SWELLING CHARACTERISTICS
OF HYDROXY-ALUMINUM
INTERLAYERED CLAYS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

In the past two decades considerable attention has been given to the occurrence, formation, and properties of hydroxy-cation materials in the interlayer spaces of the expansible layer silicates. Hydroxy-aluminum (hydroxy-Al) appears to be the principal component of the non-exchangeable material which is found in vermiculite and montmorillonite of soils and sediments, but under specific environmental conditions hydroxy-Fe and hydroxy-Mg interlayers may also be important. Dioctahedral expansible layer silicates are frequently interlayered. Clay properties altered by interlayer material include cation exchange capacity (CEC), cation-fixing ability, and shrink and swell properties, all of which have considerable impact on agricultural and engineering practices.

The bulk of the literature on this subject is concerned with the occurrence, formation, and removal of the interlayers. Although differential thermal and infrared analyses have been used in interlayer studies, the principal research tool has been X-ray diffraction. To this author's knowledge, no work has been done specifically on the macroscopic swelling of clays treated with hydroxy-Al interlayers.

The purpose of this investigation was to determine the influence of hydroxy-Al treatments on macroscopic swelling and related properties of montmorillonitic clays.

CHAPTER II

REVIEW OF LITERATURE

Montmorillonitic and vermiculitic clays are generally referred to as expansible layer silicates because of their ability to adsorb polar molecules on all layer[1] surfaces. The accumulation of polar molecules in the clay interlayer spaces forces the layers apart, resulting in swelling of the clay. Most silicate clays, however, do not exhibit swelling for reasons which will be discussed below.

Soils which exhibit large volume changes on wetting or drying generally contain considerable amounts of swelling clays. However, soil swelling is complicated by other factors, such as particle arrangement in the soil matrix and the presence of air- and water-filled voids. These complications, however, do not detract from the importance of clay swelling in soils of agricultural and engineering significance.

Clay-Water Interaction

There are essentially two types of clay-water interactions which have been described to account for the swelling exhibited by clay: (1) hydration of the exchangeable ions and the exposed clay surfaces,

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[1] The terms "layer" and "interlayer" are herein used as recommended by the Nomenclature Committee (1966-67) of the Clay Minerals Society (Brindley et al., 1968).

often referred to as crystalline swelling, and (2) macroscopic swelling, an osmotic effect caused by the presence of exchangeable cations near the surfaces of the clay layers. The first mechanism takes place at relative vapor pressures of less than 1.0, a condition seldom found to exist in natural soils. The clay-water relationship of particular interest in soils, therefore, is that which is affected by the osmotic mechanism.

Crystalline Swelling

Hydration of exchangeable cations and clay surfaces takes place in two stages. In the first stage, water is adsorbed from a moist atmosphere by a dry clay as a result of the hydration energy of the exchangeable cations on the surfaces of the clay. The binding energy of this water varies with the cation species present, but in all cases the energy is quite high, as evidenced by the fact that this water of hydration is not completely removed from the clay until a temperature of ca. 300° C is reached (Grim, 1968).

In the second stage of crystalline swelling, the water forms hydrogen-bonds with the oxygen or hydroxyl surfaces of the clay layers. The energy of these bonds is not nearly as high as that of cation hydration, but the attraction energy is high enough to cause clay surfaces to adsorb water from a moist atmosphere. Four discrete layers of water form on the surfaces of Na-montmorillonite at 99% relative humidity (Norrish, 1954) and the basal spacing at this stage of hydration is approximately 20 angstroms (A). At this point the clay has taken up about 0.5 g water/g clay and, if the clay particles were previously in closest packing, has roughly doubled its dry volume.

Potassium-saturated montmorillonite contains one or two layers of water at 100% relative humidity (Harward, Carstea, and Sayegh, 1969).

Since the soil atmosphere is near 100% relative humidity under all but extreme conditions (Page, 1955), one would generally expect soil clay surfaces to be fully hydrated. Shrinking and swelling of soil clay, then, should seldom be due to differences in the hydration state of the clay surfaces.

Macroscopic Swelling

When swelling clays come in contact with free water, large quantities of water are adsorbed and the formation of gels and sols results. This process is herein referred to as macroscopic swelling. The amount of water adsorbed, and thus the amount of swelling, is controlled by several factors, among which are: (1) the density and location of cation exchange sites, (2) the concentration and species of cations in the clay-water system, and (3) the presence or absence of binding forces in the interlayer spaces. In soil one would also have to consider, among other things, the influence of particle arrangement (cf. Emerson, 1959) and particle size distribution.

Cation Exchange Sites

Brindley and MacEwan (1953) found that, if the surface charge density of a mineral was between 0.6 and 1.4 negative charges per unit cell, the mineral expanded; with more or fewer charges, the mineral did not expand without drastic chemical treatment. The results of Quirk and Theng (1960) support these findings. When the charge density of a montmorillonite sample was decreased from 1.0×10^{-7}

meq/cm^2 to 0.6 x 10^{-7} meq/cm^2, the ability of the sample to swell was reduced from 5.0 to 0.62 g water/g clay.

Foster (1955) found no relationship between the swelling of various Na-montmorillonites and their exchange capacities. Instead, she found a relationship between swell and octahedral substitution in the minerals. Harward and Brindley (1966) reported that synthetic beidellites having tetrahedral substitution swelled less than synthetic montmorillonites having octahedral substitution.

The dependence of swell on source of charge was further borne out by the work of Harward et al. (1969). They reported that beidellite solvated with glycerol vapor resulted in the equivalent of a one-layer complex, whereas montmorillonite formed a two-layer complex. A probable explanation is that tetrahedral substitution allows less dissociation of the exchangeable cations, resulting in fewer osmotically active cations to produce swelling.

Concentration and Species of Cations

The silicate clay particle, with a deficit of positive charges in its crystalline structure, has often been viewed as a kind of osmometer (cf. Bolt, 1956), the clay particle itself acting as the semipermeable membrane holding the exchangeable cations within a definite distance from the surface. This distance, the extent of the diffuse double layer, is determined by the concentration and species of ions in the ambient solution. Since diffuse double layers do not overlap each other, large double layers result in large separation of particles.

For any cation, the diffuse double layer is greatest in pure water and decreases with increasing salt concentration. Thus, a clay flake immersed in a concentrated salt solution will swell when the salt concentration of the solution is decreased (cf. Norrish, 1954; Rowell, 1963). The swell is caused by the dilute solution moving into the interlayer spaces due to the lower osmotic potential of the interlayer solution.

The hydrated size of the cations also influences the thickness of the diffuse double layer and thus the amount of swelling. Highly hydrated ions such as Na^+ and Li^+ dissociate considerably from the surface and result in a thick double layer. Ions such as K^+ are less highly hydrated and form thinner double layers. Divalent and trivalent ions dissociate very little, form thin double layers, and exhibit little swelling.

It might be noted here that the confining pressure necessary to prevent a clay-water system from expanding is referred to as the clay swelling pressure. Calculated swelling pressures agree fairly well with experimental findings for Na-montmorillonite (Warkentin and Schofield, 1962), but leave much to be desired for Ca-clay systems (Aylmore and Quirk, 1962).

Binding Forces

The influence of clay mineral type on swelling has already been alluded to in the discussion of charge density and location. It should be noted that 1:1 layer phyllosilicates such as kaolinite and halloysite do not take up water between the layers because of hydrogen bonding between the hydroxyl surface of one layer and the oxygen surface of an adjacent layer. The resultant attractive energy is sufficiently strong to prevent the surfaces from hydrating, With a few exceptions, the montmorillonite-saponite and vermiculite groups are the only clay minerals which swell. However, the presence of several materials on the layer surfaces of these clays is known to have considerable effect on the clay properties. Removal of iron oxides in preparation for clay mineralogical analysis is generally recommended (Jackson, 1956; Kunze, 1964), although Harward, Theisen, and Evans (1962) reported that such treatments removed interlayer materials and changed the mineralogical composition of soil clays. Rich (1968) listed numerous examples of interlayer material in soil and sediment smectites and vermiculites. Such material may bind clay layers together and affect their swelling properties.

The State of the Problem

In an excellent critical review, Martin (1962) described the literature in the field of clay-water interactions as "an overwhelming morass." The major difficulty he found in evaluating the published data was that the clay surfaces used by the various investigators were rather poorly defined. The absolute necessity of careful preparation of the clay surfaces due to their sensitivity to alteration was also emphasized by Bates (1958) and Davey and Low (1968).

Beyond the problem of poorly defined systems and experimental conditions (e.g., "A Na-montmorillonite was prepared."), the literature is further complicated by the existence of differing concepts of the physical nature of the individual clay particle and of the clay-water system. More than a casual reading of an article is usually required to decipher the author's "school of clay thought."

Some workers (cf. van Olphen, 1963, p. 93-95) visualize the clay particle as being stiff enough to stand on "edge" and support considerable weight before bending. Rebound of bent particles is mentioned as a reason for swell when a load is removed from a clay soil (Means and Parcher, 1963). Still others (McAtee and Wells, 1967; Beutelspacher and Van der Marel, 1968) have presented evidence that clay particles are thin and pliable, some resembling large sheets and some barely visible specks a few angstrom units in diameter. Ramon and Jackson (1965) considered curling of clay layers to be indicative of their high flexibility.

The existence of kaolinite as large, well-ordered stacks of layers is generally accepted, but visualizing the minerals of the montmorillonite group in this manner is probably erroneous (cf. Bates, 1958, p. 37). At best, the particles appear to exist as irregular flakes which are individually so thin that the edges are hard to discern against the background of electron micrographs (Bates, 1958, p. 38).

The "clay-water system" can vary from an extremely dry clay material with a minute amount of water of hydration to a suspension containing a fraction of a percent of clay. Obviously, the properties of the various systems will be quite different and attention must be given to describing the system under consideration. Further care is necessary in comparing results obtained with different systems.

Hydroxy-Al Interlayers in Clays

MacEwan (1950) reported a soil clay which showed a 14-A X-ray diffraction peak that shifted toward the 10-A region when the clay was heated to 540° C. Since such heating normally collapses montmorillonite to 10 A, he concluded that some material was irregularly distributed between the clay layers, preventing them from touching when water was expelled.

Since this first report of interlayering in soil clays, hydroxy interlayers have been the subject of considerable research. Rich (1968), in his recent review of the literature on this subject, found the following to be generally true. (1) Vermiculites and smectites in soils and sediments are often partially interlayered. (2) The dioctahedral forms are the most frequently interlayered; the principal component of the interlayer is hydroxy-Al. (3) The most favorable soil conditions for interlayer formation are pH 4.6-5.8, frequent wetting and drying cycles, and low organic matter content. (4) When soil clays are deposited in a marine environment, Mg may fill out the partially filled Al interlayers. (5) Gibbsite formation may be either enhanced or retarded by expansible layer silicates, depending on the OH/Al ratio and the Al content of hydroxy-Al interlayers.

Rich (1968) lists some 50 literature references reporting interlayers in soils and sediments. He also lists several methods used for synthesis of interlayers, to which can be added yet another, the hydrolysis of Al amalgam (Ahlrichs, 1968). Methods of interlayer removal and the consequences of interlayer formation in clays are also discussed.

Effect on Clay Properties

As would be expected, the presence of interlayers has considerable effect on the chemical and physical properties of the clays. Cation exchange capacity and specific surface area are reduced (Rich, 1960; Sawhney, 1960; Frink, 1965). Infrared spectra are altered

(Weismiller, Ahlrichs, and White, 1967), as are X-ray diffraction and differential thermal analysis patterns. Titration curves (Schwertmann and Jackson, 1964) and several other clay properties (Davey and Low, 1968) are also altered as a result of the presence or absence of these materials.

Nature of the Interlayer Material

Considerable work has been done on the characterization of hydroxy-Al interlayers. It seems apparent that the products of artificial interlayer formation are more complex than simple Al hydroxides. Rich (1968) reviews the hydrolysis products which have been suggested. These include various polyvalent Al hydroxides, polymeric chains, and ring-like structures. McAtee and Wells (1967) produced a positively charged hydrous aluminum sol which appeared as small cubic to hexagonal crystalline particles in electron micrographs.

Hsu and Bates (1964) suggested that when OH^- ions are added to an Al salt solution, they link the Al^{3+} ions together to form stable ring structures. At OH/Al molar ratios of 0-2.1, single rings of 6+ charge or double rings of 8+ charge are produced. Ratios of 2.25-2.7 produce a continuous series of higher polymers which increase in size and total charge as the OH/Al ratio is increased, but decrease in net positive charge per Al atom. Infrared studies by Weismiller et al. (1967) of interlayers formed at an OH/Al ratio of 1.5 supported an interlayer model of single ring polymers lying planar in the interlayer space. Their work also indicated the possibility of larger polymers at higher OH/Al ratios.

It has been generally found that, at an OH/Al ratio of approximately 3, gibbsite forms as a separate species outside of the clay interlayers. A similar observation has often been made in systems of lower ratios, but conflicting results on this point are not uncommon (Rich, 1968). Turner (1967) noted that reactions involving Al and bases are still not well understood and, until they are, it is unlikely that much progress can be made in the problems of reacting clays and Al. Rich (1968) commented on the complexity of hydrolysis of Al^{3+} ions in water and on the added complexity of their hydrolysis and polymerization near clay surfaces. It was further pointed out by Hsu (1968) that the heterogeneity of the cation exchange sites of montmorillonite influences the nature of the hydroxy-Al interlayers formed. He warned that caution is needed when comparing results obtained under different experimental conditions, and in correlation of laboratory results with occurrence of interlayers and gibbsite in nature.

The literature contains ample evidence of interlayers in montmorillonitic and vermiculitic clays. X-ray analyses have shown that such clays swell less than their non-interlayered counterparts. However, the commonly used X-ray analyses are limited to relatively small basal spacings and dry samples. There is a need to test the hypothesis that macroscopic swelling of clays is also reduced by the presence of interlayer material. The study reported below has this as its purpose.

CHAPTER III

MATERIALS AND METHODS

Clays and Their Preparation

The two clays used in this study were Camargo bentonite collected from the open-pit mine site near Camargo, Oklahoma, and Panther Creek bentonite[1] from Panther Creek, Mississippi.

Samples of approximately 200 g were suspended in 20 liters of 0.5% Na_2CO_3 by stirring portions in a malt mixer, then combining in a large crock. The clays were agitated overnight and allowed to settle, after which the clear supernatant liquid was siphoned off and the clay resuspended in 20 liters of deionized water. After a second wash with deionized water, the clay remained dispersed.

The clay fraction, $<2.0\ \mu$ equivalent spherical diameter (ESD), was separated by gravity sedimentation. The Camargo sample presented a special problem in that, with each subsequent resuspension and sedimentation cycle, approximately the same amount of $<2.0\ \mu$ ESD material stayed in suspension. Finally, after 25 such cycles, the separation was terminated.

The $<2.0\ \mu$ fraction was further divided into coarse clay (2.0-0.2 μ ESD) and fine clay ($<0.2\ \mu$ ESD) fractions. The latter fraction

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[1] Purchased from Whittaker, Clark, and Daniels, Inc., New York.

was actually a combination of fine and medium clays, but will be referred to in this study as fine clay. Separation was made using, at different times, a Sharples supercentrifuge and Servall refrigerated supercentrifuge with continuous flow attachment. The former was run at 33,000 rpm with a flow rate of 600 ml/min. Conditions for fine clay separation on the Servall centrifuge were 14,000 rpm, flow rate of 100 ml/min, at 15° C. Resuspension of the clay after each centrifugation was done by stirring the clay with water on a malt mixer and making the volume to 16 liters before recentrifuging. A total of 14 centrifugations was made in the fractionation of the Camargo clay, and 7 centrifugations in the fractionation of the Panther Creek sample.

The clays were concentrated by flocculation with NaCl, washed once with deionized distilled water, and stored as suspensions.

Formation of Hydroxy-Al Interlayers

Method

Sufficient stock clay suspension to give 3.00 g clay was diluted to 600 ml with deionized distilled water and the resulting 0.5% clay suspension placed in a Waring blender. With the blender operating at high speed, the desired amount of $\underline{N}$ $Al_2(SO_4)_3$ and $\underline{N}$ NaOH was added dropwise from burettes into the agitated clay suspension. The rates of addition were regulated so that the addition took between 20 and 30 min. An attempt was made to keep the rates of addition of the two solutions approximately the same as the ratio of the amounts to be added.

Since the samples tended to heat up due to the action of the blender and the chemical reactions taking place, the suspensions were cooled for a few minutes after about half of the required amount of the solutions had been added.

The samples were aged in plastic bottles at a constant temperature of 22° C for one year, with occasional shaking.

Treatments

Each of the four clay fractions (Camargo coarse and fine and Panther Creek coarse and fine) received six different interlayer treatments which consisted of the various combinations of two OH/Al molar ratios (1.5 and 2.7) and three levels of Al (2, 8, and 16 meq Al/g clay). To facilitate discussion, the samples and treatments will be identified by number as indicated in Table I.

Citrate Extraction

Five aged, interlayered samples and a freshly interlayered sample (Sample #25) were extracted with N Na citrate to test the hypothesis that original clay properties are restored by removal of interlayer material. Aliquots of the selected samples (Samples #4, 10, 16, 19, 22, 25) containing 1.00 g clay were heated with 100 ml N Na citrate for 1 hour at 90° C. The samples were then centrifuged, the supernatant liquid discarded, and another 100 ml of the extractant added. A total of six extractions was performed and the clay was then tested along with the interlayered samples.

Analysis of Aged Interlayered Samples

A flow diagram (Figure 1) shows the order and procedures used for analyzing the Al-interlayered samples. Briefly, the following was done.

TABLE I

IDENTIFICATION OF SAMPLES AND TREATMENTS

Sample No.	Clay	OH/Al Molar Ratio	Meq Al/g Clay
1	Camargo coarse	2.7	16
2		2.7	8
3		2.7	2
4		1.5	16
5		1.5	8
6		1.5	2
7	Camargo fine	2.7	16
8		2.7	8
9		2.7	2
10		1.5	16
11		1.5	8
12		1.5	2
13	Panther Creek coarse	2.7	16
14		2.7	8
15		2.7	2
16		1.5	16
17		1.5	8
18		1.5	2
19	Panther Creek fine	2.7	16
20		2.7	8
21		2.7	2
22		1.5	16
23		1.5	8
24		1.5	2
25*	Panther Creek coarse	2.7	16

*A non-aged sample comparable to Sample #13.

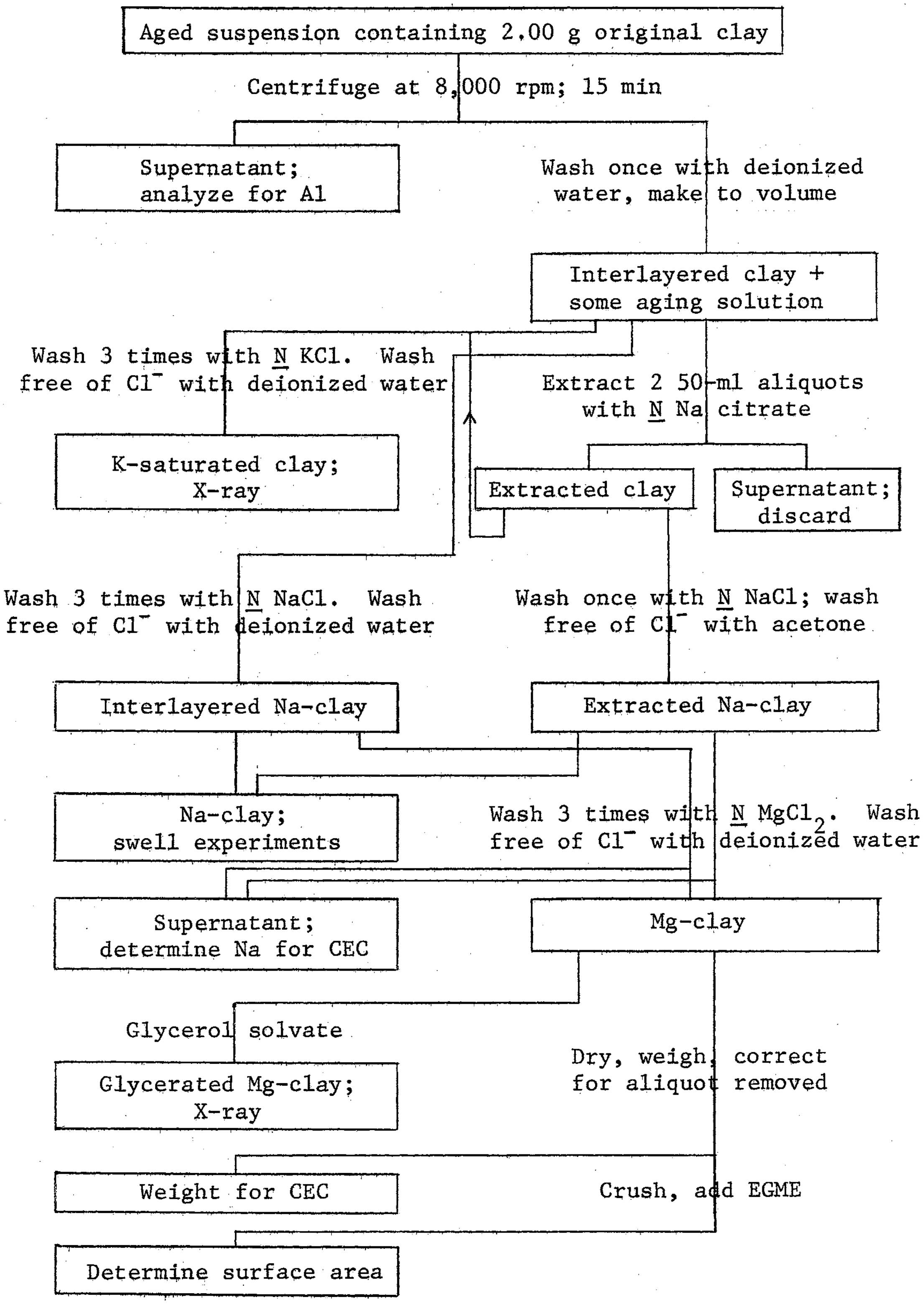


Figure 1. Flow Diagram Showing Steps in Analysis of Interlayered Clay

The bottles were shaken and two-thirds of the suspension immediately measured out. The samples selected for citrate extraction were divided in half; one half was extracted, the other half was not. After centrifugation, the samples were Na saturated with N NaCl and freed of excess salt by washing with deionized distilled water. One aliquot of the Na-saturated sample was taken for swelling measurements and another aliquot was K saturated for X-ray analysis. Sodium was replaced by washing with N $MgCl_2$ and Na determined by atomic absorption spectrophotometry to measure CEC. The clay was washed with water until free of Cl^- and an aliquot set aside for X-ray analysis. The centrifuge tube with the remaining Mg-clay was placed in a vacuum desiccator and dried to constant weight over P_2O_5. This weight, corrected for the aliquot taken for X-ray analysis, was used for the CEC determination.

The Mg-clay was then crushed in a mullite mortar, passed through a 60-mesh sieve, placed in a weighing bottle, and brought to constant weight over P_2O_5. Ethylene glycol monoethyl ether (EGME) was added and specific surface area determined according to the method of Carter, Heilman, and Gonzalez (1965).

Cation Exchange Capacity

Several authors (Frink, 1964; Rollins and Pool, 1968) have noted the importance of using high centrifugal forces and small samples when determining CEC of clays. In the present investigation, CEC was determined in several different ways, with the same values being obtained for all samples. Regardless of the saturating or replacing cation or the method of washing out the excess salt (i.e., water, dilute salt solution, ethanol, acetone), the clay samples were small (<0.5 g) and were centrifuged for 10 to 15 min at 10,000 rpm in a Servall SS-34 rotor (relative centrifugal force of 8,000-12,000 x *g*).

Redispersion after such centrifugation was difficult to accomplish when using the Vortex mixer, so a more rapid and efficient method was devised. A hole was drilled into the end of a polyethylene rod (1 inch in diameter x 1 inch long) and a small bolt was set in the hole with epoxy resin. The polyethylene was shaped into a rounded plug which fitted into the bottom of the 50-ml polyethylene centrifuge tubes used for CEC determinations. The plug was then screwed onto a malt mixer in place of the usual mixing blade. With the use of a rheostat, the speed of mixing could be easily varied as needed for dispersing the clay which was packed into the bottom of the tubes during centrifugation. This method proved to be most satisfactory for rapid and complete dispersion with no loss of clay.

Specific Surface Area

Preliminary studies on surface area determination using the ethylene glycol-bentonite buffer method of Morin and Jacobs (1964) resulted in good duplication within runs. However, large variation between runs made the method unusable.

The more rapid procedure of Carter et al. (1965), using EGME, proved to be more consistent and was adopted for this study. However, it should be noted that a standard bentonite sample included in each set of determinations varied by ±15%, so the surface areas measured were adjusted to minimize this variation. The mean specific surface area of the standard bentonite sample for all determinations was adjusted according to the amount the standard sample in that set differed from the mean. A similar adjustment was used by Morin and Jacobs (1964).

X-Ray Analyses

Magnesium-saturated and glycerol-solvated samples and K-saturated samples were air dried on glass slides as suggested by Jackson (1956, Paragraph 4-34). Samples were X-rayed on a General Electric XRD 6 instrument with Ni-filtered Cu K_{α} radiation generated at 50 kv and 20 ma. Slits were: 1^{o}MR beam, HR soller, and 0.2^{o} detector.

Potassium-saturated samples were X-rayed air dry and after heating at 200^{o} and 500^{o} C. The degree of shift in the basal spacing was used as an indication of interlayer stability.

Unconfined Swelling

Swelling in unconfined conditions was carried out using the technique described by Rowell (1963). About 0.02 g of Na-clay in suspension was pipetted onto an 18 x 18 mm microscope cover slip resting on a numbered aluminum wire frame and allowed to air dry. The cover slip and clay were then suspended by means of the wire frame in 30-ml beakers containing approximately 25 ml NaCl solution of the desired concentration. To prevent evaporation and subsequent changes in concentration, the samples were placed in a closed box containing a free water surface. All experiments were run at a constant temperature of 22^{o} C.

After 24-48 hours, the sample was carefully removed from the solution and the wire frame and bottom of the cover slip thoroughly but rapidly dried with filter paper. Excess water on the surface was gently dabbed off, although this was nearly impossible on highly swollen samples. The sample was weighed immediately to minimize error caused by evaporation from the clay surface. After drying in an oven at 105° C, the sample was again weighed and the "swell value" calculated. Swell value is a term coined by Rowell (1965) for g water/g dry clay.

The method proved to be quite satisfactory. Average standard deviation for all samples was 0.28 g water/g clay.

Swelling Under Applied Pressures

The more commonly used devices for measuring swelling pressure require relatively large samples. Since fractionation of large quantities of clay is a laborious process, the use of small samples is desirable. Small quantities of materials also simplify the work involved in artificial interlayer formation. Thus, methods requiring large samples were specifically avoided and the method of Warkentin, Bolt, and Miller (1957) adopted for this study.

An apparatus (Figure 2) for measuring clay swelling pressure, similar to that described by Warkentin et al. (1957) was built. The apparatus was mounted horizontally for convenience and to eliminate gravitational head effects. No other modifications of significance were made.

A slight suction was placed on the rubber membrane (Dental Dam latex rubber), forming a small cup (up to 3 ml volume). An air-free Na-clay suspension was placed in the depressed area and covered with the dialysis membrane (cellulose dialyzer tubing), care being taken to exclude all air bubbles. The cell was then bolted shut, confining

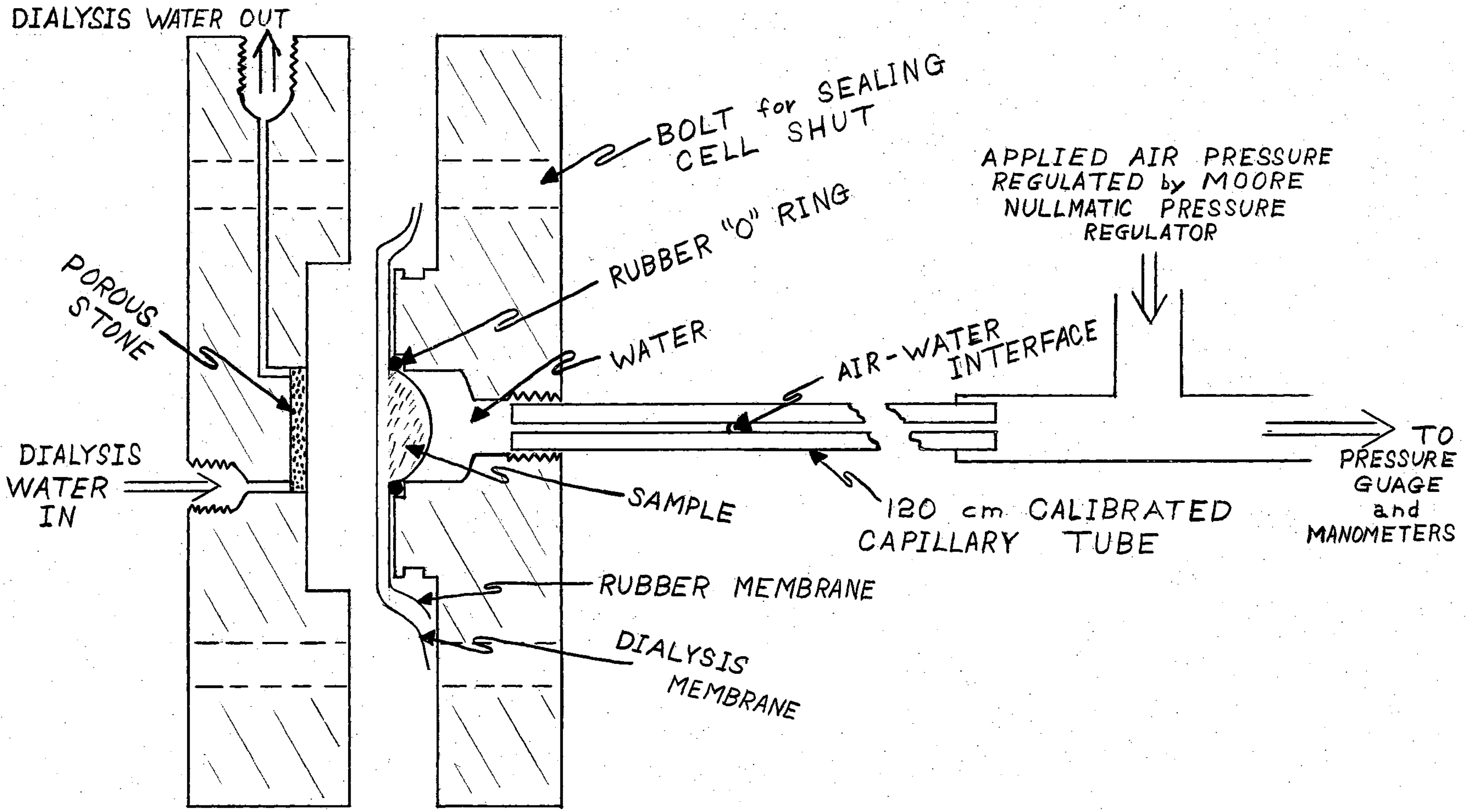


Figure 2. Apparatus for Measuring Swelling

the clay between the rubber and dialysis membranes.

The dialysis membrane rested on a porous stone through which 10^{-4} $\underline{N}$ NaCl was constantly flushed. The cavity into which the rubber membrane extended was filled with water and connected to a partially filled calibrated capillary tube. Air pressure was applied to the water in the capillary tube and thus to the clay. Changes in volume of the clay-water system were noted by the changes in position of the air water interface in the capillary. Constant pressure was maintained by a Moore "Nullmatic" pressure regulator.

The desired pressure was applied and changes in the position of the air-water meniscus in the capillary recorded. Equilibrium was reached after about 4 hours under 1.0 and 2.0 atmospheres (atm) of applied pressure and in about 24 hours under 0.01 atm applied pressure.

When all desired measurements had been made, the pressure was quickly brought to zero and the cell disassembled. The clay was removed from the membranes, using small strips of dried and weighed filter paper, and immediately placed in a tared weighing bottle. The operation was done as rapidly as possible to avoid loss of water from the clay sample.

After the bottle containing the wet clay and the paper strips had been weighed, the sample was dried at 105° C, and weighed dry. Thus the water held by the clay at the end of the swelling experiment was obtained. Water content at the other applied pressures was calculated from the measurements made on the calibrated capillary tube during the course of the experiment.

CHAPTER IV

EXPERIMENTAL RESULTS

As noted in Chapter II, several clay properties are altered by the presence of interlayers. In general, CEC and surface area decrease, while X-ray patterns show differences in basal spacings of interlayered clay minerals. Surface area and CEC are frequently used as indications of the extensiveness of interlayer coverage on the surfaces. The amount of basal spacing shift following heat treatment indicates the stability of the material.

In this study the above clay characteristics were analyzed before interlayering, after interlayering, and after removal of artificially formed interlayers by Na citrate extraction. Analyses of the data allowed postulation of the nature of the interlayer material.

Indications of Interlayer Formation and Stability

Cation Exchange Capacity

The CEC of the original clay fraction was high, as shown in Table II. Treatments with 16 meq Al/g clay reduced the CEC to zero in all but one case, and for this case (Sample #7) the CEC was reduced to 3% of its original value. This was found to occur immediately upon interlayer formation (Sample #25) and to persist during 1 year of aging.

TABLE II

SUMMARY OF DATA

Sample Number	Al left in soln. (% of added)	CEC (meq/ 100g)	Surface Area (m^2/g)	Basal Spacings (A)				Swell Values* (g water/g clay)	
				Mg-Sat Glycerol	K-Sat			Rowell Method	Warkentin Method
					25°C	200°C	500°C		
Aged Interlayered Samples									
1	1	0	440	19.3	17.0	14.4	13.5	1.6	
2	0	8	562	19.0	15.5	10.4	12.6	1.8	
3	0	87	787	18.2	13.4	12.6	10.9	2.8	
4	45	0	472	21.3	16.0	14.0	13.2	1.4	
5	42	34	740	18.8	14.2	13.1	11.5	2.2	
6	13	96	924	18.4	12.7	11.9	10.6	3.4	
CC**		129	937	17.8	--	10.8	10.0	3.0	2.2
7	0	4	582	19.4	16.0	14.6	13.1	0.64	
8	0	47	774	18.5	15.0	13.2	11.9	0.71	
9	0	113	863	18.2	13.2	12.3	10.8	6.8	3.5
10	37	0	626	20.5	16.2	14.2	13.1	0.43	
11	26	61	775	18.0	14.2	12.7	11.3	0.80	3.5
12	0	96	884	18.2	13.0	11.4	10.5	4.4	
CF**		131	943	18.2	11.3	10.6	10.1	30.2	12.0
13	0	0	346	22.1	17.0	14.5	13.4	1.2	
14	0	0	471	20.1	16.4	14.4	13.2	0.80	
15	0	58	649	18.4	13.1	14.0	10.9	3.7	
16	45	0	456	22.6	15.9	13.6	11.8	1.0	
17	31	11	554	19.4	14.2	12.8	10.6	0.92	
18	0	59	708	18.5	12.4	11.8	9.8	5.6	
PC**		91	740	17.1	11.5	10.3	9.9	3.6	2.1
19	0	0	590	21.8	16.8	14.0	13.0	0.50	3.4
20	0	42	619	19.2	15.4	13.2	12.3	0.91	3.4
21	0	85	781	18.2	13.1	11.1	10.7	12.9	6.3
22	40	0	570	22.1	16.8	14.4	13.3	0.45	4.0
23	28	46	742	18.8	13.2	11.5	11.2	1.1	
24	0	68	855	18.2	13.2	10.9	10.4	4.3	
PF**		108	868	17.6	11.0	10.3	9.9	15.8	9.8
Freshly Interlayered Sample									
25	--	0	150	22.1	--	14.7	14.2	--	
Citrate-Extracted Samples									
4		137	948	18.2	12.4	11.7	10.2	10.5	6.0
10		133	968	18.2	12.4	11.0	10.2	27.1	8.2
16		97	770	18.2	12.2	10.6	10.0	24.0	8.2
19		104	912	18.2	12.3	11.0	10.2	34.0	
22		103	926	18.0	12.1	10.4	10.0	34.4	13.3
25		91	760	18.2	12.1	11.0	10.2	26.6	

*Rowell swell done in 5 x 10^{-3} N NaCl. Warkentin swell done in 10^{-4} N NaCl.

**CC=Camargo coarse, CF=Camargo fine, PC=Panther Creek coarse, PF=Panther Creek fine.

When an intermediate amount of hydroxy-Al (8 meq Al/g clay) was used, the resulting CEC ranged from 0-46% of the original value. The coarse clays showed somewhat greater reduction than the fine clays. This could be due to a concentration of the interlayer material near the layer edges, resulting in a blocking of layer exchange sites. Such an "atoll" arrangement of interlayer material was proposed by Frink (1965). Further support of this explanation is found in the greater CEC reduction of the Panther Creek coarse as compared with the Camargo coarse. Panther Creek had larger particles than Camargo, as evidenced by a lower specific surface area. With equal amounts of interlayer material, the CEC of large particles would be more affected by edge blockage than would the CEC of small particles.

The range in CEC of various samples treated with 2 meq Al/g clay was quite small, 63-86% of the original. It appears that insufficient polymers were present to cause blocking and only the exchange sites actually covered were inactivated, leaving those not covered free for exchange reactions.

Samples treated with different OH/Al ratios showed different reductions in CEC; the higher ratio had the greater reduction (cf. Table II: Sample #2 vs. #5 and #8 vs. #11). However, this effect is confounded by the higher amount of Al left in solution by the samples treated at the 1.5 OH/Al ratio (Table II). It would seem that the effect, then, is really a reflection of the greater quantities of hydroxy-Al which had reacted with the clay.

The results suggest that the effects being observed are not dependent on a single factor and bear out previous observations on the sensitivity of clay surfaces to alteration.

Surface Area

It was noted in Chapter III that the methods for determining specific surface area of clays leave much to be desired. Duplicate samples showed such large variation that detection of differences between clays or OH/Al ratios could only be made at the 60-70% level of statistical significance. However, the differences between samples treated with different Al:clay ratios were large, and use of the data seems justifiable.

Interlayering had the expected effect of lowering the specific surface area. At the high ratio, surface area was approximately halved, while at the low ratio there was little to no reduction. At the intermediate ratio it was reduced by 25%. Evidently, the number of polymers produced at the lower ratios was neither enough to completely cover all the clay surfaces nor to completely block the edges. Polar molecules such as those used for surface area determination could thus be adsorbed on the surfaces not covered by interlayer material. At high Al:clay ratios, sufficient polymers were present either to cover the layer surfaces, completely filling the clay interlayer with hydroxy-Al polymers, or to thoroughly block the edges, forming an atoll. In this case, the surface area measured was equivalent to the clay's external surface area.

X-Ray Analyses

Many of the treatment effects noted in the CEC and surface area determinations were also observed in the X-ray analyses of K-saturated interlayered clays. (1) The Panther Creek and Camargo clays responded similarly to all treatments. (2) Little difference was noted between the two OH/Al ratios. (3) The greatest alteration in clay properties occurred in the treatments where the 16:1 Al/clay ratio was applied. (4) Little alteration occurred where 2 meq Al/g clay was reacted. (5) The fine clays collapsed slightly more and swelled slightly less than the coarse clays.

The basal spacing calculated from the center of the principal diagnostic peak is shown in Table II. This abbreviation may have led to inaccuracies due to the occasional broadness of peaks, but the procedure permitted a more concise presentation of the data.

All the data indicated that there was material in the interlayer spaces. The increases in basal spacings were greatest at the highest Al:clay ratio and smallest at the lowest ratio. The interlayer material itself collapsed considerably upon heating (cf. Table II: Sample #1, from 6.0 to 3.5 A; Sample #24, from 2.2 to 0.5 A).

At room temperature the basal spacings of the K-saturated interlayered samples were all considerably greater than the 12.4-12.8 A spacing expected of interlayered montmorillonites (Whittig, 1965). Heating at 300^{o} and 500^{o} C caused a progressive decrease in the basal spacings. The samples treated with small amounts of Al had spacings very near those of the non-interlayered clays, while the samples treated with large amounts of Al had spacings of ca. 13 A. These data again indicate the influence of the quantity of interlayer material on clay properties.

The large spacings (up to 22 A) of the Mg-saturated and glycerol-solvated samples, along with evidence from the swelling experiments, indicate that, until the interlayered clays are dried, they are still not collapsed. If Sample #3 is taken as an example, it is noted

(Table II) that the K-saturated basal spacing of the clay at room temperature was 17.0 A, an increase of 5.5 A over the non-interlayered sample. The same difference is noted between the basal spacings of the treated and non-treated samples when they were Mg-saturated. This is taken as evidence that the sample still adsorbed glycerol on its surfaces, even though the CEC was totally inactivated and the surface area reduced by 50%. This was not the case if the sample was allowed to dry. Air-dried samples showed no signs of swelling, even when allowed to soak in water for several days.

It might be noted here that the thickness of the layer is increased considerably by the precipitation of interlayer material on the surfaces. Assuming the density of the precipitate to be the same as that of the clay, an interlayer thickness of 2 A would increase the weight of "clay" by 20%. This would, in effect, lower the CEC measured; the same effect would be noted on the surface area determined. Thus, the CEC would be lowered as much as 17% simply by the increased weight of the clay-hydroxy-Al mixture without any reaction with or blocking of the exchange sites. The effect would, of course, be greatest in treatments where high Al:clay ratios were used and least where low ratios were used. Using experimental data from Sample #5, calculations were made (Table III) which support this point.

Recoverability of Clay Properties and Effect of Aging

Extraction of aged samples with N Na citrate recovered all original clay properties tested (Table II). Because of the time involved, only selected samples were extracted and only one procedure used. The samples extracted had all received 16 meq Al/g clay, the treatment which resulted in the greatest alteration of clay characteristics. It was assumed that interlayers formed at lower Al:clay ratios would likewise be completely removed by the extraction procedure. With a milder extraction (Hsu, 1968), this assumption may not be valid.

TABLE III

DILUTING EFFECT OF INTERLAYER MATERIAL ON CEC OF SAMPLE #5

Original clay concentration	3.0 g/600 ml
Clay concentration after addition of 24.0 ml N $Al_2(SO_4)_3$ and 12.0 ml N NaOH	3.0 g/636 ml
Wt of clay in 106 ml suspension	0.50 g
Wt of interlayered clay found by washing and weighing 106 ml Sample #5	0.53 g
Percent increase in wt of clay due to interlayer material	6.0%
Decrease in CEC due to gain of wt	5.7%

In order to obtain an indication of the effect of aging on interlayer stability and consequent effects on clay properties studied, two experiments were conducted. (1) The CEC of Sample #5 was determined after 7 months aging, as well as after 1 year. (2) A duplicate of Sample #13 (designated as #25) was prepared and analyzed at the time analyses were made on the aged samples.

The CEC of Sample #5 decreased from 129 to 51 meq/100 g after 7 months aging, and to 34 meq/100 g after 12 months aging. These data suggest that interlayer formation in this sample was continuing over the whole aging period and may not have been at equilibrium at the end of 1 year.

Sample #25 was analyzed about 2 hours after preparation. Cation exchange capacity was zero and surface area was reduced from 740 to 150 m^2/g. X-ray analysis of the samples heated to 500° C showed a slight but significantly larger spacing in the freshly prepared sample than in the aged sample. This, taken with the lower surface area of the fresh sample, suggests a possible rearrangement of the interlayer material on the surfaces during aging.

Swell Experiments

Preliminary Studies of Untreated Clays

Non-Swell of Coarse Clays

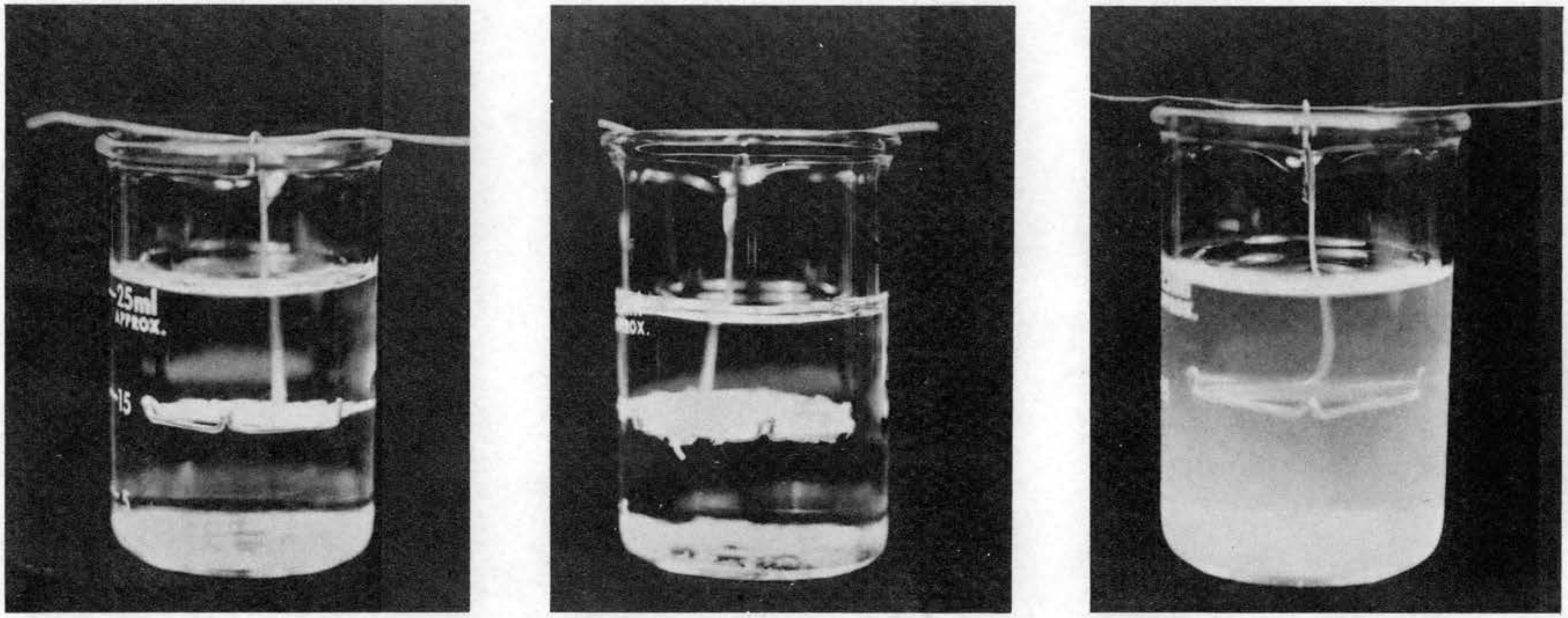
Initial efforts to measure swelling of non-interlayered coarse clays were made according to procedures found in the literature (Warkentin et al., 1957; Warkentin and Schofield, 1962). Swelling pressure was consistently lower than predicted by theory (Bolt, 1956) and substantiated by experimentation (Warkentin et al., 1957; Warkentin and Schofield, 1962). For example, theoretically, swelling pressure at a calculated layer separation of 100 A is 0.9 atm (cf. Warkentin et al., 1957). Experimental values of 0.3-0.5 atm were generally found.

Bolt (1956) has shown that incomplete removal of salts can result in reduced swelling. Therefore, a sample of Panther Creek coarse clay was washed 20 times with deionized distilled water, with no significant change in swelling noted. Jonas and Roberson (1966) concluded that higher structural charge density of the coarse fractions of montmorillonite was responsible for reluctance of that fraction to expand in atmospheres of high relative humidity. However, specific surface area and CEC measurements showed that the charge density of the two fractions was the same. Lack of parallel orientation was also dismissed as the cause of the problem, since this geometric arrangement would increase rather than decrease the swelling pressure.

Contrasted with the lack of swell of the coarse clay fraction was the swell exhibited by the fine clay. It is apparent from data shown in Table IV that the fine clay fractions expanded to values very near theoretical, while the coarse clay was essentially non-swelling. The results of unconfined swell are included in Table IV and provide additional evidence of the non-swelling of coarse clay. From these results and others to be discussed in the following section, it seems that attractive forces not accounted for in the parallel charged plate model of Bolt (1956) were acting in the coarse clay system to prevent swelling.

Swelling Curves of the Fine and Coarse Fractions

Another interesting observation was made when the non-interlayered clays were allowed to swell in NaCl solutions (cf. Figure 3) of varying concentrations (Rowell's method, 1963). Swelling curves (Figure 4) showed two effects which indicated dissimilar attractive forces in the fine and coarse clays. First, the fine clays swelled considerably as the concentration of the solution decreased, whereas the coarse clays



Slightly Swollen
Swell Value ca. 3

Highly Swollen
Swell Value ca. 30

Dispersed

Figure 3. Typical Stages in Swelling of Na-Montmorillonite Using Method of Rowell (1963).

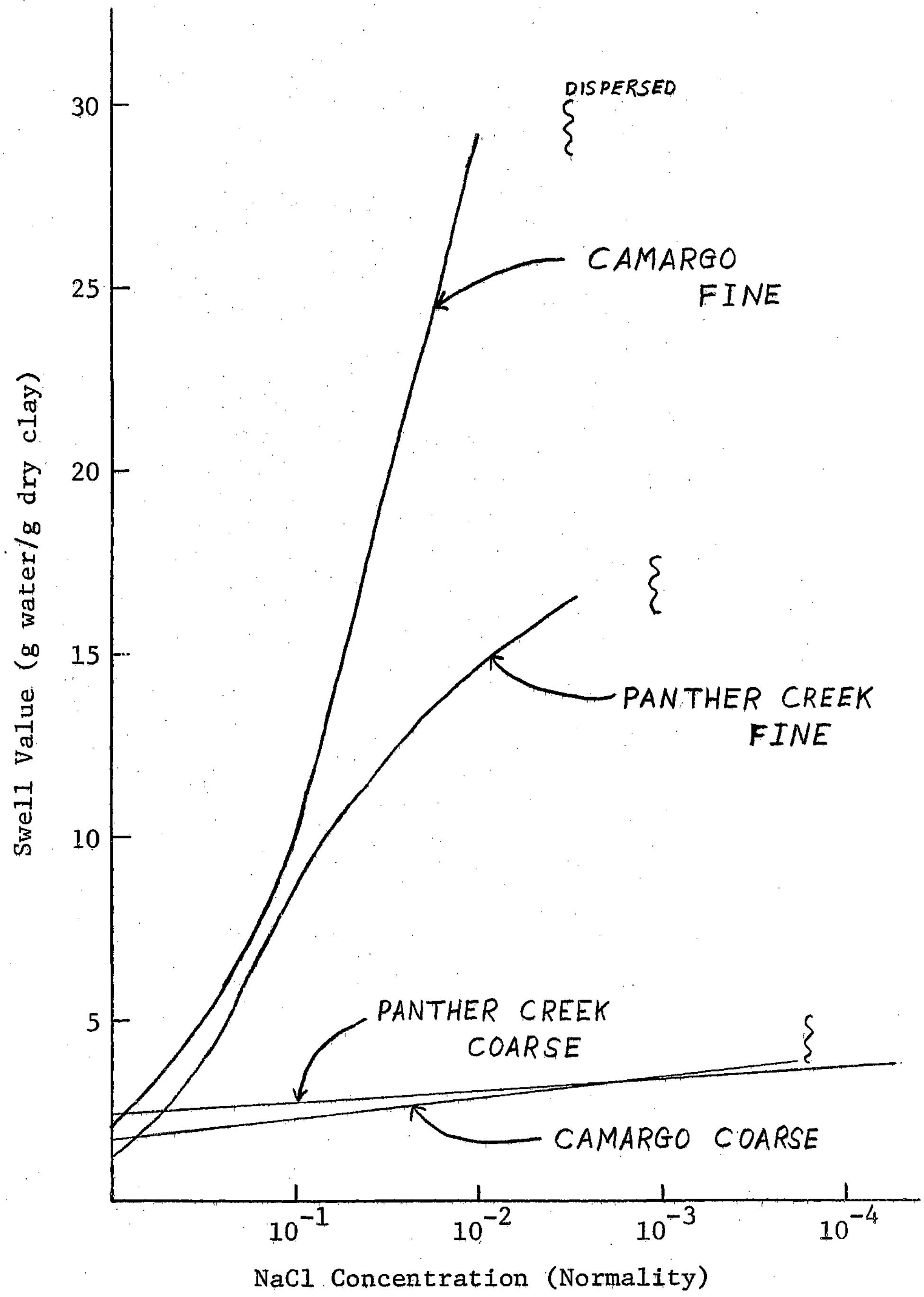


Figure 4. Swell Curves of Na-Clays Before Artificial Interlayering

showed very little swelling. Just before dispersion the fine clays held 15-30 g water/g clay; the coarse clays held 3-5 g water/g clay. Second, the fine clays dispersed at higher salt concentrations than did the coarse clays. It will be recalled (Table II) that the surface area and CEC of the two Camargo fractions were essentially the same. Under similar conditions the two fractions would be expected to have the same osmotic forces (repulsive forces), and any differences in swelling characteristics could thus be attributed to differences in the attractive forces.

TABLE IV

SWELL VALUES OF CLAYS UNDER CONFINED[1] AND UNCONFINED[2] CONDITIONS

Clay	Confining Pressure (atm)						Unconfined
	2.0	1.0	0.5	0.1	0.05	0.01	
Camargo coarse	1.5	1.7	---	2.1	---	---	3.0
Camargo fine	2.4	3.1	4.0	7.3	9.7	12.2	30.2
Panther Creek coarse	1.8	---	---	2.0	---	2.1	3.6
Panther Creek fine	2.5	3.2	4.3	7.4	8.6	9.8	15.8
Montmorillonite (theoretical[3])	2.6	3.8	5.4	11.4			

[1] Using apparatus of Warkentin et al. (1957); dialysis solution 10^{-4} N NaCl.

[2] Using method of Rowell (1963); solution 5 x 10^{-3} N NaCl.

[3] Warkentin et al. (1957).

Testing the Hypothesis

The main hypothesis tested in this study was that the macroscopic swelling of clays is reduced by the presence of Al-interlayers. In preceding sections the presence of artificially formed interlayers in four montmorillonitic clay fractions has been demonstrated and discussed. This section deals with the swelling properties of the artificially interlayered clays.

Artificially Interlayered Samples

Unconfined Swell

Swelling was essentially stopped in clays treated with the high Al:clay ratio (16:1), as shown by the swell values (Table II) of Samples #1, 4, 7, 10, 13, 16, 19, and 22. This would be predicted from the complete blockage of the CEC in those samples, since without exchangeable ions there would be no osmotic force acting to separate the layers.

However, similar results were obtained with samples treated with 8 meq Al/g clay, even though as much as half of the CEC remained. The binding effect of the interlayer material was apparently stronger than the repulsive force resulting from the presence of exchangeable ions, and separation of the layers was prevented.

The amount of interlayers at the two higher Al:clay ratios was sufficient to prevent swelling of all clays for all treatments. However, at the lowest Al:clay ratio (2 meq Al/g clay), the effect of small amounts of interlayer material on clay swelling could be observed. A 20-85% reduction in swell values of the fine clays was found

(Table II: Samples #9, 12, 21, 24), the 2.7 OH/Al ratio reducing swell less than the 1.5 ratio. The treated coarse clays swelled very little, as was expected from the non-swelling behavior of their untreated counterparts.

Swell Under Applied Pressures

This portion of the study differed from unconfined swell in that a force of varying magnitude was applied to counteract the repulsive force. The applied pressure at equilibrium was thus a measure of the net repulsive force of the system.

The results reported here were obtained using the apparatus of Warkentin et al. (1957) and a dialysis solution of 10^{-4} N NaCl. This salt concentration was more dilute than that used in the unconfined swell experiments so that greater swelling pressures could be developed. The more dilute concentration was not used in the unconfined swell experiment because dispersion of many samples was encountered at such low concentrations.

Results were consistent with unconfined swell and brought out some additional characteristics of the materials being studied. Non-swelling samples had unconfined swell values which were considerably lower than the confined swell values. Conversely, samples which swelled had larger unconfined than confined swell values (Table V). This was probably due to the manner in which samples of the two experiments were treated. In preparation for unconfined swell, the clay was allowed to air dry from suspension on a glass cover slip, whereas for confined swell the clay was placed in the apparatus as a suspension and was never dried before testing. The dehydration of the hydroxy-Al interlayer material was probably irreversible and, once dried, it did not take up water. Furthermore, dehydration prevented any re-expansion of the interlayers by binding adjacent layers. Less complete removal of the water in the confined system resulted in higher swell values for those samples.

TABLE V

EFFECT OF SAMPLE DRYING ON SWELL VALUES

Sample	Swell Value	
	Unconfined Swell[1] (Dried)	Confined Swell[2] (Not dried)
10	0.43	3.5
19	0.50	3.4
20	0.91	3.4
22	0.45	4.0
21	12.9	6.3
Panther Creek fine (untreated)	15.8	9.8
4 (extracted)	10.5	6.0
10 (extracted)	27.1	8.2
22 (extracted)	34.4	13.3

[1] In 5×10^{-3} N NaCl.

[2] In 10^{-4} N NaCl.

Samples which swelled more in the unconfined than confined conditions were those with little interlayering or those which had been citrate extracted. The effect being observed was that of the applied pressure resisting the osmotic pressure. It should be noted, however, that the accuracy of the determination at very low pressures (below 0.1 atm) is subject to considerable variation.

Citrate-Extracted Samples

Striking results of unconfined swell of the citrate-extracted samples afforded an explantion of several of the observations discussed previously and provided evidence in support of the hypothesis that interlayer material causes reduction in clay swelling. As the data in Tables II and VI show, the citrate-extracted samples had the largest swell values of any samples--even larger than the original untreated samples. Although the CEC, surface area, and X-ray showed some differences between the extracted and original samples, the differences were not as great as those found for the swell values.

The very large (3- to 7-fold) increase in swell values of the coarse fractions upon citrate extraction, taken with the concomitant slight increase in CEC and surface area, indicate that the agents which are preventing swell take up little room on the layer surfaces and occupy few cation exchange sites.

These results suggest the presence of small amounts of interlayer material in the original clays. Such an occurrence is somewhat unexpected, since interlayer materials are generally thought to be products of clay weathering. The clays used in this study were from bentonite deposits and would not be expected to have such materials. However, Rowell (1963) has reported that removal of iron oxide (0.58% by weight) from the <0.05 μ fraction of Wyoming bentonite increased the swell value by about 10%.

TABLE VI

COMPARISON OF PROPERTIES OF CLAYS BEFORE AND AFTER CITRATE EXTRACTION

Clay	CEC (meq/100g)	Surface Area (m^2/g)	Swell Values[1] (g water/g clay)	Basal Spacing (A)	
				Mg-sat glycerol	K-sat 500°
Camargo coarse					
Original	129	937	3.0	17.8	10.1
Extracted	137	948	10.5	18.2	10.2
Camargo fine					
Original	131	943	30.2	18.2	10.1
Extracted	133	968	27.1	18.2	10.2
Panther Creek coarse					
Original	91	740	3.6	17.1	9.9
Extracted	94	765	25.8	18.2	10.0
Panther Creek fine					
Original	108	868	15.8	17.6	9.9
Extracted	104	919	34.2	18.1	10.1

[1] Method of Rowell (1963).

[2] In 5 x 10^{-3} N NaCl.

The naturally occurring interlayer material is suspected to be small, randomly scattered "islands" of Fe, Al, or Si oxides or hydroxides which bind the layers together, preventing swell. When these are removed by citrate extraction, the layers are free to swell.

CHAPTER V

DISCUSSION AND CONCLUSIONS

In the course of the study it was found that, despite a large measured surface area and a high cation exchange capacity, the coarse clay fractions (2.0-0.2μ) of the two bentonite samples studied swelled very little before dispersing. Conversely, the fine clays swelled to large volumes before dispersing in dilute salt solution. This behavior suggests that different forces are active in the two fractions.

Since the fine and coarse fractions had essentially the same charge densities, in like solutions the osmotic (repulsive) forces would be the same for the two fractions. The different swell behavior must be explained by dissimilar attractive forces.

The experimental results suggest that the attractive force in the coarse clay is of a strong, non-elastic type, whereas that of the fine clay is weaker and more elastic. As the repulsive force increases (i.e., NaCl concentration decreases), the strong, "non-elastic" attractive force in the coarse clay allows the layers to expand very little (from 2 to 4 g water/g clay). When the repulsive force becomes greater than the attractive force, the clay suddenly goes from a state where the layers were an average of ca. 80 A apart to a dispersed state. On the other hand, the weaker, "elastic" attractive forces of the fine clay allow water to enter rather easily and the layers expand to large average distances without dispersing. Finally, the repulsive force becomes greater than the attractive force and the fine clay disperses.

The strong, "non-elastic" forces of the coarse clay are suspected to be randomly distributed islands of interlayer material which bind adjacent layers together by eloctrostatic bonds. Results from samples treated with hot Na citrate lend strength to this explanation. After such treatment, Samples #4, 16, and 25 attained swell values of the same order of magnitude as the untreated fine clays (Table II), a 3- to 7-fold increase. These results show that use of methods such as that proposed by Fink, Rich, and Thomas (1968) is possible only with samples freed of interlayer materials.

If one assumes the parallel plate model and calculates the distance between the clay layers (cf. Bolt, 1956; Fink et al., 1968), it is found that, just prior to dispersion, the layers of Camargo coarse were 80 A apart. The interlayer islands do not explain why the clay could expand up to an average layer separation of 80 A. Hydrous polymers would not be expected to exist in the form of polymeric chains of such length. A more realistic picture of the system may be as diagrammed in Figure 5. In such a system the interlayer material occurs randomly on the surfaces and the clay can expand freely in the areas where adjacent layers are not bound together. Thus the swollen clay layers would have a "bumpy" appearance, being swollen in some areas and held together in others. The average distance between the layers could then be large without the bonds holding them together being long. This model assumes that the clay layers are flexible and may be folded back on themselves or rolled on the edges.

When the interlayer material is absent, the clay swells as described for the fine clay. The clay takes up about 30 times its weight

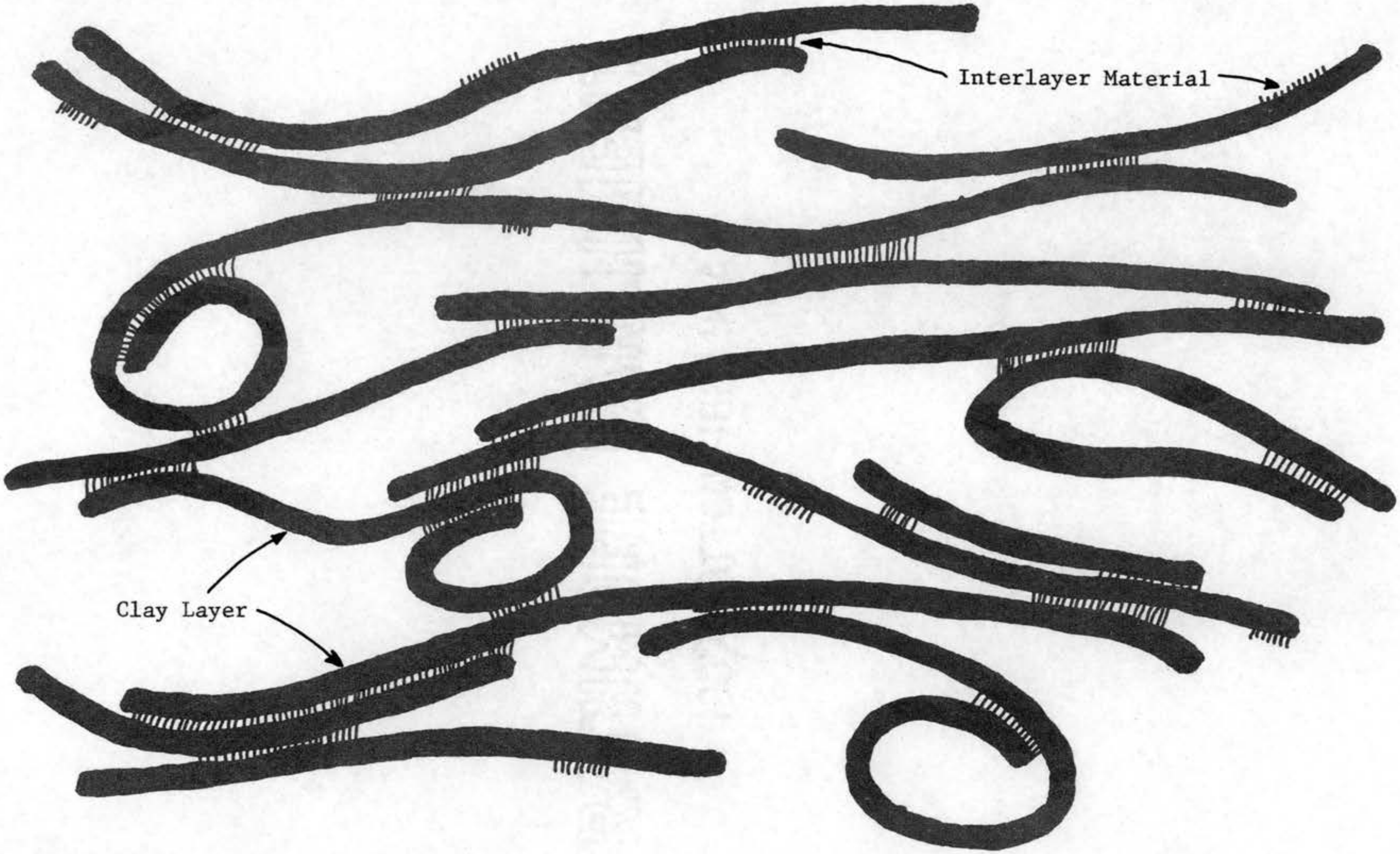


Figure 5. Proposed Model for Structure of Interlayered Montmorillonite in Water

in water before it finally disperses. In such a system a long-range attractive force holds the clay particles together in a gel before dispersion.

Numerous investigators have advanced explanations for the formation and stability of clay gels. Part of the lack of agreement stems from the various "schools of clay thought" mentioned in Chapter II. Van Olphen (1963, cf. p. 151-152) favors the model where bonds between the negatively-charged faces (planar surfaces) of the clay layers and the positively-charged edge surfaces result in a "house of cards" arrangement of particles in the gel. Rowell (1965) proposed the formation of pores between clay micells during swelling as an explanation of the large amounts of water taken up by oriented clays. Evidence reviewed by Low (1968) strongly favors an edge-to-edge or a face-to-face arrangement and points to the limited evidence for the edge-to-face model. Mungan and Jessen (1963) proposed a hinge structure where shared water molecules of the bound water layer form a hinge between adjacent clay layers, allowing parts of the layers to be free to swell while the other parts remain attached to each other.

The results of this study do not allow the favoring of one model over another. It is obvious, however, that removal of materials from the surfaces of the silicate clays, especially those of large ESD, results in an enhancement of their ability to swell.

Artificial interlayering of the samples showed that very large amounts of interlayer material can completely inactivate the cation exchange sites and reduce the surface area to about half its original value. This reduction in surface area seems small in light of the often-expressed concept of a montmorillonite clay crystal many layers thick. If such were the case, one would expect a large (95% or so) decrease. However, if the clay exists largely as individual particles or particles only a few (2-10) layers thick, one would expect surface area reductions on the order of those found in this study. The data of Stahnke (1968)[1] on external and internal surface areas of soil clays corroborates this view.

Of particular significance is the marked effect that small amounts of interlayer material have on swelling, while having much smaller effect on other clay properties. This was brought out most dramatically by the swelling of the coarse clays after citrate extraction. It is interesting to speculate how soils might swell if the "swelling" clays they contain were not interlayered.

Further studies related to this problem might include artificial interlayering of soil clays as a means of stabilizing soils for engineering purposes and studies of soil clay swell.

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[1] C. R. Stahnke, 1968. The genesis of a chrono-climo-sequence of Mollisols in west-central Oklahoma. Ph.D. thesis. Okla. State U., Stillwater, Okla.

CHAPTER VI

SUMMARY

The presence of hydroxy-Al polymers artificially precipited on the interlayer surfaces of fine and coarse clay fractions of Panther Creek and Camargo bentonites was verified by CEC, surface area, and X-ray diffraction measurements.

Non-treated clays were found to have a strong attractive force which prevented swelling; its effect was considerably greater in the coarse than in the fine clay fractions. Treatment with hot N Na citrate resulted in 2- to 7-fold increases in swelling. Amorphous Fe, Si, or Al are considered to be the agents binding the layers together.

All four clay fractions reacted similarly to artificial interlayering. At the high Al:clay ratio (16 meq Al/g clay) CEC was completely lost, surface area reduced to one-half its original value, and a basal spacing of ca. 13 A exhibited after K saturation and heating at 500° C. No macroscopic swelling occured in samples so treated. At smaller concentrations of hydroxy-Al, the clay properties were less drastically altered.

Extraction with Na citrate restored the original CEC, surface area, and basal spacings to the clays and resulted in slight enhancement of CEC and surface areas of the coarse fractions.

Evidence presented supports the hypothesis that macroscopic swelling of montmorillonitic clays is greatly reduced by small amounts of interlayer material. Reduced swelling occurs even when other clay properties may be only slightly different from non-treated samples. Indications are that interlayer materials occur naturally in clays from bentonite deposits.

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VITA 3

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