the rate of expansion per amount of water varied somewhat from one montmorillonite to another.

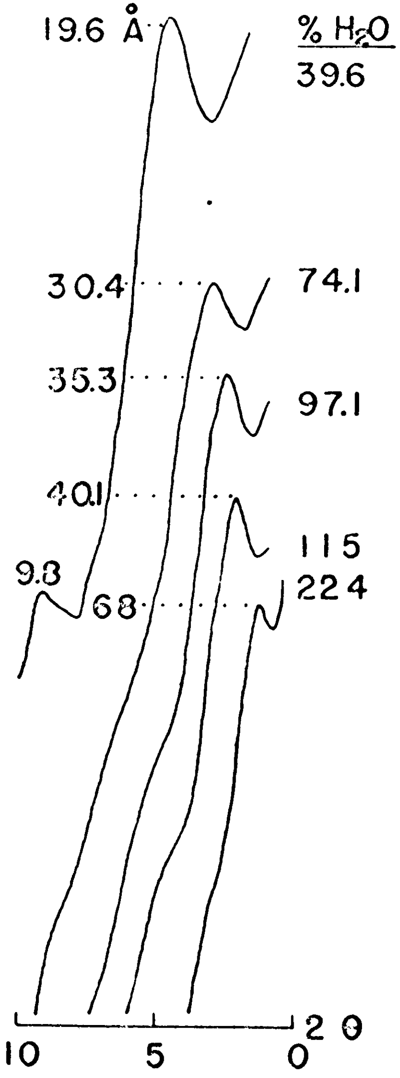
Fig. 7—Smoothed X-ray diffraction patterns of 2 to 0.08μ Na-montmorillonites



Na-NONTRONITE

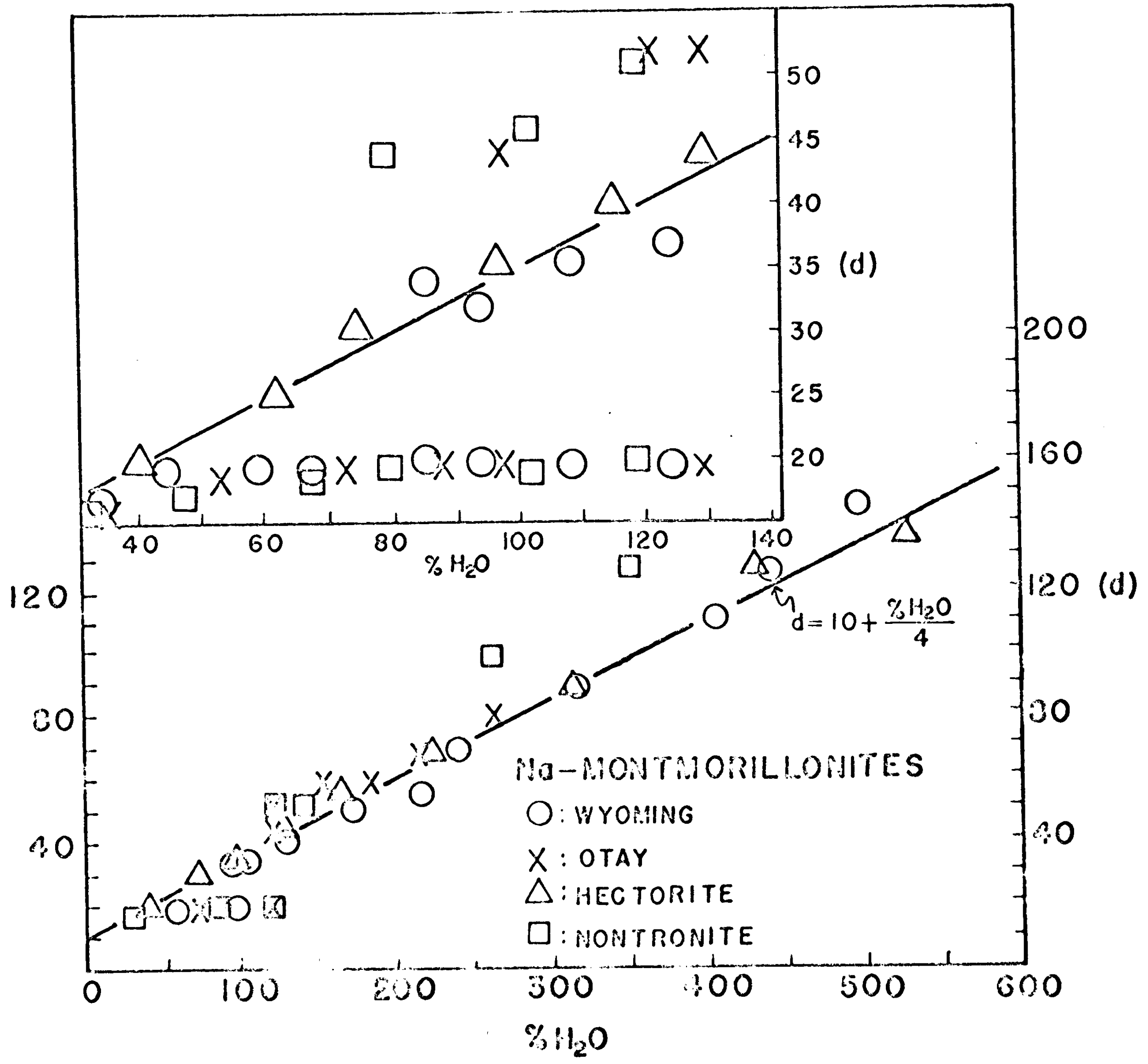


Na-OTAY



Na-HECTORITE

Fig. 8—Lattice (001) spacings of 2 to 0.08μ Na-montmorillonites vs. water percentage.

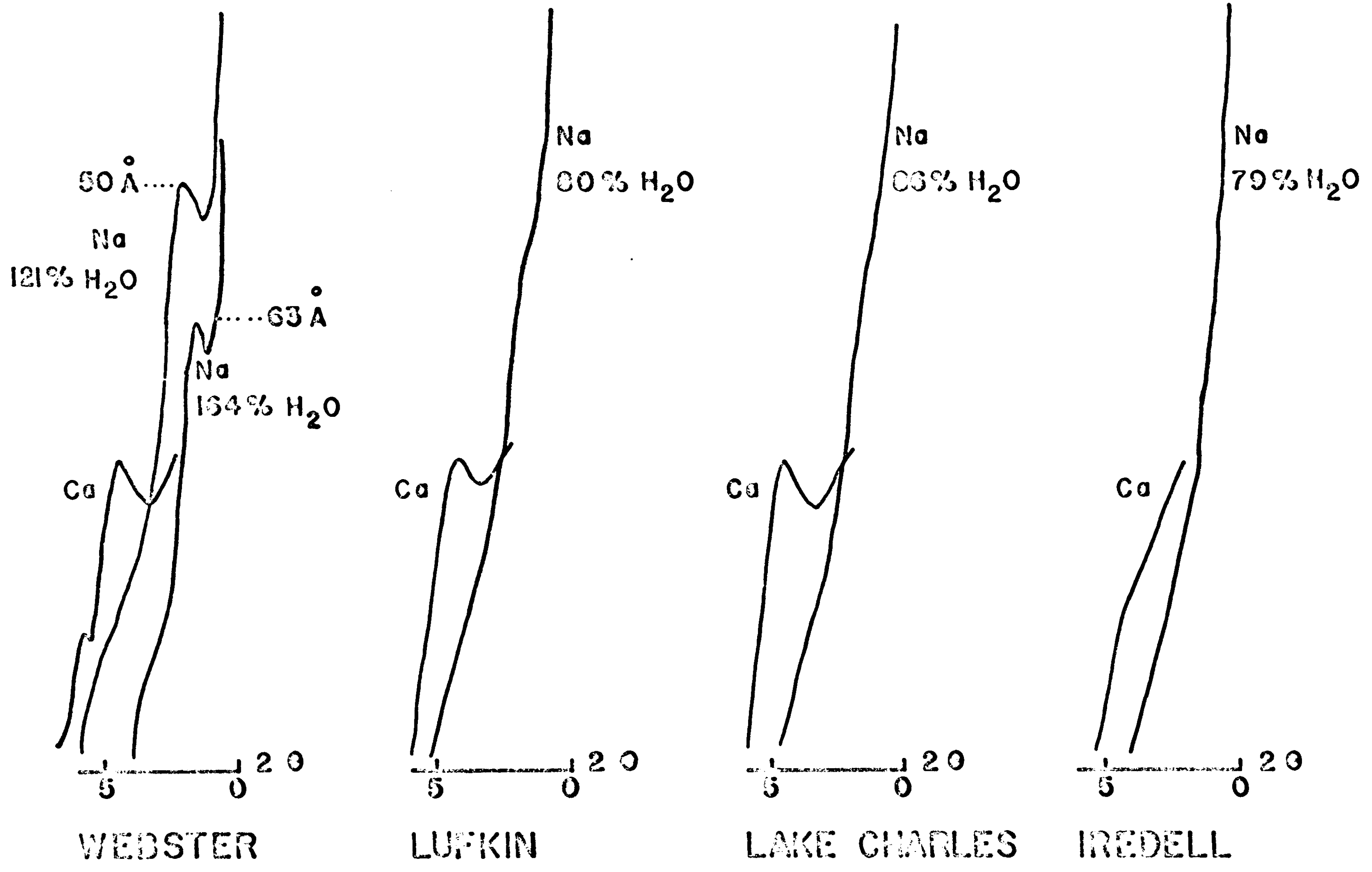


Na-MONTMORILLONITES
○ : WYOMING
X : OTAY
△ : HECTORITE
□ : NONTRONITE
$d = 10 + \frac{\% H_2O}{4}$
% H_2O
0
100
200
300
400
500
600
40
80
120
160
200
120 (d)
40
60
80
100
120
140
20
25
30
35 (d)
40
45
50

The experimental techniques also were applied to study swelling properties of several Na-saturated soil clays, all known to contain a large proportion of montmorillonite. Results showed that the soil montmorillonites used, differ in the regularity with which they expand at high water contents. Fig. 9 shows X-ray diffractograms of several of the expanded Na-soil clays. The two Webster patterns indicate that the montmorillonite present has expanded regularly, in the first case to 50A, and then, at the higher water content, to 63A. Except for the Webster sample, evidence for regular swelling was slight. The Lufkin and Lake Charles clays did show an indication of regular expansion, but not to the untutored eye. The Iredell and all others tested showed no evidence of crystalline expansion in the osmotic swelling region.

Regular expansion of certain of these soil clays possibly could have been facilitated through improved experimental techniques. A probable cause of failure may have been that part of the very fine montmorillonite fraction was lost during the removal of excess salts. Even though the final washes were carried out with methanol and the suspensions were centrifuged for one-half hour at 14,000 rpm., there was still a tendency for the Na-montmorillonites to remain slightly dispersed.

Fig. 9—X-ray diffractograms of expanded Na-soil clays.


50 Å
Na
121% H_2O
63 Å
Na
164% H_2O
Ca
5
0
2θ
WEBSTER
Na
80% H_2O
Ca
5
0
2θ
LUFKIN
Na
86% H_2O
Ca
5
0
2θ
LAKE CHARLES
Na
79% H_2O
Ca
5
0
2θ
IREDELL

Another possible explanation for the poor X-ray diffraction patterns for the Na-soil clays may be due to a very large variation of interplanar spaces in the expanded phase, thus preventing sharp intensity maxima. The surface charge density in soil montmorillonites is probably highly heterogeneous; this would in turn cause a large variation in the interlayer force fields. Thus in a free-swelling system, equilibrium between the forces of attraction and expansion, could be attained only by unequal expansion of the clay plates. The more heterogeneous the charge density becomes, the broader and less intense will be the resulting X-ray diffraction peaks.

Effect of saturating cation on swelling characteristics

The major differences in swelling properties observed in this study are ascribed to the particular saturating cation and modification of this cation effect by mineralogical characteristics of the particular clays.

Divalent calcium has a strong electrostatic attraction for the clay plates and prevents free osmotic expansion of the montmorillonite lattice. Expansion is, therefore, mainly due to hydration of the interlayer calcium ions, and is stopped at about a 10A thickness of water. Additional water added to the system after this maximum spacing is obtained, probably enters between groups of clay platelets and results in intraparticle expansion.

Li- and Na-saturation allowed extensive expansion of the montmorillonites. Despite some similarities, however, there were impressive differences. Of the two ions, lithium has the higher hydration energy. This results in a larger hydration shell for Li^+ than for Na^+ and consequently, a weaker attraction for specific charge sites on the clay. It is thought that the stronger effective charge of Na^+ is responsible for the discontinuous expansion exhibited by three of the clays. When Na^+ is the saturating cation, and the clay is tetrahedrally charged (at least to some degree), the point charges on the clay are sufficiently strong to cause the clay to resist expansion until sufficient water is added to overcome this strong attractive interaction between the cation and the clay surface, and dissociate them.

Further evidence that this explanation is realistic is furnished by the results obtained for the swelling of Na-hectorite, in that this sample expanded freely and linearly in the region where the other Na-montmorillonites exhibited the discontinuity in expansion.

Hectorite, unlike the other montmorillonites examined, possesses charge sites only in the octahedral layer (Table 2). The relatively large distance from the seat of the charge in the octahedral layer to the planar oxygen surfaces, where this charge deficiency is expressed, results in a diffusion of the charge, rather unformally, over the planar oxygen surfaces, rather than as a point charge as is the case for charge sites originating in the tetrahedral layers. This reduction in the point charge effect for hectorite allows the sodium ions to be easily dissociated from these basal oxygen surfaces, thus permitting free-expansion of the clay plates at a much lower water content than for clays having tetrahedral charge sites.

It appears that when the montmorillonites were either Na^+ or Li^+ saturated, the major factor which controlled swelling was the differential osmotic activity between the interlayer water and the external water. Specific attractive forces between Na^+ and tetrahedral charge sites arrested free expansion over a limited water range but these were overcome as more water was added. In the case of hectorite, all the charge is located in the octahedral layer and sodium saturation was not sufficient to stop free expansion. When Li^+ was the saturating cation the osmotic force was great enough to overshadow any attractive force in all four of the clays. Calcium saturation prevented interlayer expansion beyond about 20A, although intraparticle expansion between "packets" of clay platelets apparently occurred.

B. Some applications of the free-swelling characteristics of montmorillonites.

The expansion curves of the free-swelling Na- and Li-saturated specimen type montmorillonites in water systems are shown in Figures 10 to 15. The data have been plotted according to equation [4], so that the inverse of the slopes equals the internal surface areas and the intercepts provide a measure of the externally associated water. The results have been compiled in Table 3.

The plotted data in Figures 10 to 15 show that for all cases, the d-spacings increase linearly, with increasing amounts of water, up to fairly high water contents. In this linear expansion region each additional increment of added water goes into the interstitial regions to swell the clay lattice, while the quantity of external water remains constant.

Eventually, however, as more and more water is added to the system some of the montmorillonites reach a point where their rates of expansion gradually begin to decrease. It can be shown that this decrease in rate of expansion may be attributed to continuously increasing amounts of water hydrating the external surfaces. Thus:

$$W_t = W_{ex} + W_i$$

Fig. 10—Free-swelling of Na-saturated Wyoming bentonite in a water system (where d is the spacing of the expanded montmorillonite in Angstrom units, where u is a constant which is equal to 2 x 10^4 $(A \cdot m^2)/g$, and where W is equal to the total weight of the water in the system in grams).

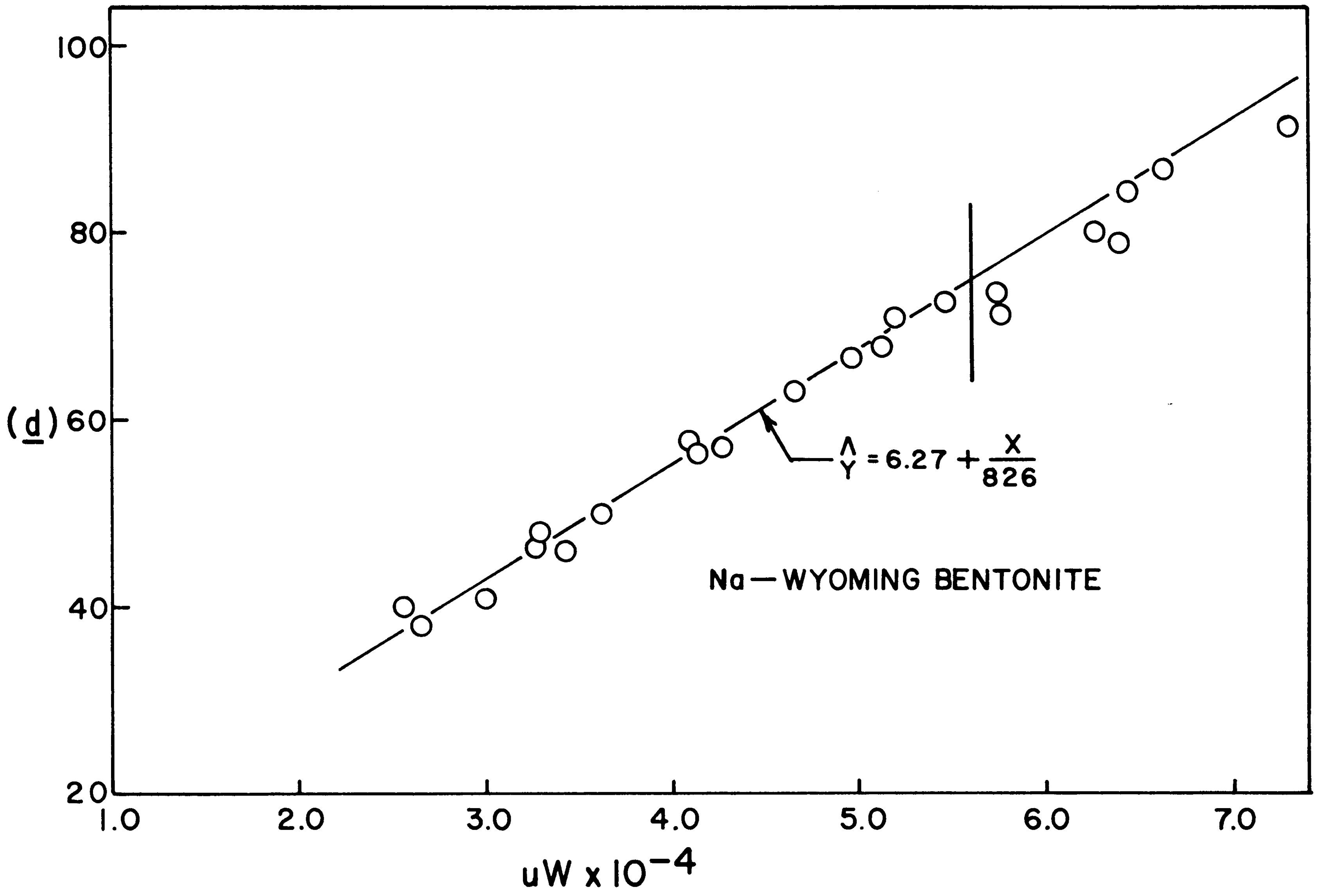

100
80
(d) 60
40
20
1.0
2.0
3.0
4.0
5.0
6.0
7.0
uW x 10^-4
$\hat{Y} = 6.27 + \frac{X}{826}$
Na — WYOMING BENTONITE

Fig. 11—Free-swelling of Na-hectorite in a water system.

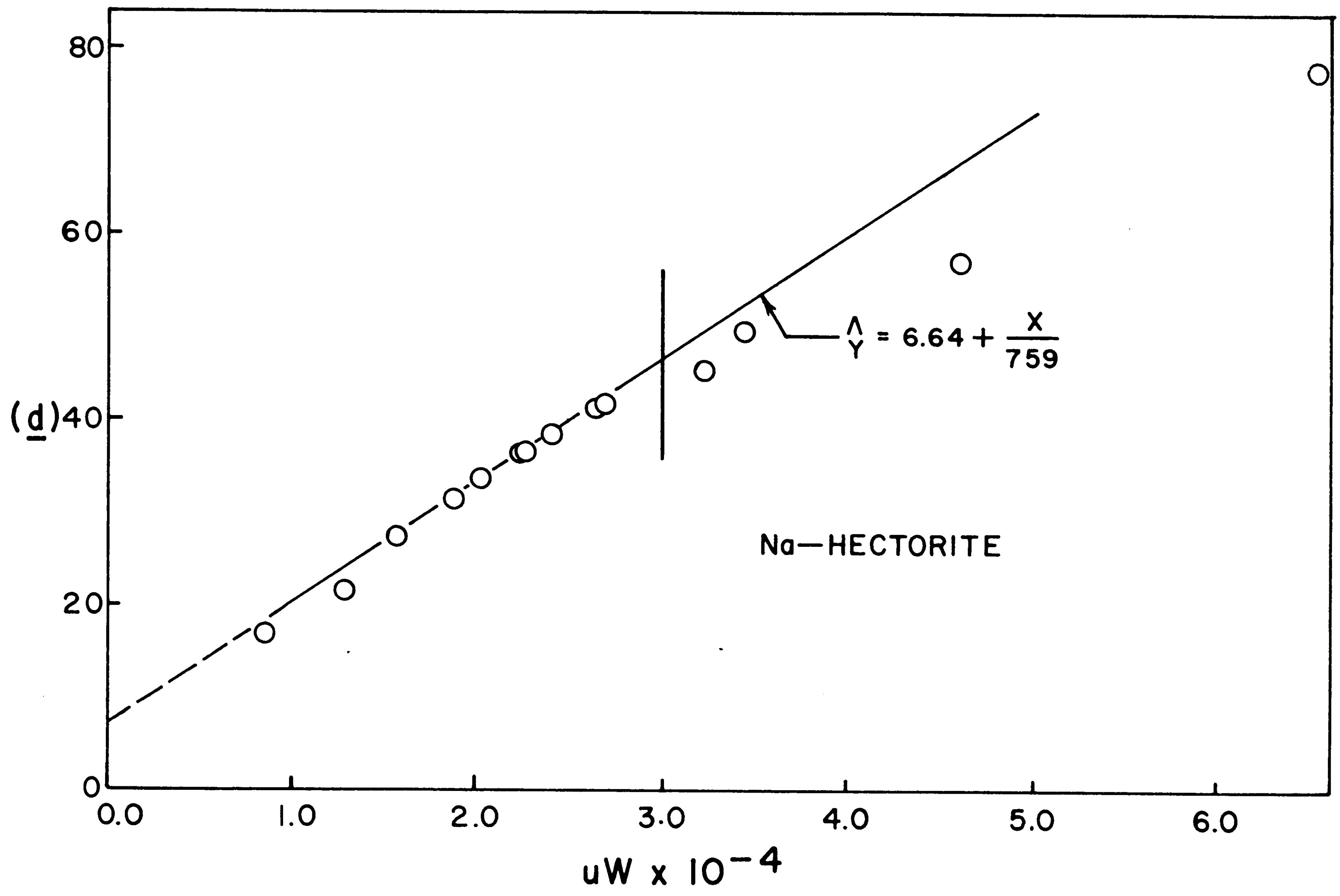

80
60
(d)40
20
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
uW x 10^{-4}
$\hat{Y} = 6.64 + \frac{X}{759}$
Na—HECTORITE

Fig. 12—Free-swelling of Li-saturated Wyoming bentonite in a water system.

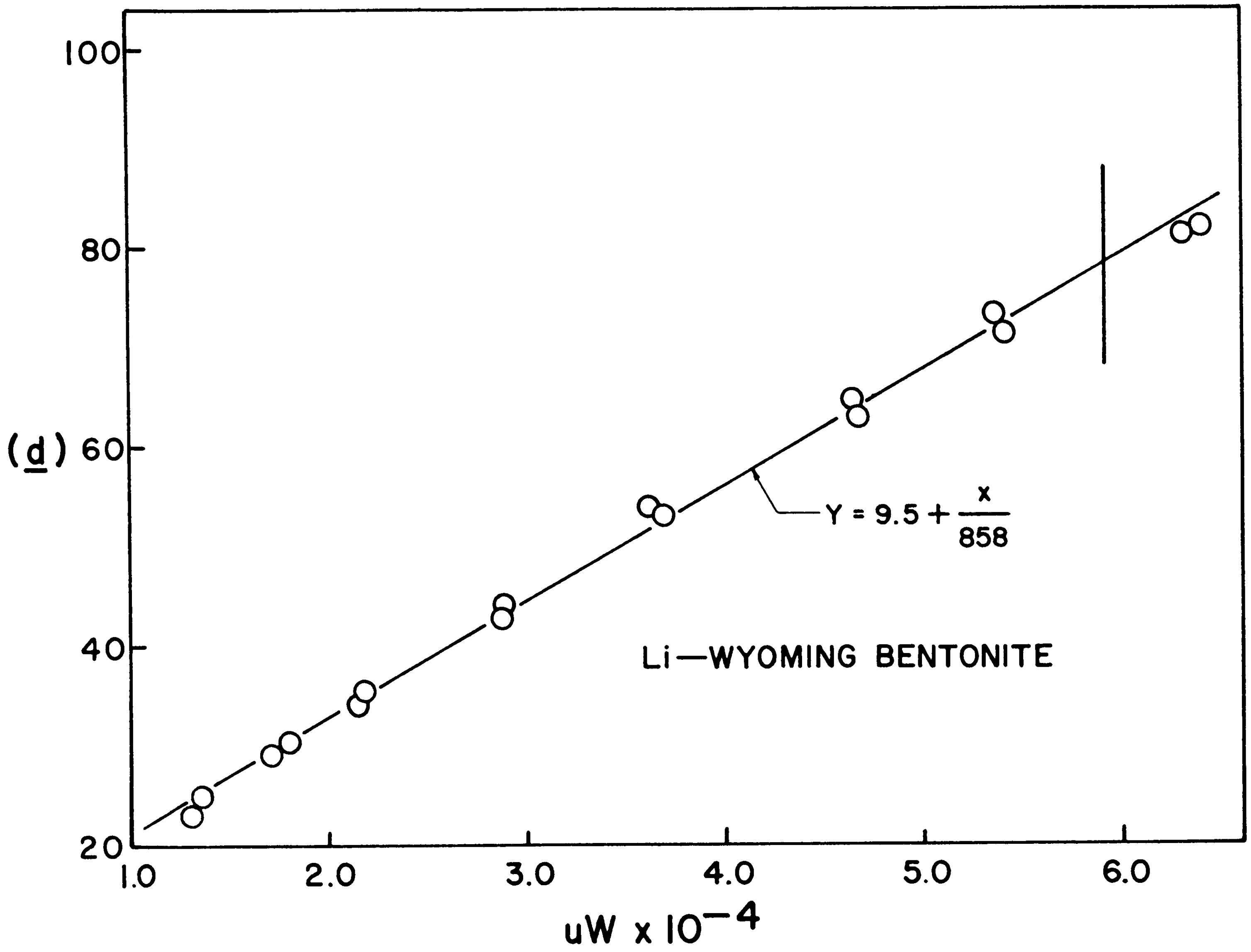

100
80
(d) 60
40
20
1.0
2.0
3.0
4.0
5.0
6.0
uW x 10⁻⁴
Y = 9.5 + x/858
Li—WYOMING BENTONITE

Fig. 13—Free-swelling of Li-hectorite in a water system.

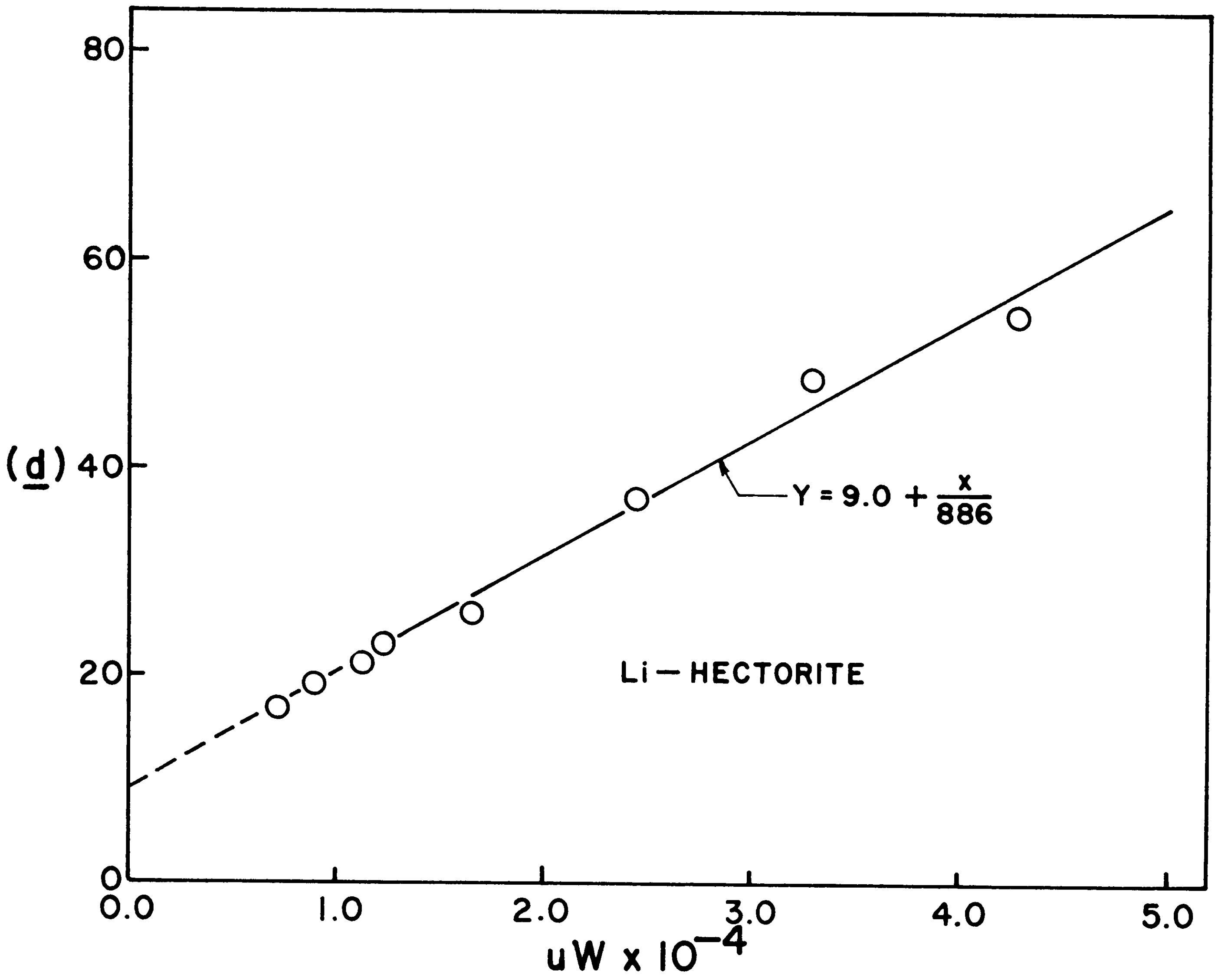

80
60
(d) 40
20
0
0.0
1.0
2.0
3.0
4.0
5.0
uW x 10^{-4}
$Y = 9.0 + \frac{x}{886}$
Li — HECTORITE

Fig. 14—Free-swelling of Li-saturated Otay bentonite in a water system.

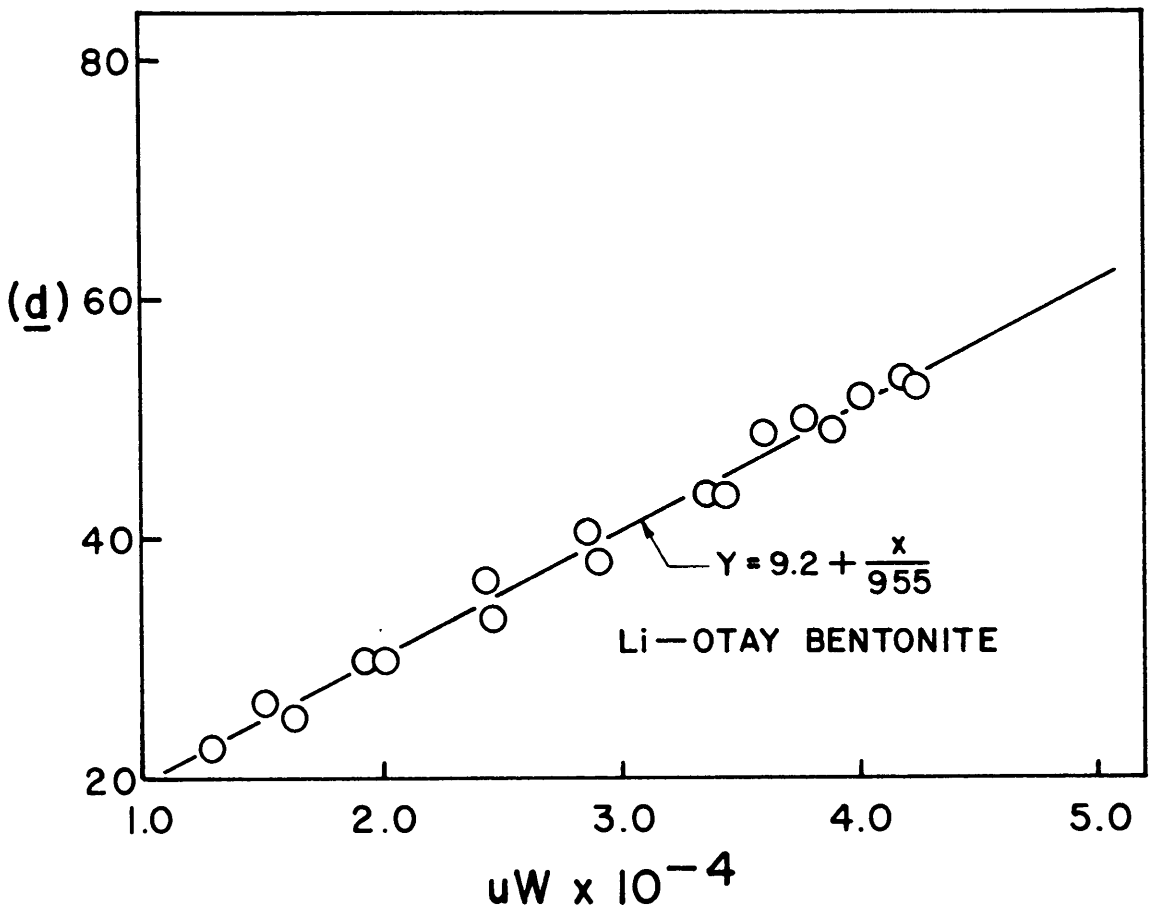

(d)
80
60
40
20
1.0
2.0
3.0
4.0
5.0
uW x 10^{-4}
$Y = 9.2 + \frac{x}{955}$
Li—OTAY BENTONITE

Fig. 15—Free-swelling of Li-nontronite in a water system.

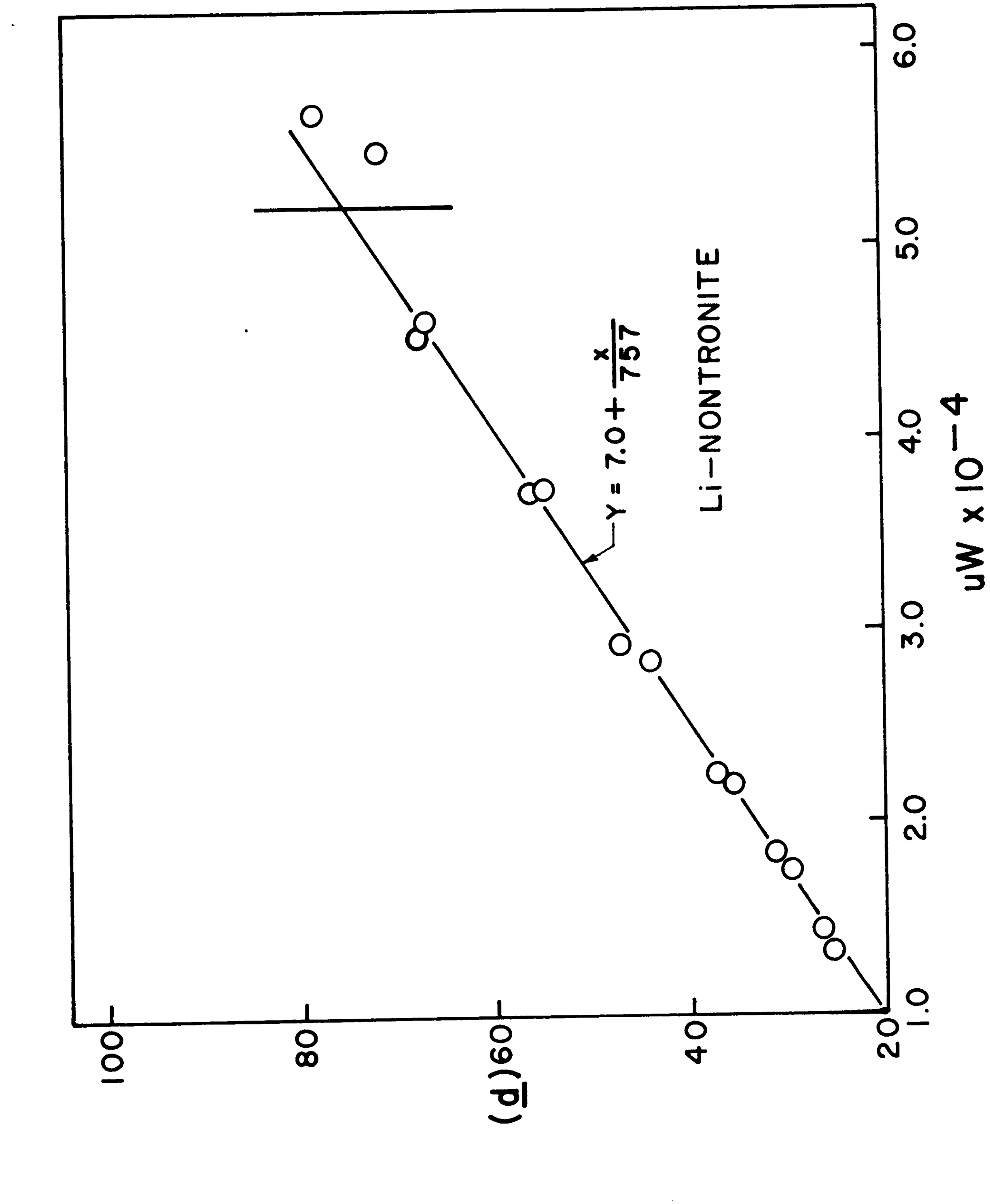

(d)
100
80
60
40
20
1.0
2.0
3.0
4.0
5.0
6.0
uW x 10⁻⁴
Y = 7.0 + x/757
Li—NONTRONITE

Table 3—Internal surface areas and percent external water for speciman type montmorillonites.

Clay (0.08-2µ)	Internal surface area Swelling data	 Theoretical	External water
	m²/g	m²/g	%
Na-Wyoming bentonite	826	746	12.8
Li-Wyoming bentonite	858	757	−0.4
Na-hectorite	759	765	10.6
Li-hectorite	886	771	1.8
Li-Otay bentonite	955	762	1.0
Li-nontronite	757	687	9.1

where W_t, W_{ex}, and W_i refer to total, external and internal grams of water per gram of sample respectively. If we assume a density of 1.000 for the internal water, we may write:

$$W_i = \rho d(S_i/M)$$

or

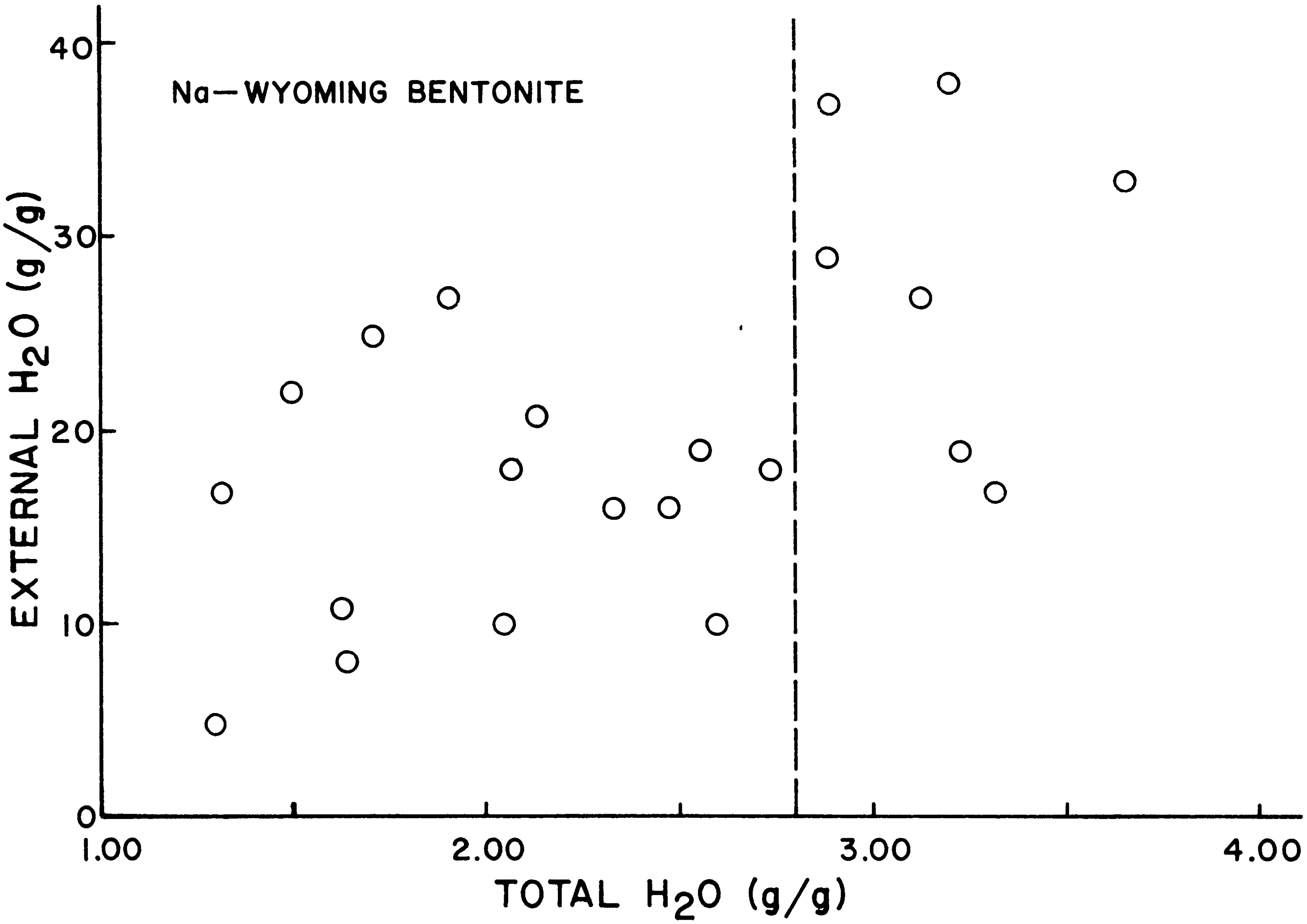
$$W_t = W_{ex} + \rho d(S_i/M)$$

where ρ is the usual water density conversion factor; where d is the (001) diffraction peak of the expanded montmorillonite; and where (S_i/M) is the internal area per gram of sample (all quantities are in cgs units).

Since the internal planar surface area remains constant as the plates expand, it is possible to determine W_{ex} for each experimental data point. If W_{ex} remains constant as W_t increases, a plot of W_t versus W_{ex} should give a straight line with zero slope. If W_{ex} increases at a constant rate as W_t increases the plot should be linear with positive slope but if W_{ex} increases at an ever increasing rate as W_t increases, the plot should be curvilinear with positive slope.

The expansion data for Na-Wyoming bentonite has been so plotted (Fig. 16). Results suggest that the amount of external water does remain constant up to about 2.8 grams

Fig. 16—Plot of the external water versus the total water over the free-swelling range studied for Na-Wyoming bentonite (grams of H_2O per gram clay, g/g).


Na—WYOMING BENTONITE
EXTERNAL H_2O (g/g)
40
30
20
10
0
1.00
2.00
3.00
4.00
TOTAL H_2O (g/g)

water per gram clay, then begins to increase with increasing water content. Unfortunately, the scatter of the data points was quite large.

Two similar plots were obtained from the swelling data of two soil clays (Fig. 22). Both linear plots of external water versus total water have nearly zero slope, and the scatter of points is much less than for the Na-Wyoming bentonite.

The preconditions set on equation [4] only specify that the linear portion of the expansion curve be long enough to determine satisfactorily the parameters of slope and intercept. Thus, it is possible to disregard non-linear portions of the curve. This practice was followed in Figures 10 to 15, where the upper data points were omitted if there was evidence the plots were no longer linear. We see that all the expansion curves for the Na- and Li-montmorillonites did possess linear portions.

In order for the expansion curve to be linear, i.e. for the amount of externally associated water to remain constant as additional increments of water are added to the system, the hydrating forces of the interlamellar regions must be several orders of magnitude greater than the hydrating forces of the external surfaces. Another contributing factor is the large proportion of internal surface compared to external surface (Table 1). A detailed study of the various hydrating forces, however, is beyond the scope of this dissertation.

Table 3 compares the internal surface areas of these montmorillonites, as obtained from the swelling data, to the theoretical planar surface areas as calculated by using the a,b, cell dimensions and the molecular weights (Jackson, 1956, p. 331). Cell dimensions were either taken from A.P.I. Project 49. (1951, Report No. 7) or were determined from the 060 X-ray reflection, and the relation $a = b/\sqrt{3}$ as suggested by Brindley (1961, p. 29). Molecular weights were calculated from the molecular formulas given in A.P.I. Project 49. (1951, Report No. 7).

Agreement between the experimental and theoretical surface areas for the two Na-montmorillonites is reasonably good. The value of 826 m^2/g for Na-Wyoming bentonite is a bit too high, yet is close to the commonly accepted value of 800 m^2/g. The experimental value of 759 m^2/g for the Na-hectorite is slightly less than the theoretical area. This is what one would expect because the internal area should be equal to the total planar surface area, minus that small amount of planar surface area which is external to the individual "packets".

The Li-montmorillonite data, however, was less rewarding;

the experimentally determined areas were considerably higher than expected. The plots (Figures 12 to 15) were all linear, yet the rate of expansion in all cases was inadequate to give surface areas that agreed with the theoretical values. One also notes that the experimentally obtained values for percent external water for the Li-montmorillonites are unreasonably low (Li-nontronite may be an exception).

It was originally thought that Li^+ would be a better choice than Na^+ as the interlamellar saturating cation. This supposition was based on the data of Norrish (1954) and Foster et al. (1955) and also from the data of Phase I of this report. All of these studies showed that Li-montmorillonites, in general, swelled linearly over a greater range than Na-montmorillonites, and particularly at lower water contents where the smaller d-spacing would permit a more accurate determination by X-ray diffraction. The choice, apparently, was a poor one.

It is possible that this unexpected swelling pattern for the Li-montmorillonites may be due to lithium's peculiar hydrating properties. Hendricks et al. (1940), in a comparison of the dehydration properties of a number of mono-ionic-montmorillonites, found that Li^+ was the only alkali metal that showed high energy hydration characteristics. They found 3.3 water molecules associated with each Li^+

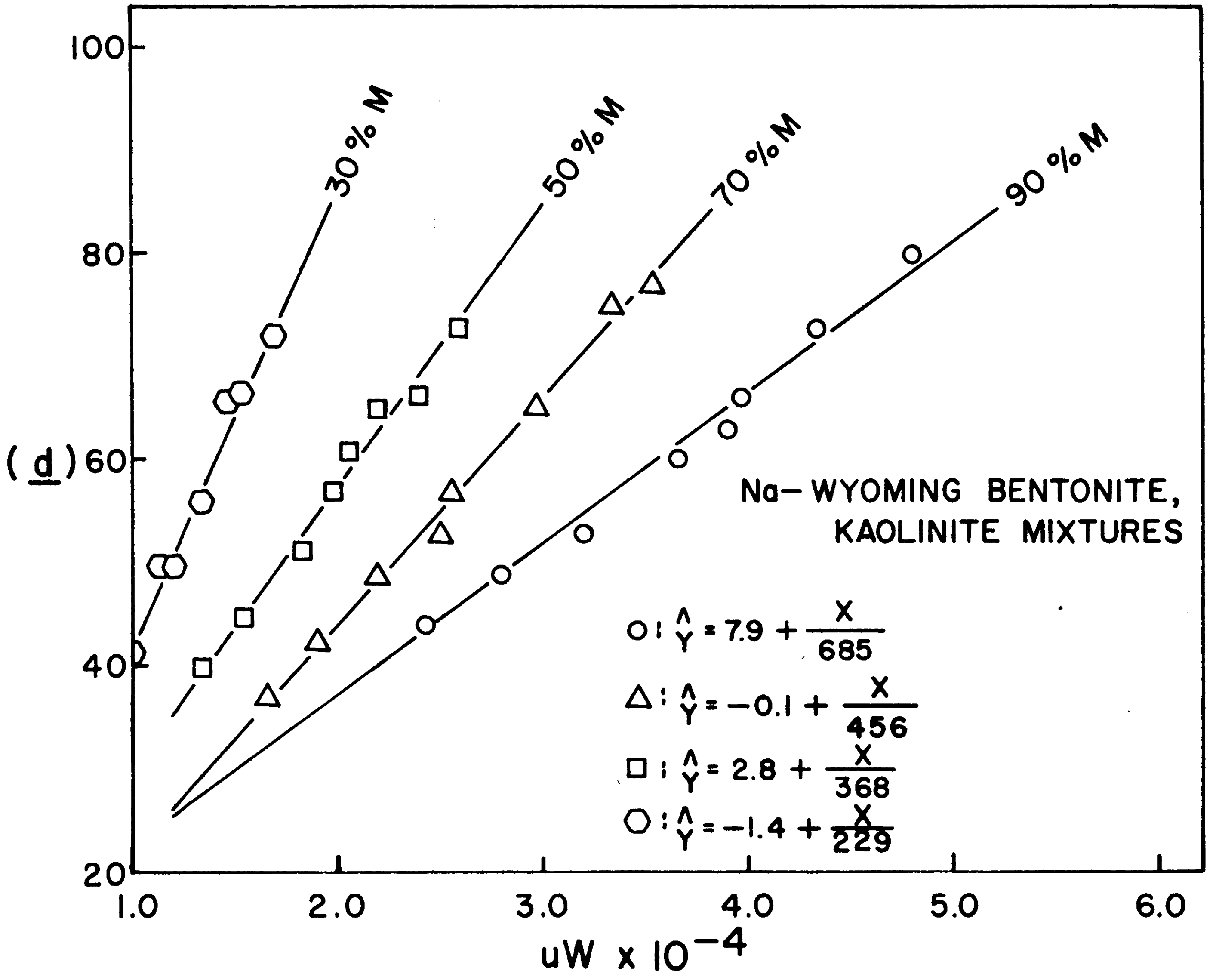
ion. Forslind (1950) points out that due to the high electronegativity of Li^+ ions, they are able to attain a covalent-ionic resonance with attached water molecules. The other alkali metals, however, are unable to do so.

In order to influence the results of this experiment, it would be necessary that the Li^+ ions' spheres of activity unduly influence the water structure (density or specific volume) in the osmotic swelling region. Any effect on water density at water contents below the osmotic region, however, should not change the slopes of the curves in the free-swelling region, but should only displace the curves, either up or down, thus altering the values of the y axes intercepts.

Osmotic expansion of Li-montmorillonites begins at about 50 percent water. For a montmorillonite with 800 m^2/g of internal surface area, this corresponds to a half-thickness of the interlayer water of only 6A or only about two water layers. It is thus reasonable to suppose that the Li^+ ions may indeed alter the interlayer water structure in the osmotic swelling region, thus affecting the pattern of swelling. More work needs to be done on this.

To test the validity of equations [6] and [8], the expansion characteristics of several mixtures of Na-Wyoming bentonite and -kaolinite were studied. Fig. 17 shows the

Fig. 17—Free-swelling of the montmorillonite fraction in Na-saturated Wyoming bentonite,-kaolinite mixtures (where d is the spacing of the expanded montmorillonite in Angstrom units, where u is a constant which is equal to 2×10^4 $(A \cdot m^2)/g$, and where W is equal to the total weight of the water in the system in grams).


30 % M
50 % M
70 % M
90 % M
Na- WYOMING BENTONITE,
KAOLINITE MIXTURES
○ : $\hat{Y} = 7.9 + \frac{X}{685}$
△ : $\hat{Y} = -0.1 + \frac{X}{456}$
□ : $\hat{Y} = 2.8 + \frac{X}{368}$
⬡ : $\hat{Y} = -1.4 + \frac{X}{229}$
(d)
100
80
60
40
20
1.0
2.0
3.0
4.0
5.0
6.0
uW x 10^{-4}

swelling curves for four separate levels of montmorillonite. We see that as the proportion of montmorillonite in a mixed clay system decreases, the rate of swelling increases.

It turns out that this rate of increase is described by a hyperbolic function. Rearranging equation [8], we get:

$$M(d - 9.4) = \frac{u(W - \Theta)}{S_i/M}$$

where the terms on the left side of the equation remain constant at any constant water level.

The results from Fig. 17 have been calculated according to equation [9], and are listed in Table 4. We see that the experimentally determined surface areas agree remarkably well with the corresponding theoretical values. Unfortunately, there was too much variation in the values for the amount of external water to detect any definite trend. Therefore, no attempt was made to evaluate L and L'.

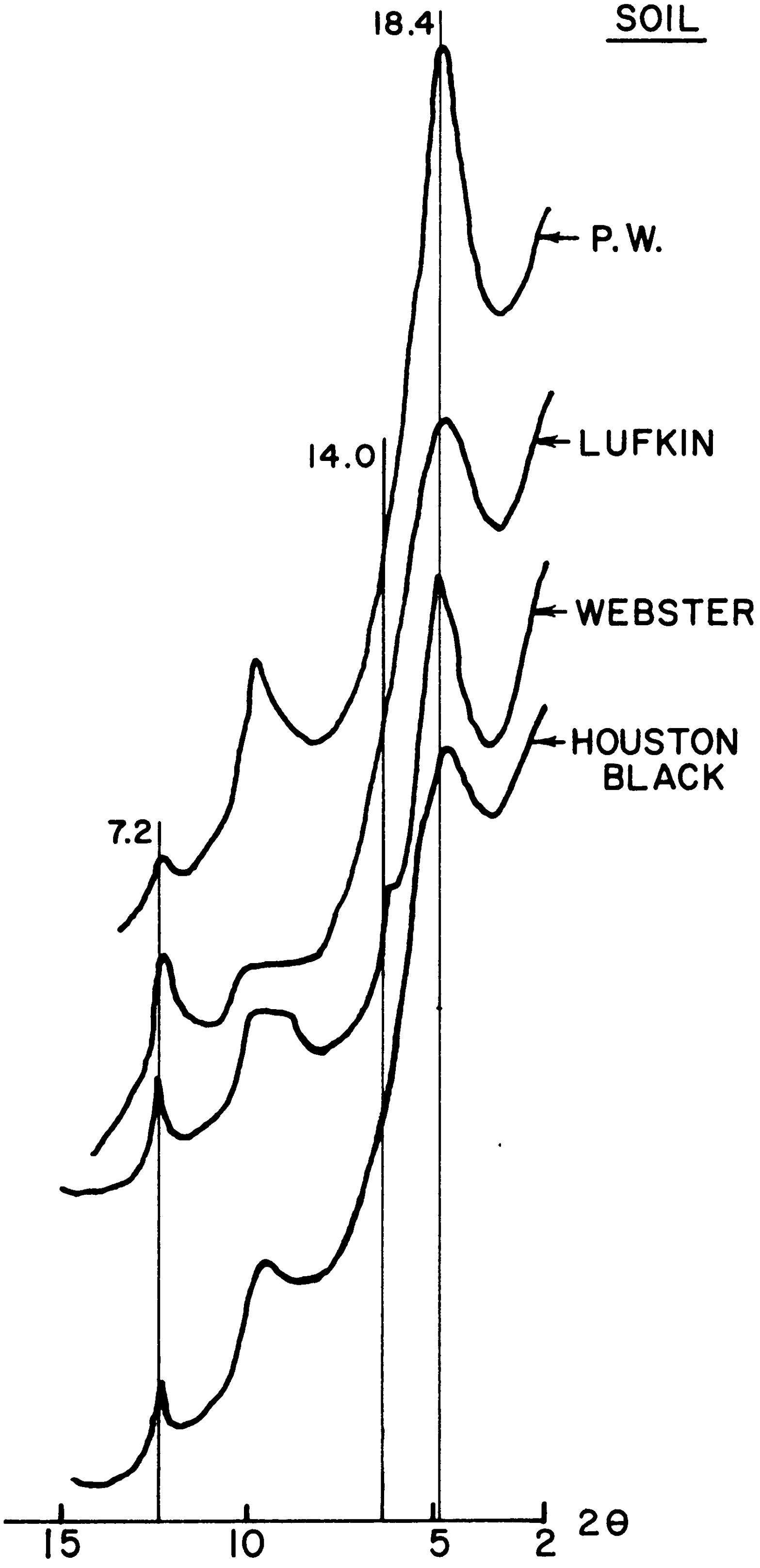
The procedure was next applied to four soil clays, all known to be high in montmorillonite. Fig. 18 shows the X-ray diffraction patterns of $<2\mu$, Mg-saturated and glycerol solvated samples of these clays. All patterns show a strong reflection at about 18.5A, which is the diagnostic peak for montmorillonite. All four soil clays contained other non-swelling, or limited-swelling, clay minerals, as exemplified by the peaks at 7.2A (probably

Table 4—Internal surface areas and percent external water for Na-saturated Wyoming bentonite, -kaolinite mixtures.

Percent Wyoming bentonite	Internal surface area Swelling data	 Theoretical[1]	External water
	m^2/g		%
100	826	746	12.8
90	685	671	5.1
70	456	522	21.7
50	368	373	12.1
30	229	224	12.4

[1] Based on calculated planar surface area.

Fig. 18—X-ray diffractograms of the Mg-saturated and glycerol solvated, <2µ fractions of the soil clays used in study (hkl reflection maxima in Angstrom units; P.W. refers to Prince William sample).



SOIL CLAYS (Mg—GLYCEROL)

kaolinite) and 14A (probably vermiculite).

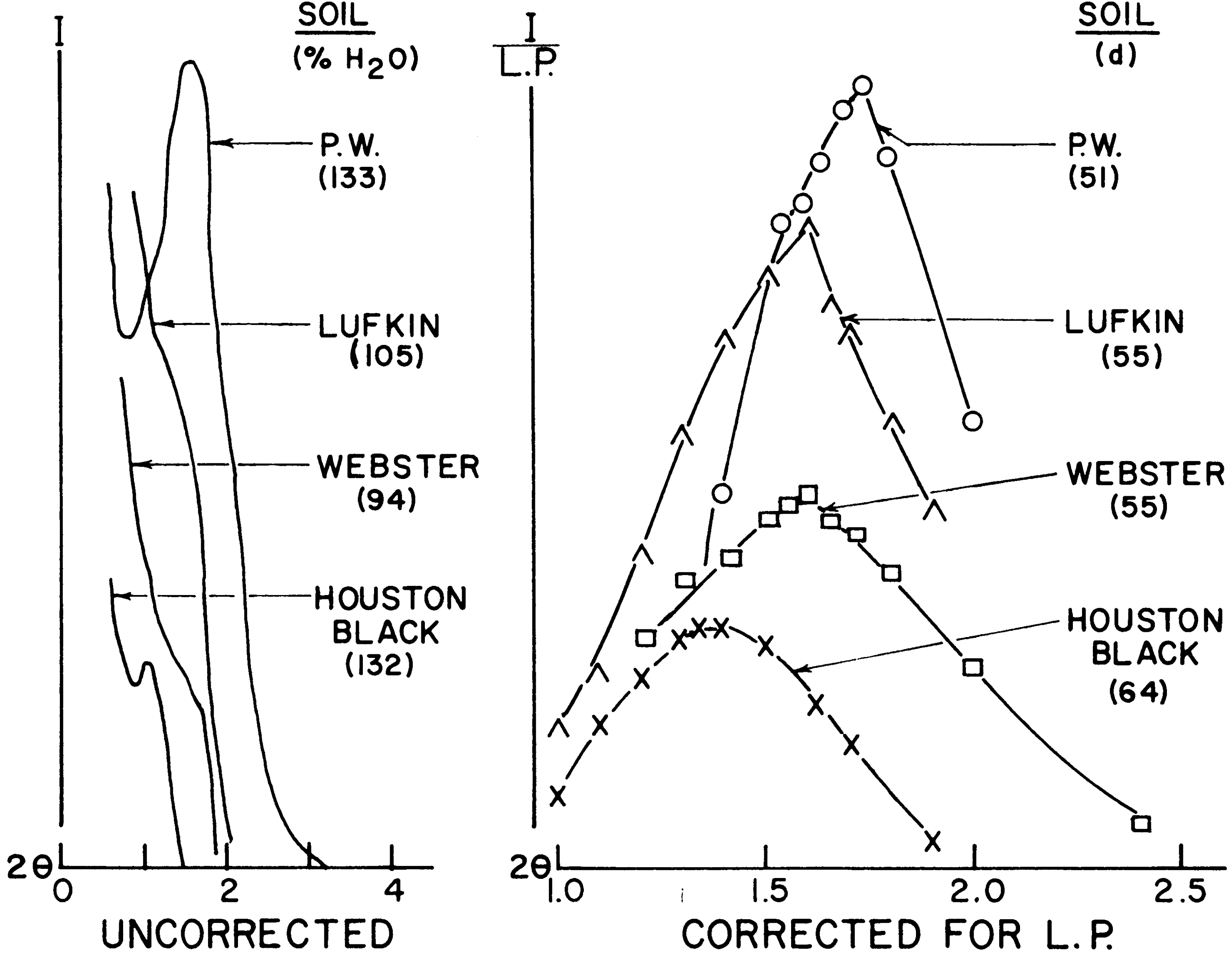
Fig. 19 shows a typical low angle X-ray diffractogram for each of these soil clays in the free-swelling expansion region. The corresponding plots for the patterns after correction for the combined Lorentz and polarization factors are also shown. The d-spacings were always taken from the modes of the corrected patterns.

The plots of d-spacing versus uW for three of the soil clays appear in Fig. 20. The scatter of points is quite small (Fig. 22) - in spite of often having to be content with rather diffuse diffraction peaks. The data for the soil clays are summarized in Table 5.

The swelling characteristics of Na-saturated clay from Houston Black soil, however, were very irregular. Fig. 21 shows that the scatter was quite large. Also, the y axis intercept at 29.8A is too high. (An intercept greater than 9.4A implies that there is less than a zero amount of external water—which is impossible).

Two explanations for this irregular expansion behavior are postulated: (1) small amounts of organic matter may still be present in the interlamellar regions, and inhibit swelling, or (2) the charge density of some layers of the montmorillonite fraction may be too high to permit regular expansion. If the magnitude of charge density of

Fig. 19—Typical X-ray diffractograms of the free-swelling montmorillonite fractions of Na-soil clays, with their accompanying plots after correction for the combined Lorentz and polarization factors (L.P.).



I
SOIL
(% H_2O)
P.W.
(133)
LUFKIN
(105)
WEBSTER
(94)
HOUSTON
BLACK
(132)
2θ
0
2
4
UNCORRECTED
I / L.P.
SOIL
(d)
P.W.
(51)
LUFKIN
(55)
WEBSTER
(55)
HOUSTON
BLACK
(64)
2θ
1.0
1.5
2.0
2.5
CORRECTED FOR L.P.

Fig. 20—Free-swelling of Na-soil clays in water systems (where d is the spacing of the expanded montmorillonite in Angstrom units, where u is a constant which is equal to 2 x 10^4 $(A \cdot m^2)/g$, and where W is equal to the total weight of the water in the system in grams).

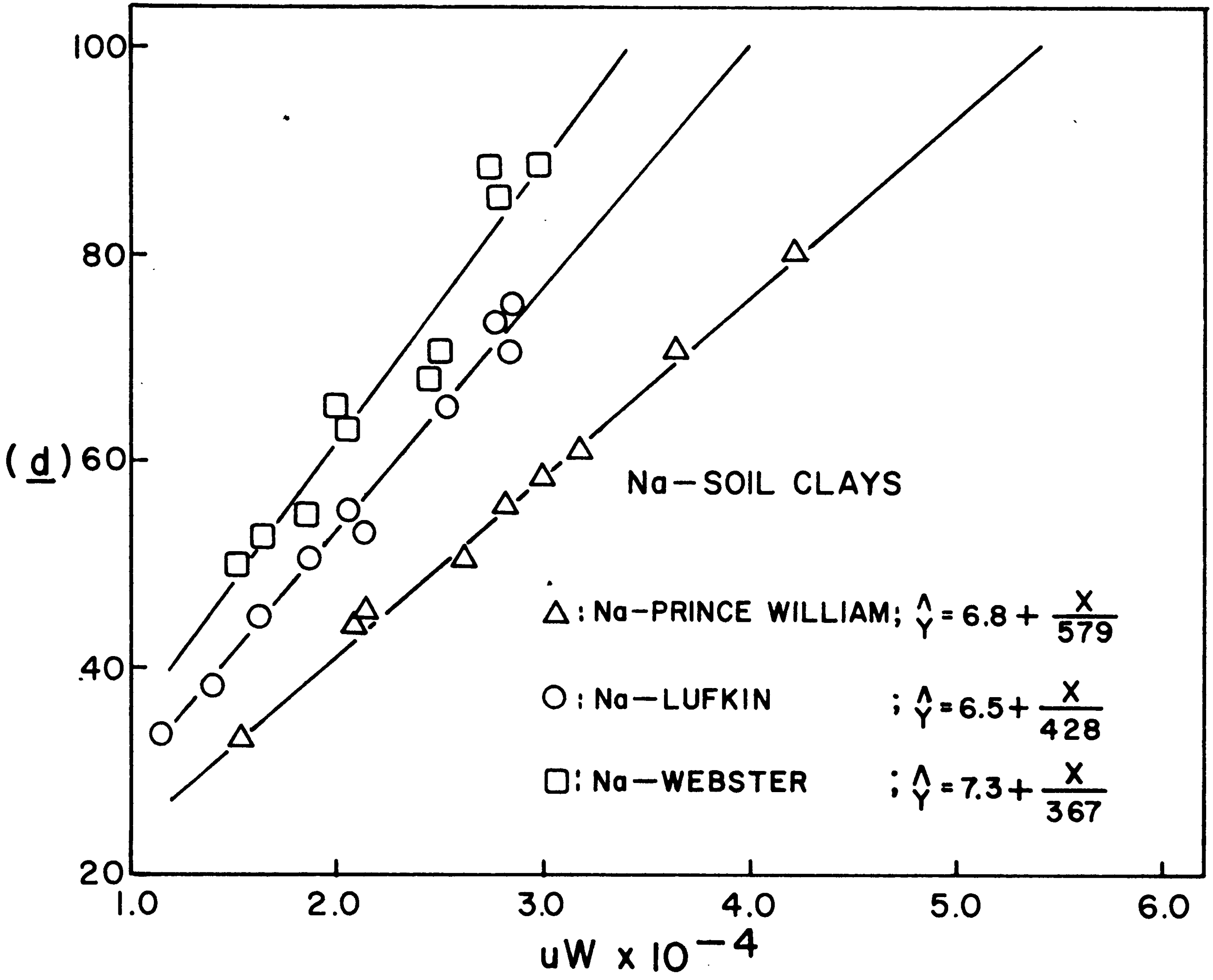

100
80
(d) 60
40
20
1.0
2.0
3.0
4.0
5.0
6.0
uW x 10^{-4}
Na—SOIL CLAYS
△ : Na—PRINCE WILLIAM; $\hat{Y} = 6.8 + \frac{X}{579}$
○ : Na—LUFKIN ; $\hat{Y} = 6.5 + \frac{X}{428}$
□ : Na—WEBSTER ; $\hat{Y} = 7.3 + \frac{X}{367}$

Fig. 21—Swelling of Na-Houston Black in a water system.

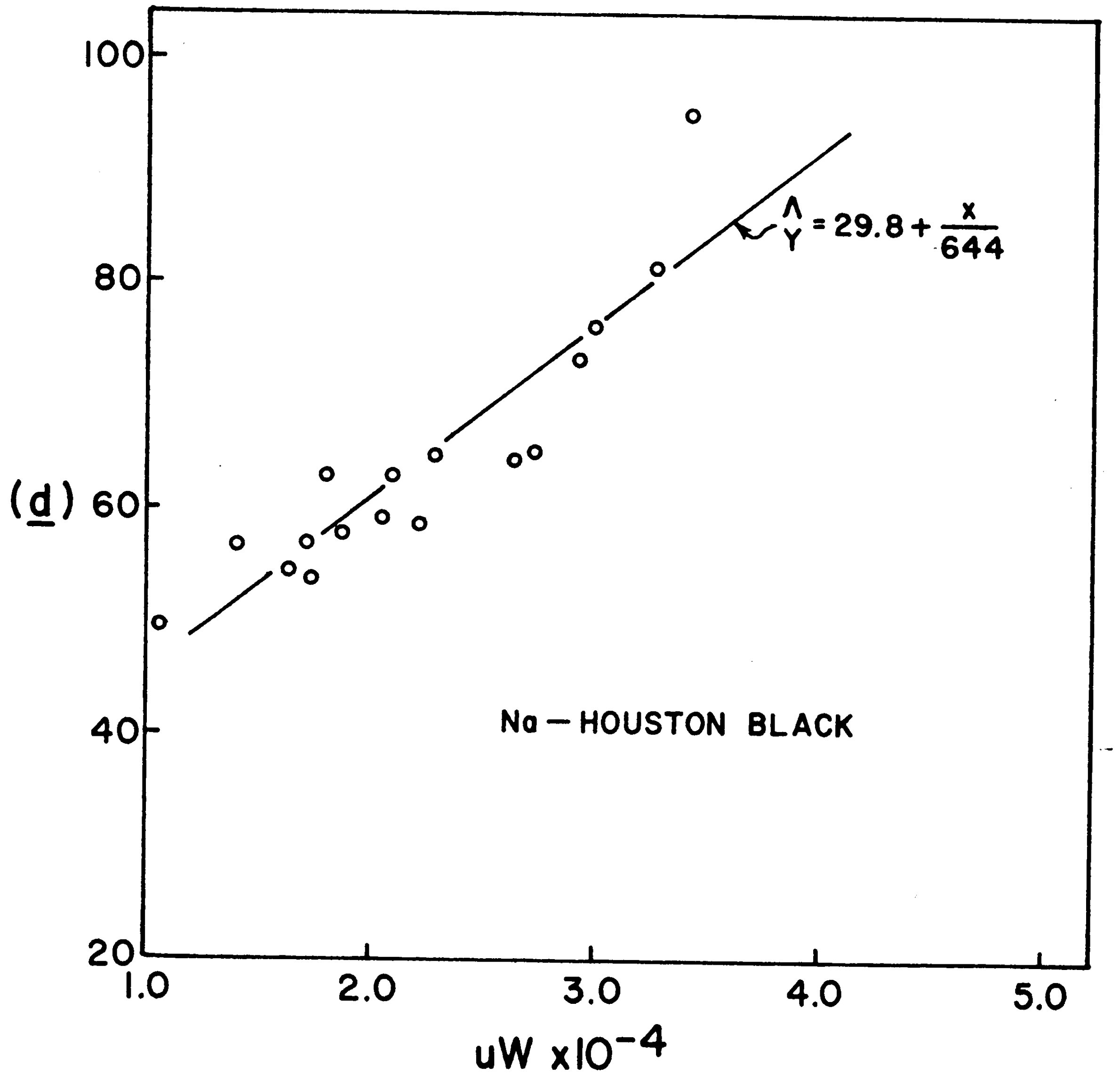

(d)
100
80
60
40
20
1.0
2.0
3.0
4.0
5.0
uW x10^{-4}
$\hat{Y} = 29.8 + \frac{x}{644}$
Na — HOUSTON BLACK

Fig. 22—Plot of the external water versus the total water over the swelling range studied for Na-Lufkin and Prince William.

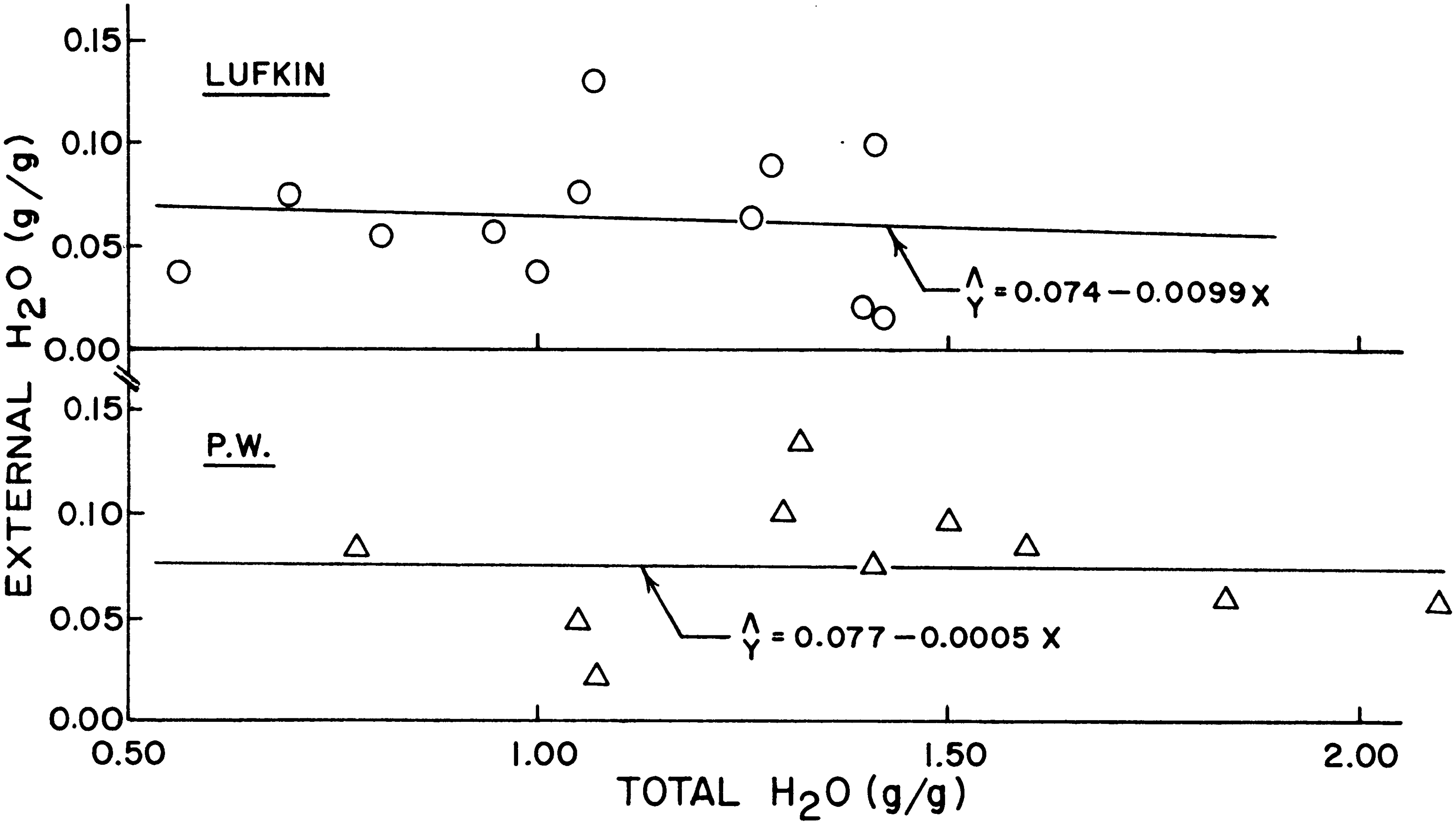

LUFKIN
$\hat{Y} = 0.074 - 0.0099X$
P.W.
$\hat{Y} = 0.077 - 0.0005X$
EXTERNAL H_2O (g/g)
0.15
0.10
0.05
0.00
0.15
0.10
0.05
0.00
0.50
1.00
1.50
2.00
TOTAL H_2O (g/g)

Table 5—Experimentally determined parameters of internal surface area, external water and montmorillonite in soil clays.

Soil clay	Internal surface area	External water	M$^{1.}$	C.E.C.$^{2.}$
	m^2/g	%	%	me/100g
P.W.	579	7.5	72	85.6
Lufkin	428	6.2	53	68.1
Webster	367	3.9	46	66.3
Houston Black	644	---	--	94.0

1.Based on internal surface area of 800 m^2/g using equation [10] .

2.Based on exchangeable Na$^+$, at 300C dry weight basis.

the montmorillonite approached that of vermiculite, one might expect a rather random situation as to whether the individual Na-saturated plates expanded osmotically or not. Houston Black clay was found to have a CEC of 94 me/100g, (Table 5), which is high for a soil clay, and thus supports the 2nd postulate. A study of the swelling characteristics of this clay after Li^+ saturation might resolve this problem.

The percentage of montmorillonite in the three soil clays: Prince William, Lufkin, and Webster, has been calculated from the swelling data (Table 5), by use of equation [10] . To do this it was necessary to assume some value for the internal surface area per gram of montmorillonite. The commonly accepted value for Wyoming bentonite of 800 m^2/g was selected. The values for θ, the external water, were calculated from the respective y axis intercept values shown in Fig. 20.

It was originally assumed that θ was a constant for any one particular soil or clay mixture, but it was also assumed that the value of θ should be a function of the type and relative proportions of the various clay minerals present in the mixture. As already stated, no trend in the value of θ could be found for the Na-Wyoming bentonite, -kaolinite mixtures, due to a large amount of scatter in the calculated values of θ. Another attempt was made to detect such a trend by plotting the experimentally obtained values of the external water versus the internal surface area for all the Na-montmorillonites (Fig. 23). Again the scatter is too great to detect any significant trend. However, we see that θ seems to fluctuate randomly about a mean of 0.10 = 0.05 gram water per gram clay. This relatively large fluctuation in θ is misleading, in that the values of θ are quite small compared to the total amount of water in the clay system.

Thus, as the theory indicates, we normally can safely substitute the average value of θ into equation [11]; then after assuming a surface area of 800 m^2/g for the montmorillonite present in the sample, we can solve directly for the amount of montmorillonite (M) present for each data point of d and W.

A nomograph for the determination of the amount of montmorillonite present in a clay mixture has been prepared (Fig. 24) with the aid of equation [11]. Again, the assumptions were: (1) $(S_1/M) = 800\ m^2/g$, and (2) $\theta = 0.10\ g/g$. To find percent M, one merely determines the intersection of d and $\%H_2O$. A similar nomograph was previously prepared by Fink and Thomas (1965) assuming a value of 0.50 for θ. This value is now known to have been too large.

Fig. 23—Plot of the experimentally determined values of external water versus internal surface area.

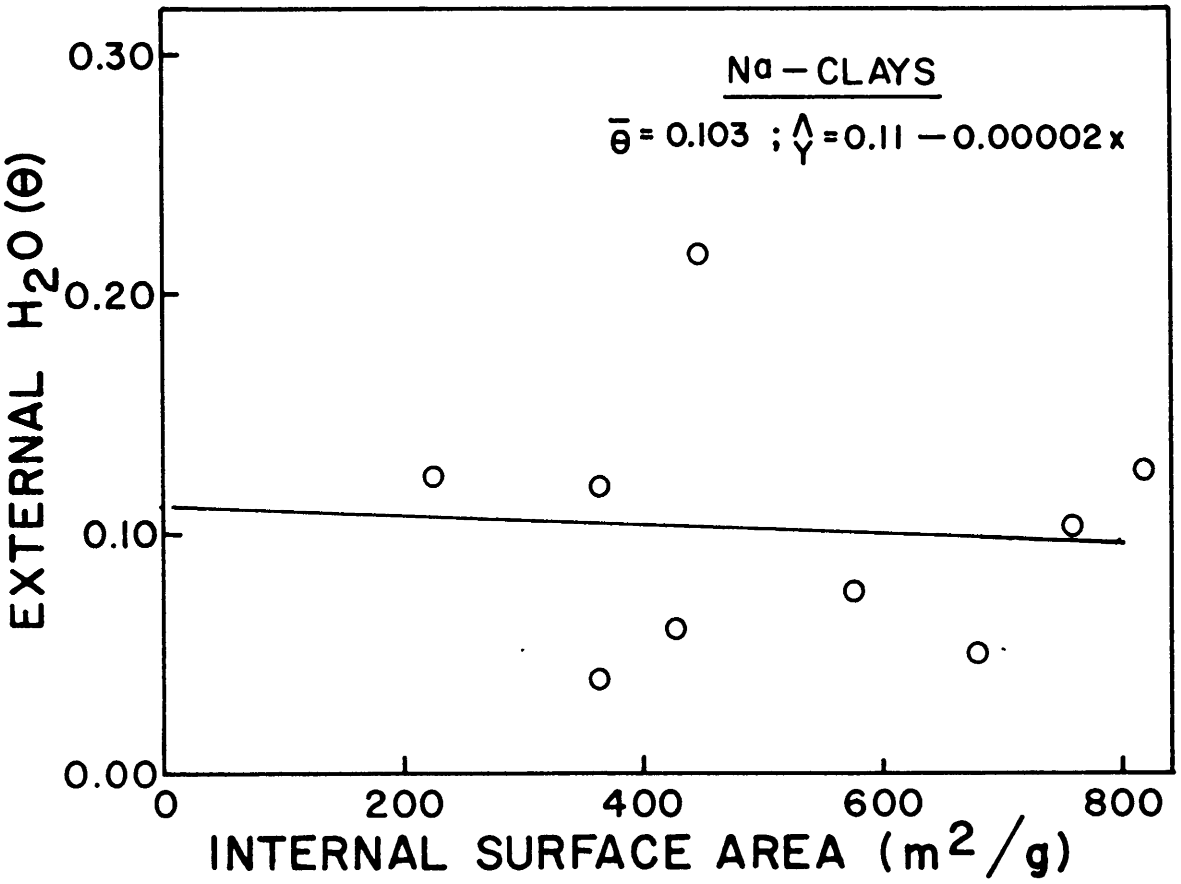
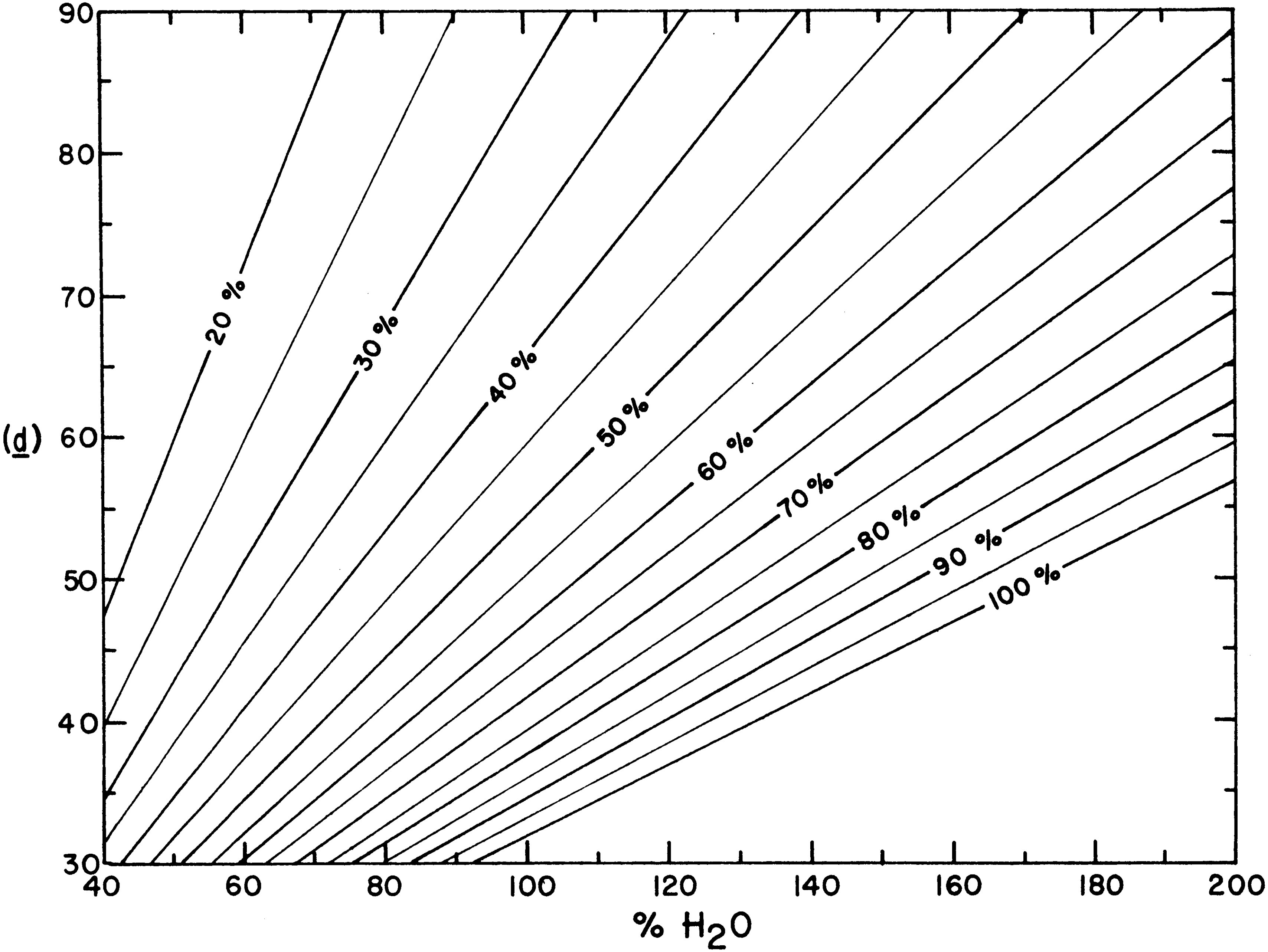

Na – CLAYS
$\bar{\theta} = 0.103$; $\hat{Y} = 0.11 - 0.00002x$
EXTERNAL H_2O (θ)
0.30
0.20
0.10
0.00
0
200
400
600
800
INTERNAL SURFACE AREA (m^2/g)

Fig. 24—Nomograph for determination of percent montmorillonite in a clay mixture, using free-swelling data.


(d)
90
80
70
60
50
40
30
40
60
80
100
120
140
160
180
200
% H_2O
20 %
30 %
40 %
50 %
60 %
70 %
80 %
90 %
100 %

It would be advantageous to know something about the errors one could expect in solving for M if one assumed incorrect values for θ or S_i/M. This has been attempted graphically in Figures 25 and 26. The plots were determinded using equation 11 .

In Fig. 25 we see that the error in the determination of the amount of montmorillonite (M) in the system due to an error in the selection of the value for the amount of external water (θ), not only depends on the amount of error in θ, but also depends on the total amount of water in the system, and on the amount of montmorillonite present. For example, if θ actually equals 0.20 instead of the assumed 0.10 (i.e. $\Delta\theta = 0.10$), the error in M at 0.40 grams of water per gram of clay at the 30% M level will be 0.10 grams of montmorillonite - or about a 30 percent error. At 1.0 gram of water per gram of clay this error has been reduced to only 0.03 grams of montmorillonite - or only about a 10 percent error. Of course at the higher montmorillonite levels the percentage error, fortunately, will be much less.

The proportionate error in the amount of montmorillonite in the system ($\Delta M/M$) due to assuming the incorrect value for the amount of internal surface area per gram of montmorillonite (S_i/M) is shown in Fig. 26. This error

Fig. 25—Calculated possible error in determination of montmorillonite (M) in a clay mixture by assuming an incorrect value for the amount of external water (θ); based on $\theta = 0.10$ g/g.

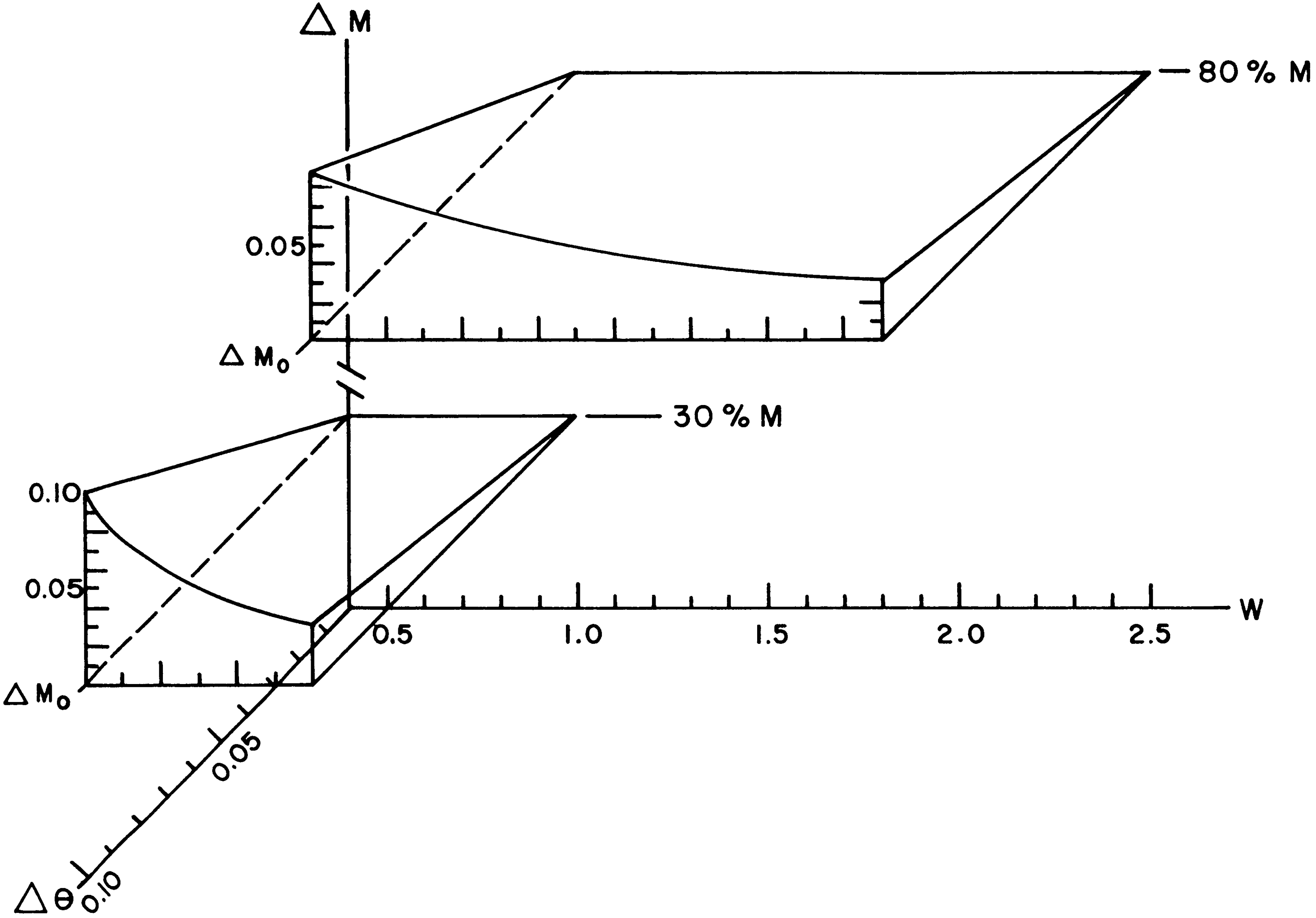
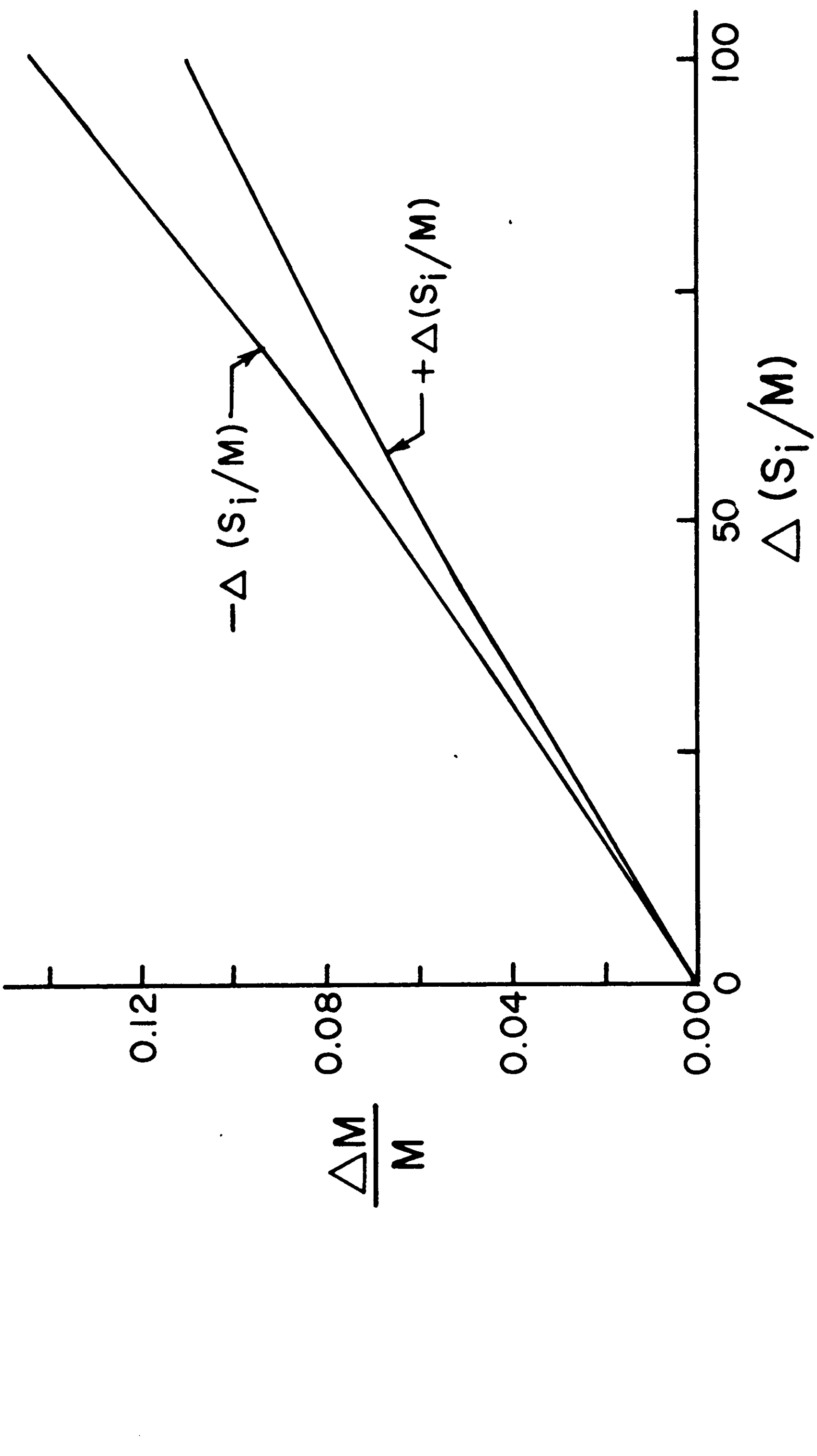

ΔM
80 % M
0.05
ΔMo
30 % M
0.10
0.05
ΔMo
0.5
1.0
1.5
2.0
2.5
W
0.05
0.10
Δθ

Fig. 26—Calculated possible error in determination of montmorillonite (M) in a clay mixture by assuming an incorrect value for internal surface area per gram of montmorillonite (S_i/M); based on $(S_i/M) = 800\ m^2/g$.


$\frac{\Delta M}{M}$
0.00
0.04
0.08
0.12
0
50
100
$\Delta\,(S_i/M)$
$-\Delta\,(S_i/M)$
$+\Delta\,(S_i/M)$

is independent of the amount of water and the amount of montmorillonite in the system. It is only dependent on the magnitude (positive or negative) of the error involved in assigning a value to the internal surface area of the montmorillonite present in the sample. For example, if S_i/M actually equals 700 m^2/g instead of the assumed 800 m^2/g (i.e. $\triangle(S_i/M) = 100$), the proportionate error in M will be about 0.13; if S_i/M equals 900 m^2/g, the proportionate error in M will be about 0.09.

XI Summary and conclusions

Free-swelling properties of montmorillonites in water systems were studied using X-ray diffraction techniques. Four specimen type montmorillonites (Wyoming bentonite, Otay bentonite, hectorite and nontronite) and several soil clays were selected. In Phase I of the study the differential swelling properties were related to type of cation on the exchange complex and to variations between the mineralogical properties of the montmorillonites.

It was found that all Ca-montmorillonites expanded in a step-wise manner to a maximum spacing of about 20A; all Li-montmorillonites expanded linearly with water contents greater than 35 percent; sodium saturated Otay and Wyoming bentonites and nontronite showed a discontinuity in their expansion patterns up to about 110 percent water, then linear expansion at higher water contents. The Na-hectorite, however, did not exhibit this discontinuity, but rather expanded linearly over this region.

The soil clays studied in Phase I showed a large amount of individual variation in their ability to expand regularly in the osmotic swelling region. Only one soil clay (Webster) was found to exhibit distinct regular expansion in this swelling region.

It was concluded that divalent calcium with it's strong electrostatic attraction for the clay plates, prevents free osmotic swelling of the montmorillonite lattice. Interlamellar swelling in Ca-montmorillonites is, therefore, attributed mainly to various hydration states of the Ca^{2+} ions.

The main difference in the swelling characteristics of montmorillonites saturated with either Li^+ or Na^+ (i.e. the discontinuity in their expansion) is attributed to the higher state of hydration of the Li^+ ions, which permit them to be more readily dissociated from the clay surface. It is felt that the relatively strong association between the Na^+ ions and the negatively charged internal basal oxygen surfaces tend to restrict their dissociation until fairly large amounts of water are present, i.e., the energy of the associated water approaches that of free water. As water is added to the system, the plates expand, one at a time, from a low hydration state in which free-expansion is prevented by the Coulombic attraction between the cation and the clay surface, to a hydration state where the hydrating force is mainly osmotic. This osmotic force is attributed to the diffuse or double-layer distribution of the now dissociated interlayer cations.

That variations between the mineralogical properties of montmorillonites differentially influences swelling characteristics, was exhibited with the presence or absence of the discontinuity in the expansion of Na-saturated montmorillonites. Again, as in the comparison between the swelling characteristics of Li- versus Na-montmorillonites, the presence or absence of the discontinuity is attributed to the degree of dissociation of the interlayer cation from the basal oxygen surfaces. Hectorite, with its seat of charge located in the octahedral layers, permits a rather uniform diffusion of this charge over the entire basal oxygen surfaces. The other montmorillonites tested, however, with at least a part of their seat of charge located in the tetrahedral layers, concentrate this charge on the adjacent basal oxygens as a point charge. The Na^+ ions may be more easily dissociated from the surfaces when the associated negative charges are distributed uniformly over a relatively large area, than when they exist as point charges.

In Phase II of this study free-swelling properties of montmorillonites were utilized to quantitatively determine: (1) internal surface areas; (2) the amount of water which is hydrating the external surfaces; and (3) the amount of montmorillonite present. All three of these factors were studied with the pure, specimen type, montmorillonites used in Phase I, and with montmorillonites present in clay type mixtures, including soils.

It was hypothesized, that in the free-swelling region, if the plot of d-spacings in Angstroms versus a function of the total water content of the sample (uW) was linear, the reciprocal of the slope of that line should equal the internal surface area, and the y axis intercept should be directly related to the amount of external water in the system. The term u in the abscissa is a constant equal to 2×10^4 (A m^2)/g, and W is equal to the total water in the system.

Experimentally, it was found, that the internal surface area data obtained from the swelling curves of Na-saturated montmorillonites, compared favorably with theoretical values. Results for the Li-montmorillonites were less useful. It is thought that strong interactions between the Li^+ ions and the interlayer water may have altered the specific volume of that water, thus unfavorably affecting the d-spacing, and, consequently the slope of the line and the y axis intercept.

The method was also shown to be useful for determining the internal surface areas of soil clays, and, then, if certain reasonable assumptions were made, this same data provided a very good indication of the amount of montmorillonite present in the clay mixture.

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XIV Appendix

Section 1: Procedure for conversion of moisture percentages based on clay samples dried at 110C, to a 300C base.

List of Symbols

m_{110} = weight of, 110C dried, "reference" clay sample.

m_{300} = weight of above sample, dried at 300C.

Δw = weight of water removed from "reference" clay sample between 110C and 300C = $(m_{110} - m_{300})$.

M_{110} = weight of 110C dried, clay sample used in diffraction study.

M_{300} = weight of same sample, on 300C dried weight basis, as determined by calculations based on weight changes of "reference" samples.

W_{110} = weight of water removed at 110C from clay sample used in diffraction study.

ΔW = weight of water calculated to be present on clay sample, used in diffraction study, between 110C and 300C.

W_T = $W_{110} + \Delta W$

To convert moisture percentages of the samples used in the diffraction study from a 110C dried basis to a 300C dried basis, three "reference" samples of each monoionic-saturated clay were dried and weighed - first after drying at 110C (m_{110}) and then after drying at 300C (m_{300}). From this, Δw was determined for each of the three "reference" samples. The average of $\Delta w/m_{110}$ for the three samples was then obtained.

To obtain ΔW, for the samples used in the diffraction study, the following relationship was used:

$$\frac{\Delta w}{m_{110}} = \frac{\Delta W}{M_{110}} = \Delta W$$

To obtain the percent moisture, based on a 300C dried weight basis, the following relationships were used:

$$W_T = W_{110} + \Delta W$$

$$M_{300} = M_{110} - \Delta W = 1 - \Delta W$$

$$\% \ H_2O_{300} = \frac{W_T}{M_{300}} \times 100$$

Section 2: Procedure for back calculating to determine weights of air dried (25C) Wyoming bentonite and Georgia kaolinite needed to give mixtures of these two clays the desired weight proportions upon subsequent drying to 300C.

List of Symbols

m_{25} = weight of, 25C dried, "reference" clay sample.

Δw = weight of water removed from "reference" clay sample between 25C and 300C.

ΔW = weight of water calculated to be present on clay sample used in diffraction study, between 110C and 300C.

M_{25} = weight of sample, at room temperature, needed to give the correct proportion of it in a clay mixture dried at 300C.

M_{300} = weight of same sample, on a 300C dried weight basis, as determined by calculations based on weight changes of "reference" samples.

To determine the necessary amounts of the air-dry samples of Na-Wyoming bentonite and Georgia kaolinite needed to give the desired weight ratios when mixed and dried at 300C, the following procedure was followed.

Two "reference" samples of each clay were used to determine water loss between 25C and 300C. From this, the relation used in Section 1 was established to determine the water which would theoretically be lost from that portion of the clay mixture used in the diffraction study when the mixture was dried to 300C. The following relations were used:

$$M_{300} = M_{25} - \Delta W$$

$$\Delta W = \frac{\Delta w}{m_{25}} \cdot M_{25}$$

$$M_{300} = M_{25} - \frac{\Delta w}{m_{25}} \cdot M_{25}$$

$$= M_{25} \left(1 - \frac{\Delta w}{m_{25}}\right)$$

Therefore:

$$M_{25} = M_{300} \left(1 - \frac{\Delta w}{m_{25}}\right)^{-1}$$

From these relationships it was possible to use predetermined amounts of air-dry samples of the two clays used in the mixtures, and still be assured of the correct ratios of each when subsequently dried at 300C.

Abstract

Free-swelling properties of montmorillonites in water systems were studied using X-ray diffraction techniques. Four specimen type montmorillonites (Wyoming bentonite, Otay bentonite, hectorite and nontronite) and several soil clays were selected.

In Phase I of the study the differential swelling properties were related to the type of cation on the exchange complex and to variations in the mineralogical properties of the montmorillonites.

It was found that all Ca-montmorillonites expanded in a step-wise manner to a maximum spacing of about 20A; all Li-montmorillonites expanded linearly with water contents greater than 35 percent; sodium saturated Otay and Wyoming bentonites and nontronite showed a discontinuity in their expansion patterns up to about 110 percent water, then linear expansion at higher water contents. The Na-hectorite, however, did not exhibit this discontinuity, but rather expanded linearly over this region.

It was concluded that divalent calcium with its strong electrostatic attraction for the clay plates, prevents free osmotic swelling of the montmorillonite. Interlamellar swelling in Ca-montmorillonites is, there-

fore, attributed mainly to various hydration states of the Ca^{2+} ions.

The main difference in the swelling characteristics of montmorillonites saturated with either Li^+ or Na^+ (i.e. the discontinuity in their expansion) is attributed to the higher state of hydration of the Li^+ ions, which permit them to be more readily dissociated from the clay surface. It is believed that the relatively strong association between the Na^+ ions and the negatively charged internal basal oxygen surfaces tend to restrict their dissociation until fairly large amounts of water are present, i.e., the energy of the associated water approaches that of free water.

Variations between the mineralogical properties of montmorillonites was found to influence swelling characteristics, as was exhibited by the presence or absence of the discontinuity in the expansion of Na-saturated montmorillonites. Again, as in the comparison between the swelling characteristics of Li- versus Na-montmorillonites, the presence or absence of the discontinuity is attributed to the degree of dissociation of the interlayer cation from the basal oxygen surfaces. Hectorite, with its seat of charge located in the octahedral layers, permits a rather uniform diffusion of this charge over the entire basal oxygen surfaces. The other montmorillonites tested, however, with at least a part of their seat of charge located in the tetrahedral layers, concentrate this charge on the adjacent basal oxygens as a point charge. The Na^+ ions may be more easily dissociated from the surfaces when the associated negative charges are distributed uniformly over a relatively large area, than when they exist as point charges.

In Phase II of this study free-swelling properties of montmorillonites were utilized to determine quantitatively: (1) internal surface areas; (2) the amount of water which hydrates the external surfaces; and (3) the amount of montmorillonite present. All three of these factors were studied with specimen type montmorillonites used in Phase I, and with montmorillonites present in clay type mixtures, including soils.

It was hypothesized, that in the free-swelling region, if the plot of d-spacings in Angstroms versus a function of the total water content of the sample (uW) was linear, the reciprocal of the slope of that line should equal the internal surface area, and the y-axis intercept should be directly related to the amount of external water in the system. The term u in the abscissa is a constant equal to

2×10^4 $(A \cdot m^2)/g$, and W is equal to the total grams of water in the system. The free-swelling data for Na-montmorillonites compared favorably with theoretical values, while the results for Li-montmorillonites surprisingly did not.