

THE STRUCTURAL STATUS OF CLAY SYSTEMS

by

L. A. G. AYLMOORE AND J. P. QUIRK

Department of Agricultural Chemistry
Waite Agricultural Research Institute, University of Adelaide

ABSTRACT

Illite and montmorillonite have been compressed into cores under a pressure of 1200 atm. The structural status of these clays has been examined by means of detailed nitrogen adsorption-desorption isotherms and by means of electron micrographs of fracture surfaces of the clay cores. The subsequent swelling behavior of sodium and calcium clay cores has been analyzed in terms of the model derived from these measurements and the specific surface area of the clay. A generalized theory for the condensation of plate-shaped particles into domains has been proposed.

Measurements of the effect of electrolyte concentration and hydrostatic suction on the swelling of sodium- and calcium-saturated clay cores indicate that diffuse double layer theory may play a significant part in determining the swelling of monovalent clay systems but not divalent clay systems.

The magnitude of the film thicknesses apparently developed in solutions as concentrated as molar and 4 M, where the condition of ideal solutions required by diffuse double layer theory is certainly not fulfilled, seems to indicate that solution uptake is increased by a relaxation of structural strains within the clay matrix on lubrication by solutions. These strains may arise from the distortion of crystals in packing during the drying process. Such relaxations which appear to occur between pF 4 and 3 could initiate the development of a gel structure.

INTRODUCTION

The reaction of clay with water is of fundamental importance in the fields of agriculture, engineering and clay technology. From an agricultural point of view the stability of soil aggregates to processes of wetting and drying and also to mechanical stresses applied during cultivation depends to an appreciable extent upon the forces between individual clay particles and groups of clay particles. An understanding of the relationship between clay and water is therefore essential for a proper appreciation of water retention and movement in soils and the basic mechanisms involved in soil structure.

Similarly soil engineering studies are concerned with the consolidation and shear strength of the soil-water mass. These properties are determined

by the nature of the clay-water interaction as well as mechanical particle-to-particle interaction. Even for soils of loam texture which exhibit no physical swelling the interaction of clay with water results in swelling, which, although accommodated within the rigid framework of coarser particles, markedly influences soil properties.

A clay mass exists in a series of structural states depending not only on its water content but also on its history. In the dry state the structural status of a clay material can be defined by pore size distribution studies; as swelling takes place the uptake of water can be described in terms of the formation of a gel structure and the film thickness developed by clay particles in repelling one another.

Croney and Coleman (1954) and also Holmes (1955) have shown that at any given hydrostatic suction it was possible for a clay mass to have a range of different water contents depending on its previous history and also that a disturbed clay mass described a series of hysteresis loops on repeated wetting and drying. This effect of terminal pressure on the decompression curve for clays in the gel state is also well illustrated by the results of Warkentin, Bolt and Miller (1957). For many years soil engineering workers (Lambe, 1953; Parry, 1959) also have been aware of the presence of irreversible hysteresis in the water content-suction relationship of a clay material. They use such terms as "virgin consolidation curve," "rebound curves" and "overconsolidated clay."

The results of Croney and Coleman, and Holmes indicate that for a clay mass to describe what may be termed the final or minimum water content hysteresis loop it was necessary to dry the clay material to its shrinkage limit. In this state the clay matrix has settled down to a situation where the clay particles are in a state of minimum potential energy with respect to one another.

Aylmore and Quirk (1959) have suggested that as a clay-water system dries from a situation approaching the gel state (virgin consolidation curve) the formation of domains of oriented crystals and the subsequent reorientation of these domains to positions of minimum potential energy cause the actual volume of water enmeshed within the gel structure to decrease continually. A domain was envisaged as a microscopic or submicroscopic region within which the clay particles (crystals) are in parallel array. These groups of oriented crystals, or domains, are randomly placed with respect to one another throughout the clay matrix; that is, the domains are in turbulent array.

Schofield (1946) regarded the swelling of a clay matrix as arising from the development of diffuse double layers by the clay particles. He has presented a theoretical treatment based on the Gouy-Chapman diffuse double layer, to describe the film thickness in terms of the hydrostatic suction within the water surrounding the clay mass and the electrolyte

concentration of the solution external to the double layers of the clay crystals.

The role of double layers in the retention of water by montmorillonite has been investigated in a series of papers by Bolt (1956), Bolt and Miller (1955) and Warkentin, Bolt and Miller (1957). In questioning the validity of some of the conclusions of these workers, Aylmore and Quirk (1959), and Quirk and Aylmore (1960) have pointed out that the central problem, in trying to interpret the behavior of clay-water systems in terms of double layer formation at the clay liquid interface, was to separate that water which was simply enmeshed within a gel structure from the water retained by physico-chemical forces on the clay particles.

There are few satisfactory experimental data with which a comparison between the internal swelling of expanding lattice minerals and the film thickness developed on the external surfaces of clay crystals can be made. Attempts to correlate physical swelling data for clay minerals with theoretical treatments have proved less conclusive than the more direct X-ray approach.

Early Hofmann and Bilke (1936) reported that, near saturation, Na⁺-montmorillonite gave a spacing considerably greater than 30 Å. However, Méring (1946) observed that when flakes of Na⁺-montmorillonite were placed in water they increased to 20 times their volume; he concluded that the swelling took place between crystals rather than by crystalline swelling. He attributed the disappearance of the 20 Å basal reflection to disorder in the primary particles rather than their swelling. From permeability and X-ray studies Quirk (1952) concluded that Na⁺-montmorillonite expanded beyond the basal reflection of 20 Å and noted that this swelling could be controlled by high sodium chloride concentration (see also Norrish and Quirk, 1954). Norrish (1954) has shown that for concentrations (*C*) less than 0.25 N the basal spacing increased linearly with respect to $C^{-1/2}$ as predicted by Schofield's theory; however, the film thickness calculated from the X-ray spacing is less than that predicted from theory.

The present paper is concerned with an analysis of the water content-energy curves of clay cores in terms of their structure in the dry state as revealed by complete low temperature nitrogen adsorption-desorption isotherms and the surface area of the crystals. Compressed cores were used so that contributions by water enmeshed within the gel structure to the total water content would be at a minimum.

MATERIALS

Although a number of different clays were examined the results for four clays are discussed to indicate the main features of the investigation. These clays are as follows: an illite from the B horizon of a solodized solonetz in the hundred of Willalooka, South Australia; the B horizon of Urrbrae loam,

a Red-brown earth at the Waite Institute, South Australia, containing 60 percent of particles less than 2μ ; a montmorillonite from Redhill, Surrey, England and Wyoming bentonite from Upton, Wyoming, U.S.A. Willalooka illite is degraded to some extent since it has a low potassium content (4 percent K_2O) but there is no evidence of interstratification. The clay fraction of the Urrbrae loam contained 60 percent illite and 40 percent kaolinite. The illite in the Urrbrae loam appears to have similar characteristics to the Willalooka illite.

EXPERIMENTAL PROCEDURES

(a) *Preparation of Clay Materials*

Samples of clay were saturated with the desired cation by repeated washing and centrifuging using a molar solution of the appropriate chloride. Excess salt was removed by washing the materials with distilled water until they commenced to disperse or until the chloride concentration was less than 10^{-3} M. Salt-free samples of clay were obtained by dialyzing for two weeks against distilled water using "Visking" cellulose casing.

Decantation of clay suspension was carried out to remove coarse particles and the suspension was filtered in a Buchner funnel; the clay was then allowed to air-dry. Violent dispersion techniques were specifically avoided to prevent the possible disruption of any natural clay structures which might exist, particularly for the divalent clays.

The air-dry clays then were gently ground to a powder and placed in a desiccator and allowed to come to vapor equilibrium with a saturated solution of potassium sulfate ($p/p_0 = 0.96$ at $20^\circ C$). Samples (200 mg) of homoionic clays were placed in a stainless steel mold and compressed to 1200 atm pressure by means of a hydraulic jack. The water contents of the illite and montmorillonite powder in equilibrium with 0.96 relative vapor pressure were sufficient to give saturation under compression. After compression the cores were wet in stages of pF $4.7 \rightarrow 2.8 \rightarrow 2.0$ and then dried successively to 0.75 and 0.19 relative vapor pressure before drying over P_2O_5 . The water adsorption isotherms, surface areas, and pore size distributions were determined on these cores.

For Urrbrae B the natural aggregates were obtained and the cores were made after Ca^{2+} saturating by the same procedure as was used for the other clays except that coarse particles were not removed. The natural aggregates were largely Ca^{2+} saturated.

(b) *Low Temperature Nitrogen Sorption Isotherms*

Complete nitrogen adsorption-desorption isotherms for the clay materials at $78^\circ K$ were obtained using a volumetric apparatus based on the original apparatus of Emmett and Brunauer (1934) and incorporating many

of the refinements suggested by Harkins and Jura (1944) and Joyner (1949).

Sufficient weight of clay to give a surface area of approximately 100 m² was placed in the sample bulb, connected to the apparatus and outgassed at a temperature of 300 °C for 25 hr or until the pressure remained below 10⁻³ mm after isolation from the pumps for 30 min. The 300 °C outgassing temperature was adopted for most satisfactory reproducibility in the light of results obtained by Brooks (1955). Méring (1946) concluded that montmorillonite retained its hydration capacity up to a temperature of 300 °C. In the present work it was found that montmorillonite still retained its capacity for large physical swelling after outgassing at a temperature of 400 °C.

(c) *Water Content–Energy Relationships*

Water content–energy relationships for the clay materials were obtained by means of pressure plate and pressure membrane apparatus and constant humidity desiccators. The work was carried out in a room maintained at 20 ± 1/4 °C.

To facilitate comparison between solutions of different electrolyte concentration and also the calculation of surface film thickness, the solution contents are given in volume of solution absorbed per gram of oven dry (110 °C) clay.

(d) *Determination of Exchange Capacity*

Samples of the clays as previously prepared were saturated with strontium by washing with a neutral solution of molar strontium bromide. Excess salt was removed by washing with distilled water and the clays allowed to air-dry. The exchange capacities were obtained as the difference between the strontium and bromide contents determined using an X-ray spectrographic method. In all samples the bromide contents were very low.

The exchange capacities in meq per 100 g of oven dry 110 °C clay are given in Table 1.

TABLE 1.—PROPERTIES OF CLAY MATERIALS

Material	Surface Area (m ² /g)	Exchange Capacity (meq/g)	Porosity (cm ³ /g)	Particle Density (g/cm ³)
Willalooka illite	152	0.41	0.185	2.65
Redhill montmorillonite	102	1.00	0.152	2.58
Wyoming bentonite	38	1.01	0.135	2.59
Urrbrae—cores	94	0.28	0.141	2.72
Urrbrae—aggregates	91	0.28	0.191	2.72

(e) Specific Gravity and Porosity Determinations

Specific gravity of the clays was determined on the oven-dry (110 °C) material by the volume displacement method using a nonpolar liquid and 25-ml pycnometers. The apparent density of the oven-dried clay cores was determined from the oven dry mass and the overall volume of the clay cores. The volume of the clay cores was calculated from direct measurements of the dimensions obtained with a traveling microscope. For volumes of 0.1–0.2 ml this method gave better than 1 percent accuracy. The porosity was calculated from the particle density and apparent density in the usual way.

RESULTS AND DISCUSSION

Nitrogen Isotherms and Pore Size Distributions

Surface areas of the clay minerals, obtained by the application of the B.E.T. theory to the nitrogen adsorption isotherm are set out in Table 1 together with the exchange capacity, porosity of clay cores and particle density.

To illustrate the distribution of pores differential plots of the volume adsorbed per gram with respect to relative vapor pressure against relative pressure, i.e. $dV/d(p/p_0)$ against p/p_0 , were made. The equivalent pore radii calculated on the basis of the Kelvin equation are indicated on the abscissa. The linear (p/p_0) scale was considered more convenient for the purpose of illustration than a true pore size distribution plot of dV/dr against r , since the latter involves the inverse logarithmic relationship between p/p_0 and r and provides little further information.

The isotherm for the Ca^{2+} cores of Willalooka illite together with the pore size distribution are shown in Figs. 1 and 2. Similar results for Redhill montmorillonite are shown in Figs. 3 and 4.

The nitrogen adsorption isotherm of Willalooka illite and Redhill montmorillonite both show appreciable hysteresis above 0.4 relative vapor pressure followed by a small but persistent hysteresis down to a very low vapor pressure. Similar hysteresis effects in nitrogen isotherms on finely divided material have been noted by several other workers. Brooks (1955) explained the presence of hysteresis at low relative pressures (< 0.4) in the nitrogen sorption isotherms for Ca^{2+} -montmorillonite as being due to the propping apart of interlamellar spacings by residual water molecules giving rise to a structural instability of the material. This could account for the augmented nitrogen adsorption capacity on the desorption branch of the isotherm down to very low relative pressures. The disappearance of this micro-pore hysteresis after the removal of most of the water of adsorption and hydration by a prolonged outgassing for 152 hr at 25 °C and 4 hr at 60 °C

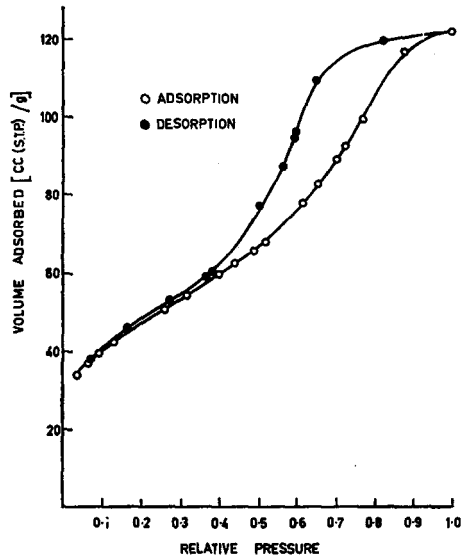


FIGURE 1.—Liquid nitrogen adsorption-desorption isotherm for Ca^{2+} Willalooka illite cores.

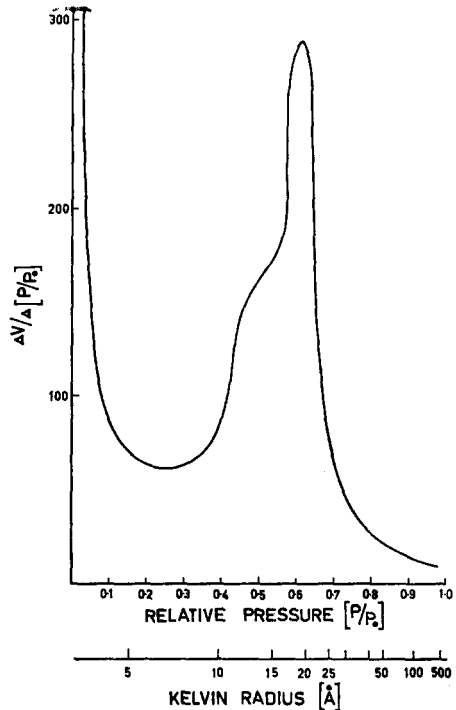


FIGURE 2.—Pore size distribution of Ca^{2+} Willalooka illite cores obtained by differentiating the nitrogen desorption isotherm.

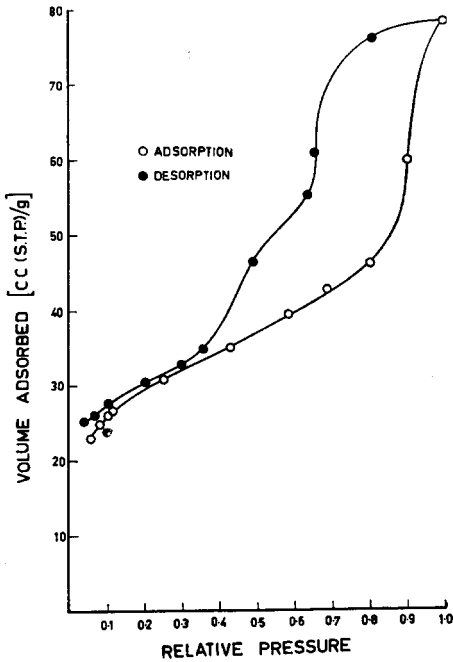


FIGURE 3.—Liquid nitrogen adsorption-desorption isotherm for Ca^{2+} Redhill montmorillonite cores.

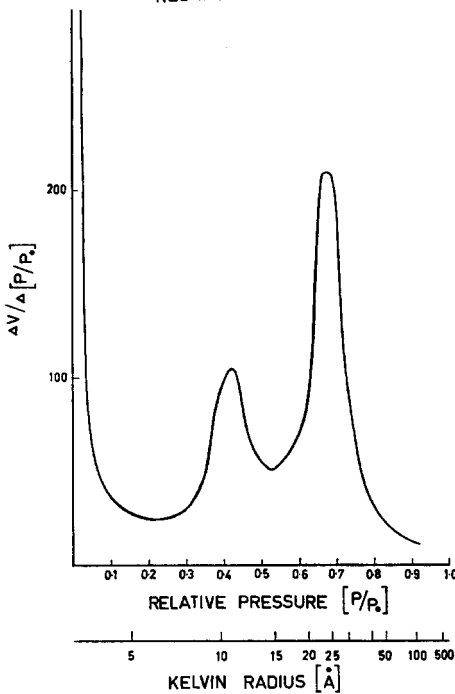


FIGURE 4.—Pore size distribution of Ca^{2+} Redhill montmorillonite cores obtained by differentiating the nitrogen desorption isotherm.

at 10^{-6} mm mercury pressure, gave support to this concept. Low relative pressure hysteresis was not, however, evident in the isotherms obtained by Brooks for native (Na^+) Wyoming bentonite and in this case he considered that the intracrystalline spacing (2.80 Å corresponding to one water layer) was too small to allow nitrogen penetration (diameter of nitrogen molecule = 4.2 Å).

McDermot and Arnell (1955, 1956) in studying the properties of brominated graphites where the situation is not unlike that for the montmorillonites with both intercrystalline and intracrystalline sorption of bromine, have also demonstrated the existence of two types of hysteresis in nitrogen isotherms for these structures with an expanding *c*-axis. These workers believed the broad hysteresis loop extending from saturation down to relative pressures of approximately 0.45 to be due to the porous nature of the graphite and designated it as "pore" hysteresis. The second type of hysteresis which they termed "swelling" hysteresis was attributed to the availability of volume within the swollen graphite crystals after removal of most of the bromine. The term intercrystalline swelling was used by these workers but the phenomenon as described is probably more aptly termed intracrystalline.

The persistence of this latter type of hysteresis in the present work on Ca^{2+} Redhill montmorillonite after the stronger outgassing procedure and its presence for the illite cores seems to indicate its origin in this case as an intercrystalline rather than an intracrystalline phenomenon. This could arise if there were any appreciable stacking of the platelike crystals of these minerals in the drying or consolidation process. Similar conditions for a structural instability as envisaged by Brooks would then occur.

The interpretation of equivalent pore radii calculated on the basis of the Kelvin equation must be made with some caution. The conventional form of the Kelvin equation relates the vapor pressure lowering above a hemispherical meniscus to the curvature of the meniscus or radius of the cylindrical pore containing the meniscus

$$r_c = - \frac{2V\gamma}{RT} \log_e p/p_0,$$

where p is the desorption pressure, p_0 the saturated pressure, V is the molar volume and γ the surface tension of the adsorbed liquid at temperature T , r_c is the radius of the cylindrical pore and the radius of curvature is

$$(1/r_c + 1/r_c) = 2/r_c.$$

For a meniscus which occurs between parallel plates whose dimensions are large compared with the distance of separation, the radius of curvature is given by $(1/r_p + 1/\infty)$ where r is half the distance of separation between plates. Thus

$$r_p = - \frac{V\gamma}{RT} \log_e \frac{p}{p_0}$$

so that

$$r_c = 2r_p.$$

Hence the conventional Kelvin radius (hemispherical meniscus) which is given in Figs. 1 and 2 can be better regarded as estimates of the average crystal separations at least for those pores that are small in comparison with plate dimensions (say $< 100 \text{ \AA}$). If Foster's suggestion (1932) is correct this estimate should be increased by twice the thickness of an adsorbed monolayer (approx. 8 \AA).

The volume of liquid nitrogen retained at any particular value of relative pressure is related to the particle size and specific surface area as is to be expected. However, almost the entire porosity of the Willalooka cores is accommodated in pores having equivalent cylindrical radii less than 33 \AA . From the differential plot it can be seen that the peak of the pore size distribution for this clay occurs at a relative pressure of approximately 0.625 corresponding to an equivalent cylindrical pore radius of 20 \AA . Since the crystal plates of this clay are probably of the order of 700 \AA across the cleavage face, this equivalent cylindrical radius may be interpreted, on the addition of twice the monolayer thickness, as a separation between crystal sheets of the order of 28 \AA . If the oven-dry porosity of the clay is divided by the specific surface area the average half distance between crystals so calculated is 13 \AA . It may be inferred, therefore, that the matrix of the Willalooka cores consists of the clay plates highly organized on a microscale into packets or domains with very few large pores between domains. It is difficult to visualize such a relatively narrow band of pore sizes arising in any other fashion than this for plate-shaped particles, although the reason for crystals remaining at such high separations in the dry state is not clear. The presence of surface irregularities on the clay crystals may be envisaged as holding the majority of the surface at appreciable separations. Alternatively the separations may be considered to arise from mutual repulsion of the surface charge distributions. In this regard the approach of one plate to another in the dry state could possibly provide a net repulsive force such as may result from the approach of a positive charge (surface cation) to a dipole considered as arising from the separation of the exchangeable cation on the adjacent sheet from the site of isomorphous replacement by the layer of oxygen atoms.

It may be argued, of course, that the crystal sheets may be very much closer within domains with a large volume of interdomainal pores of the order of 28 \AA , but unless a large proportion of the surface area is not available to nitrogen adsorption this would necessitate the presence of a considerable volume of much larger pores between domains to provide the same total porosity. Isotherms for the adsorption of polar water molecules indicate that essentially the total surface of the illites is available to nitrogen adsorption.

The peak in the pore size distribution for Willalooka illite (Fig. 2) shows a shoulder corresponding to plate separations of approximately 20 Å. On the other hand the pore size distribution for Redhill montmorillonite exhibits two separate peaks corresponding to plate separations of approximately 20 Å and 32 Å, respectively. For Wyoming bentonite these same peaks were in evidence and corresponded to plate separations of approximately 20 Å and 85 Å, respectively. The second peaks may be inter-

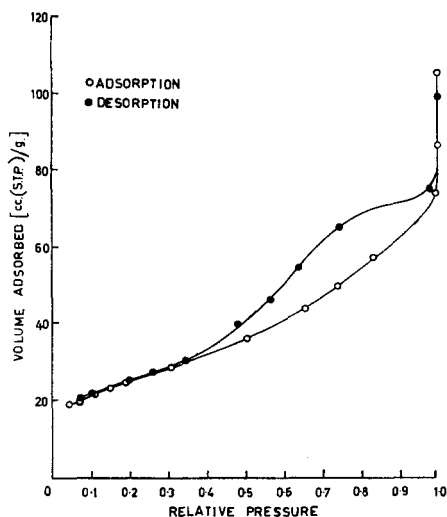


FIGURE 5.—Liquid nitrogen adsorption-desorption isotherm for Ca^{2+} Urrbrae B cores.

preted as arising from larger intradomain spacings for the montmorillonites than for the illites resulting from the contraction of the montmorillonite crystals after the formation of the clay matrix structure during the drying process. The increased separation for Wyoming bentonite probably arises from the larger number of lamellae per crystal. The first peak on each curve (indicating plate separations of approximately 20 Å in each case) may then correspond either to the areas of closest possible approach of the clay crystals in a fixed structure, as suggested for Willalooka illite, in which case some mechanical hindrance or repulsive force is implied, or else to a reshuffling of the clay crystals by surface tension forces as envisaged by Barrer and MacLeod (1954).

The comparison of the nitrogen sorption isotherms of the manufactured cores and natural aggregates of the Urrbrae loam, B horizon, shown in Figs. 5 and 6 is particularly interesting. Both isotherms are similar to that obtained for the Willalooka illite indicating a high degree of domain structure formation. Below an equivalent cylindrical pore size of 20 Å (0.625 relative vapor pressure) there are no significant differences between the cores and

natural aggregates. This may be interpreted as indicating that the intra-domain pore space is not affected to any appreciable extent by the compression process. The volume of pores between 100 Å and 200 Å is significantly reduced for the cores indicating that domains have been brought into closer packing. Quirk and Panabokke (in press) have studied the pore size distribution for pores greater than 100 Å in some detail and all these pores are eliminated by compression.

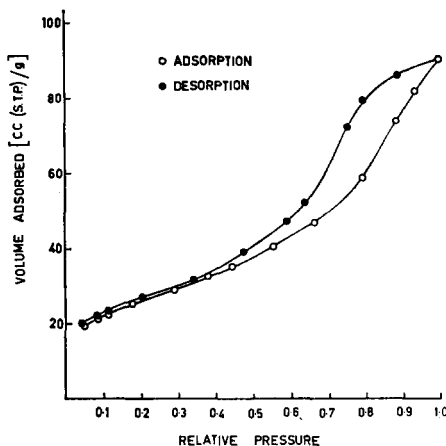


FIGURE 6.—Liquid nitrogen adsorption-desorption isotherm for Urrbrae B, natural aggregates.

An electron micrograph of the fracture surface of a Willalooka illite core obtained using a polyethylene replica technique is shown in Plate 1. The parallel alignment of the plate-shaped particles into an oriented group can be distinguished as the striated area of alternate light and dark strips. The size of the domain area for Willalooka illite (approximately $10\ \mu$ long) in comparison to the crystal size for this clay seems to indicate that a domain structure may consist not only of crystal sheets oriented and stacked but also interleaved across a considerable distance. The change in orientation of some of the particles can be clearly seen near the edge of this area.

Physical Swelling of Montmorillonite

(a) Ca^{2+} montmorillonite.—The effect of previous history on the water content of Ca^{2+} Redhill montmorillonite cores and suspensions is shown in Fig. 7. One feature is the marked hysteresis between the wetting and drying curves for the cores. This hysteresis is clearly dependent on the final wetting point since on drying to $pF\ 3$ from a suction of 1 cm the clay retains more water than on drying from 10 cm suction. The hyster-

esis is even more marked where the clay has been dried from a suspension or where it has been saturated with Na^+ and then again saturated with Ca^{2+} . The apparently more open gel network and hence the larger volume of enmeshed water (*i.e.* water held by capillary

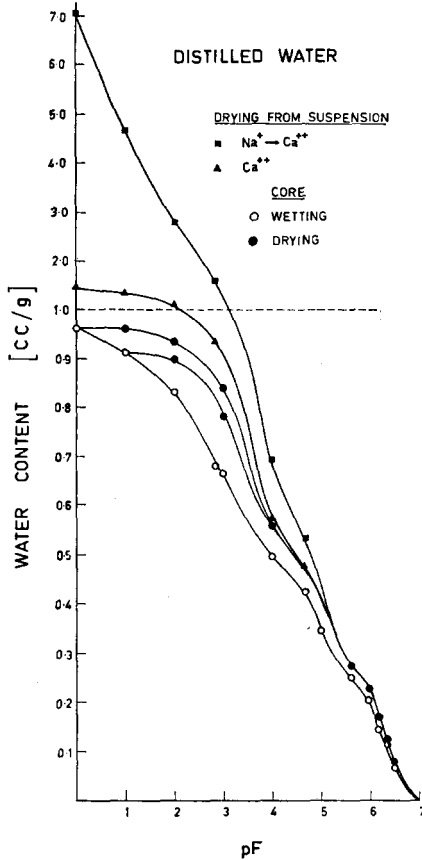


FIGURE 7.—Effect of previous history and hydrostatic suction on the water content of Ca^{2+} Redhill montmorillonite.

forces; see section on enmeshed water in the discussion) in the latter case may be considered to arise from the presence of a larger number of particles due either to the disruption of domains with the crystals retaining their entity or alternatively to the breakup of the crystals themselves whether by dispersion to the elementary silicate sheet level when Na^+ saturated or by a less complete crystal degradation. The identical surface areas obtained for the Ca^{2+} and $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ montmorillonites ($38 \text{ m}^2/\text{g}$ for Wyoming bentonite and $100 \text{ m}^2/\text{g}$ for Redhill mont-

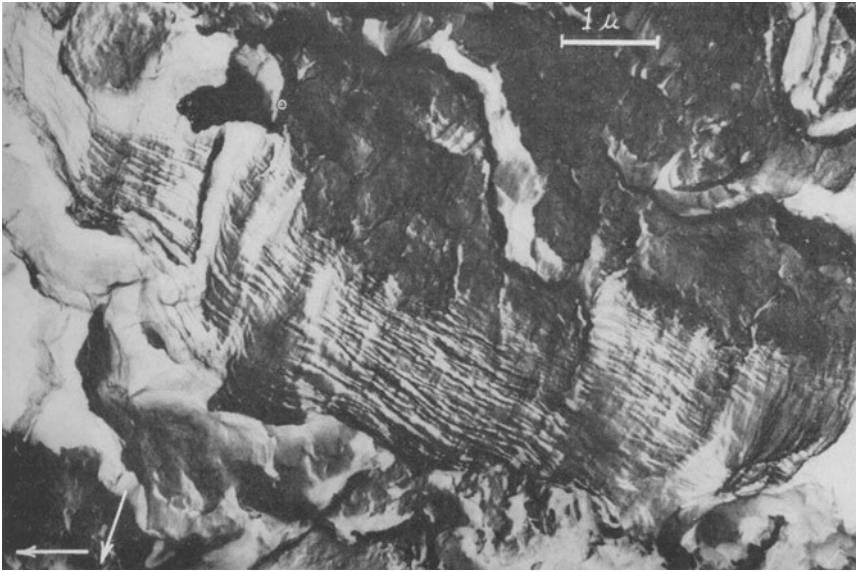


PLATE 1.—A electron micrograph of a replica of the fracture surface of a clay core of Willalooka illite. The arrows show the direction of shadowing. The interleaved and parallel arrangement of the clay crystals can be seen to extend over a considerable distance indicating that a domain is considerably more complex than the simple model.

morillonite) seem to indicate that the crystals either retain their entity throughout the treatment or else result from a statistical re-formation process which for a given type of elementary sheet tends to give the same external surface area when condensation takes place.

Despite the great differences in water content at low suctions, all the drying curves are essentially coincident at pF 5.6 (0.75 relative vapor pressure at 20 °C), the point at which normal shrinkage, as obtained from volume measurements on the cores, ceases. Air entry at this point corresponds to a Kelvin cylindrical radius of $<50 \text{ \AA}$ and since the dry cores have an appreciable volume of pores with equivalent cylindrical radii of several hundred Ångströms it may be concluded that considerable internal accommodation of swelling producing an effective reduction in pore dimensions has occurred. Note that the total volume of liquid nitrogen retained by the Ca^{2+} montmorillonite cores ($0.068 \text{ cm}^3/\text{g}$ and $0.120 \text{ cm}^3/\text{g}$ for Wyoming bentonite and Redhill montmorillonite respectively) at 0.9 relative vapor pressure (90 \AA equivalent Kelvin radius) is appreciably less than the oven-dry porosities of the cores ($0.135 \text{ cm}^3/\text{g}$ and $0.150 \text{ cm}^3/\text{g}$, respectively).

At 0.75 relative vapor pressure the intracrystalline spacing is 15.4 \AA (Mooney, Keenan and Wood, 1952) and the volume of water ($0.258 \text{ cm}^3/\text{g}$, assumed density equal to unity) corresponding to two layers of intracrystalline water plus two layers on the external surface of the crystals is only slightly less than the total volume of voids ($0.265 \text{ cm}^3/\text{g}$) obtained from volume measurements on the Redhill cores.

The results in Table 2 calculated by dividing the water contents given in Fig. 7 by the external surface area after correcting for intracrystalline water [$d(001) = 19 \text{ \AA}$] indicate a film thickness of 19 \AA at a suction of 10 atm, and this is considerably more than the predicted value on the basis of the Gouy-Chapman model which would hardly be expected to apply at this point. However, at pF 1 the film thickness of 59 \AA is a good deal lower than the theoretical expectation of 200 \AA . This film thickness of 59 \AA would be an overestimate since the large hysteresis indicates that a considerable

TABLE 2.—EFFECT OF INCREASED SUCTION ON THE FILM THICKNESS FOR Ca^{2+} MONTMORILLONITE CORES WET WITH DISTILLED WATER

pF	Water Content (cm^3/g)	Corrected for Intracrystalline Water — $d(001) = 19 \text{ \AA}$ (cm^3/g)	Film thickness (Å)	
			Calculated	Theoretical ¹
1	0.92	61	60	200
2	0.83	52	51	72
3	0.57	26	25	24
4	0.50	19	19	8

¹ 10^{-4}M CaCl_2 .

amount of the water, held in the clay structure, may not be associated directly with the clay surfaces.

The Gouy-Chapman theory as developed by Schofield relates film thickness on a charged surface to the electrolyte concentration of the solution external to the double layer of the charged surface and the hydrostatic

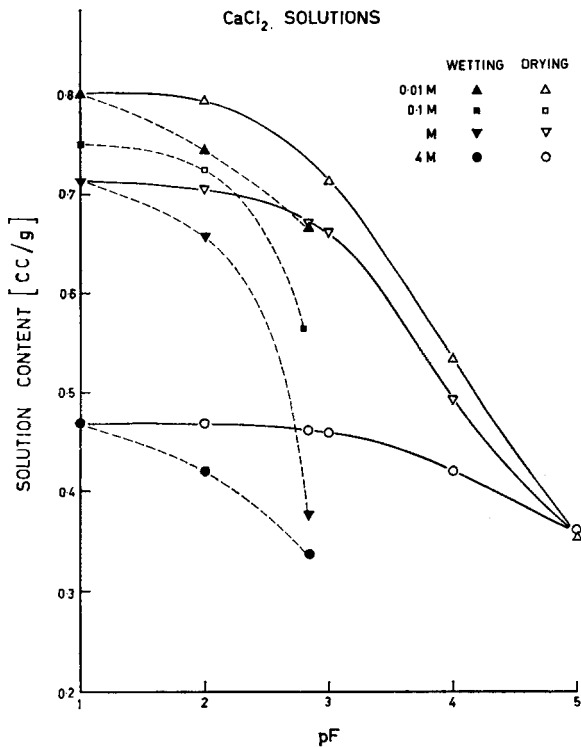


FIGURE 8.—Effect of hydrostatic suction and calcium chloride concentration on the solution content of Ca²⁺ Redhill montmorillonite cores.

suction imposed on the liquid. The results in Fig. 8 show adsorption and desorption isotherm for the montmorillonite cores over the electrolyte concentration range 4 M CaCl₂ to 0.01 M CaCl₂. All curves show a marked hysteresis and this hysteresis is particularly noticeable at pF 2.8 when the clay contains 1 M CaCl₂.

The change in the solution content from 0.72 cm³/g in molar to 0.80 cm³/g in 0.01 M does not seem large enough to indicate the presence of diffuse double layers in the system; however, it may be suggested that the particles within a domain do not show appreciable swelling owing to the presence of a potential barrier and that diffuse double layers exist between adjacent

domains. The relatively small amount of swelling (solution content increase from 0.72 to 0.92 cc/g) which takes place between molar and distilled water (10^{-4} M) may possibly be attributed to diffuse double layers forming on the external surface of the domains since their surface area would be very much less than the external surface area of the crystals which is 102 m²/g. At pF 1 the swelling in molar is very much greater than in 4 M although the external surface film thickness calculated for 4 M (basal spacing of 15.4) is 23 Å. This large change in solution content between 4 M and molar would be associated with the swelling of the whole surface including that within domains.

The film thickness calculated on wetting to pF 2.8 with 4 M CaCl₂ is 13 Å and this increases to about 23 Å at pF 1. These considerable values for this concentration cannot be regarded as the true film thickness development but probably arise from the relaxation of strains imposed on clay crystals and domains as the result of drying. On wetting, when sufficient liquid is present in the system relaxation may take place creating a gel structure. It should be remembered that as saturation exists for these cores and that the initial pore space has been invaded by intracrystalline swelling.

(b) Na⁺ montmorillonite.—The results of the effect of electrolyte concentration on the swelling of Na⁺ montmorillonite (Fig. 9) contrast with those

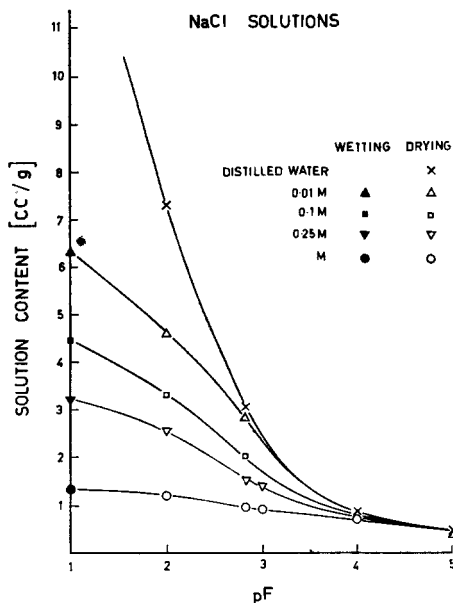


FIGURE 9.—Effect of hydrostatic suction and sodium chloride concentration on the solution content of Na⁺ Redhill montmorillonite cores.

for Ca^{2+} montmorillonite. Here solution contents of several hundred percent are obtained at pF 1 for dilute solutions and it seems apparent that diffuse double layers are forming.

The film thickness values in Table 3 were calculated by dividing the solution content by the total surface area of $760 \text{ m}^2/\text{g}$ except for molar

TABLE 3.—FILM THICKNESS FOR Na^+ REDHILL MONTMORILLONITE

M	Solution Content (cm^3/g)	Film Thickness		
		Calculated from Water Content	X-ray ²	Theoretical
1.0	1.33	102 ¹	4.5	19
0.25	3.20	42	16	33
0.10	4.45	59	25	48
0.01	6.80	83	63	114
0.0001	22.50	295	570 ³	400

¹ External surface area used and a correction applied for intracrystalline water.

² Norrish (1954).

³ Obtained by extrapolation of the X-ray results.

NaCl where the external surface area of the clay was used after correcting for intracrystalline water $d(001) = 19 \text{ \AA}$. The high value obtained by this procedure for the external film thickness in molar NaCl as compared with that obtained at a concentration of 0.25 M NaCl and also as compared with the X-ray measurements of Norrish (1954) highlights the fact that even for the swelling of compressed cores there is considerable reorganization of the structure so that a considerable proportion of the water simply is enmeshed within the gel structure rather than being associated with the clay particles in the form of a diffuse double layer. Owing to the presence of this gel structure it is only possible to say that diffuse double layer theory is obeyed in a qualitative way. It is not possible to decide whether the measurements of Norrish or the theoretical predictions by Schofield's method are more apposite.

Swelling of Illite

(a) Ca^{2+} illite.—It has been suggested that Willalooka illite possesses a highly organized structure with crystals oriented on a microscale into domains and that almost the entire porosity in the dry state arises from average separations of about 28 \AA between these oriented crystals. If this is so, the domain system in an illite has much in common with the montmorillonite crystal and provides an ideal situation for the operation of electrostatic attractions as suggested by MacEwan (1948) with the ex-

changeable cations lying between the negatively charged clay plates. In these circumstances the volume of solution not directly associated with crystal surfaces would be less significant and a more reliable estimate of the film thickness developed on the clay surfaces should be obtained by dividing the solution content by the specific surface area. The effect of

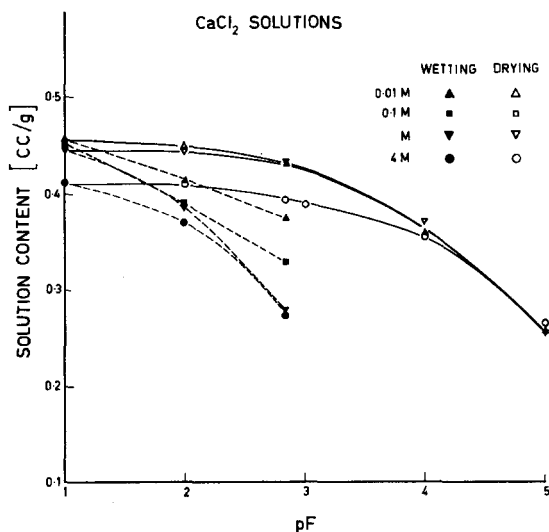


FIGURE 10.—Effect of hydrostatic suction and calcium chloride concentration on the solution content of Ca^{2+} Willalooka illite cores.

TABLE 4.—CALCULATED FILM THICKNESS (\AA) FOR Ca^{2+} WILLALOOKA ILLITE FOR DIFFERENT SUCTIONS AND ELECTROLYTE CONCENTRATIONS

Suction pF	Molar Concentration of CaCl_2				
	4.0	1.0	0.1	0.01	0.0001
1	27	30	30	30	30
2.8	18	18	22	25	25
4.0	—	—	—	—	20
4.7	—	—	—	—	18

electrolyte concentration on the swelling of the Ca^{2+} Willalooka illite cores is shown in Fig. 10. It is immediately obvious that variations in calcium chloride concentration between distilled water (10^{-4} M) and molar have little if any effect on the solution uptake by this clay at pF 1.

From Table 4 it can be seen that the film thickness calculated as above at pF 1 is essentially constant at 30 \AA for all electrolyte concentrations between 4 M and distilled water. This is reminiscent of Ca^{2+} montmorillonite which has a basal spacing of 19 \AA for all calcium chloride concen-

trations less than molar. Thirty Ångströms, whilst considerably larger than the 10 Å or thereabouts expected for a molar solution, is considerably less than 200 Å predicted by diffuse double layer development in distilled water (say 10^{-4} M). It seems reasonable to conclude that diffuse double layer concepts cannot be used to describe the swelling of this Ca^{2+} clay system even though the silicate sheets appear to be separated by a distance of 60 Å. As a potential barrier obviously exists in this system it still may be argued that diffuse double layer concepts could be applicable to Ca^{2+} clay particles which had moved across this potential barrier as a result of dispersion or mechanical work or could apply to the interaction between adjacent domains. There is, however, little indication of any such effects.

The nature of the potential barrier is not clear. MacEwan (1948, 1954) has suggested that coulombic attractive forces exist up to plate separations of 30 Å, at which separations he envisaged the formation of separate diffuse double layers by each particle. The results discussed here indicate a plate separation of 60 Å but no allowance has been made for enmeshed water in obtaining this figure so that the true plate separation could be appreciably less than 60 Å.

The electron micrograph of the fracture surface of a Willalooka illite core shows that clay crystals in the dry clay matrix are subject to considerable distortion (Plate 1). Hence Terzaghi's (1927) idea of crystal bending on drying and subsequent relaxation on rewetting could be operative in increasing the solution uptake above that which would occur if only surface film development took place, as within a montmorillonite crystal. This relaxation may account for the large hysteresis at pF 2.8 in Fig. 10. With the reduction in electrostatic attractive forces as envisaged by MacEwan at separation of about 40 Å the elastic properties of the clay crystals may be sufficient to overcome the effective potential barrier and initiate the formation of gel structures. Once the structure has undergone this relaxation of mechanical strain the increase in suction necessary to cause recompression of the structure, appears to be comparatively independent of the concentration of electrolyte present (Quirk and Aylmore, 1960).

To exclude the possibility that the restricted swelling of the Ca^{2+} Willalooka illite was due to cementing materials, samples of the Na^+ -saturated clay, which is subsequently shown to exhibit large swelling and considerable response to change in electrolyte concentration, were resaturated with Ca^{2+} . The behavior of this Ca^{2+} clay was identical with that of the material which had been directly Ca^{2+} saturated. One interesting feature was that the $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ illite suspension when dried at pF 1 in the presence of molar CaCl_2 retained $2.67 \text{ cm}^3/\text{g}$ of solution whereas the Ca^{2+} illite suspension retained $1.79 \text{ cm}^3/\text{g}$. This difference is attributed to domain breakdown in the preparation of the Na^+ clay. The domains evidently re-formed on drying.

(b) *Na⁺ illite*.—The effects of concentration of sodium chloride solution on the drying curves of Willalooka illite after wetting to pF 1 are shown in Fig. 11. There is a continuous rapid reduction in swelling with increasing sodium chloride concentration as would be expected from diffuse double layer considerations. At pF 1 the solution uptake is reduced from 8.41 cm³/g for distilled water to 0.482 cm³/g for normal sodium chloride solution. This latter water content is only slightly greater than that for Ca²⁺ Willalooka illite in distilled water, indicating that for molar NaCl the potential barrier

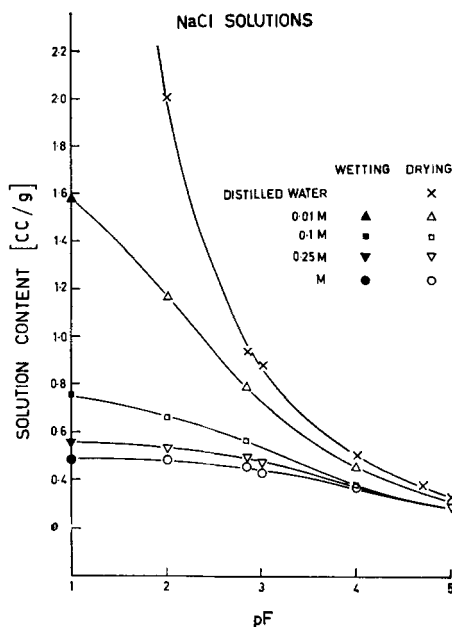


FIGURE 11.—Effect of hydrostatic suction and sodium chloride concentration on the solution content of Na⁺ Willalooka illite cores.

has not been exceeded. The same is true for the 0.25 M solution where the film thickness calculated as before is 37 Å. In 0.1 M NaCl there is a considerable increase to 50 Å and in 0.01 M the calculated film thickness is 106 Å. These large film thicknesses for Na⁺ Willalooka in dilute salt solutions suggest the possibility of the formation of a diffuse double layer once the potential barrier has been exceeded. When the film thicknesses obtained by dividing the solution content in Fig. 11 by the specific surface area are compared with the theoretical diffuse double layer value (Fig. 12) it can be seen that the agreement for low suctions is good over the range 10⁻¹ to 10⁻⁴ M NaCl. However, no allowance has been made for water that is simply enmeshed in the structure. Even though this would be at a mini-
9*

imum for Willalooka illite because of its highly organized structure, this correction probably would bring the calculated film thickness in 10^{-2} and 10^{-1} M NaCl closer to those calculated for Na^+ -montmorillonite from the X-ray results of Norrish (1954). At these respective concentrations film

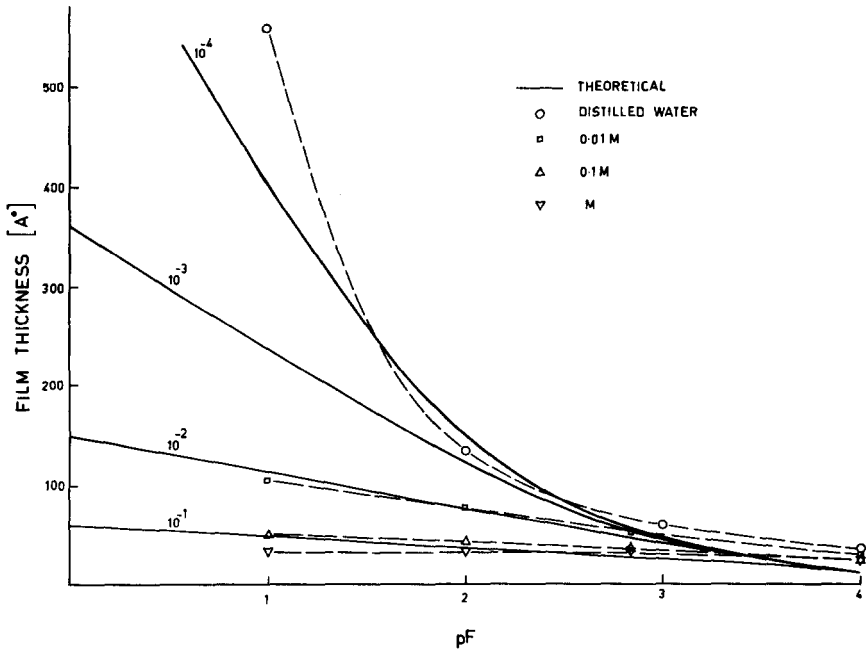


FIGURE 12.—A comparison of calculated and theoretical film thicknesses for Na^+ Willalooka illite cores. The calculated film thicknesses were obtained by dividing the solution content by the specific surface area.

thicknesses of 62 and 23 Å are found for oriented flakes of Na^+ -montmorillonite in free solution.

Cores, of the Urrbrae, B horizon, clay show very restricted swelling for divalent ion and high electrolyte concentration monovalent ion systems and large swelling in dilute monovalent ion systems similar to that observed for the Willalooka illite, indicating that domain structure effects are also very apparent for this clay. This contrast in behavior between the Na^+ and Ca^{2+} illite is very similar to the contrast in behavior between Na^+ and Ca^{2+} montmorillonite and reinforces the suggestion that a domain of illite crystals is similar to a montmorillonite crystal since both, when Ca^{2+} saturated, show limited swelling because of the existence of a potential barrier. In this regard a montmorillonite crystal may possibly be regarded as a particular type of domain with the single lamellae constituting the basic units instead of entire crystals as in an illite domain.

The potential barrier limiting the swelling between Ca^{2+} illite crystals would appear to be clearly different from that which limits the crystalline swelling of Ca^{2+} montmorillonite since much greater distances of separation are involved. Furthermore if illite crystals approached within 5 Å of one another as montmorillonite or vermiculite lamellae do on drying, limited swelling would be expected since the surface density of charge of the illite crystals (2.7×10^{-7} meq/cm²) is considerably greater than vermiculite (approx. 2×10^{-7} meq/cm²) which gives a maximum lamellae separation of about 5 Å when saturated with sodium or calcium. This potential barrier is overcome by Li^+ -vermiculite. However, an alternative explanation of the restricted swelling of the Willalooka illite when Ca^{2+} saturated and in high electrolyte concentration monovalent solutions could be the existence of vermiculite-like bonding at very small areas of closest approach of crystals within domains. Hence the swelling that occurs in these cases may result largely from interdomainal interactions.

GENERAL DISCUSSION

(a) *Enmeshed Water*

If the swelling and shrinkage of clay systems were entirely due to the development and contraction of diffuse double layers, the systems would be expected to exhibit little hysteresis. The existence of potential barriers as observed by Norrish (1954) could contribute to hysteresis effects. However, the nature of the irreversible hysteresis observed in the saturated state seems to indicate that structural alterations due to particle readjustment are of major importance in determining this hysteresis (Schofield, 1935). It therefore seems reasonable to suggest that while some of the water is directly associated with the surfaces of the clay particles, some is retained by surface tension forces within a gel structure arising from mechanical interactions of the clay particles. The chief experimental difficulty in trying to test the applicability of diffuse double layer theory, as adapted by Schofield (1946), to the swelling of clay systems is to separate the relative contributions of the two mechanisms to the total water content.

The retention of water within the gel structure can be regarded in the following way. When a rigid porous material, initially filled with liquid, dries out under falling vapor pressures, pores (capillaries) of particular dimensions will empty at particular vapor pressures. The remaining liquid is held under a hydrostatic suction which is transmitted to the walls, but, as each pore empties, the stresses on the walls due to this cause will fall to zero. If, however, the material is easily deformed, the increase in the suction in the liquid will cause a reduction in the size of the pore, and evaporation will be delayed until a lower vapor pressure is reached, by which time the suction has further increased. This mechanism is clearly distinct from

the loss of water from double layers as the result of reducing the vapor pressure or increasing the applied hydrostatic suction. Barkas (1948) has discussed the shrinkage of wood gels in these terms.

Before considering the consequences of this model it is necessary to consider how the gel structure can arise for a compressed clay core or natural clay structure. The electron micrograph (Plate 1) of Willalooka illite shows a region of oriented particles and it is immediately obvious that this region is of considerable extent and conforms in a general way to the idea of the parallel alignment of particles. It can be noticed, however, that this arrangement is far from simple since there is considerable interleaving and bending of the individual crystals. Aylmore and Quirk (1959) have described such a region as a domain. Because the term "domain" could also be taken to mean micro-aggregate the terminology used by coal research workers may be more meaningful. Biscoe and Warren (1942) use the term turbostratic groups to convey the idea that the groups contain particles in a parallel or stratified arrangement and also that the groups with respect to one another are in turbulent array. The above interpretation of the electron micrograph for Willalooka is supported by the peak which occurs in the pore size distribution indicating plate separations between 10 and 30 Å (Fig. 2).

The gel structure appears to form at high suctions (approx. 10–50 atm) and in the presence of strong salt solutions. This would suggest that it is initiated by a mechanical rather than a physico-chemical mechanism although the degree of gel structure development is related to the electrolyte concentration. Terzaghi's (1927) idea of crystal bending on drying and subsequent relaxation on rewetting is probably operative in the formation of this structure. The gel structure development probably is dependent to a certain extent on the removal or decrease in attractive forces rather than an increase in repulsive forces between adjacent clay crystals. It has been suggested that in the presence of sufficient liquid, strains due to crystal bending will tend to relax. However, when the solution between the charged surfaces is 4 M CaCl_2 the ion distribution would be such that one ion would be only 5 Å from its neighbor and the water in this region would be largely in the state of dielectric saturation. As the concentration of ions is decreased the attractive force would be lessened since this proportion of water showing dielectric saturation in the vicinity of the clay particles would decrease. This suggestion could explain the larger relaxation in molar NaCl than in molar CaCl_2 , but of course it would not explain the increase in solution content at $pF1$ from 0.80 to 0.92 cm^3/g for Redhill montmorillonite when 0.01 CaCl_2 and distilled water are used as the wetting liquid. It is interesting to note that Redhill montmorillonite has a much greater tendency to form a gel structure than Willalooka illite, indicating a more extensive or stronger domain structure for the latter material.

(b) Turbostatic Groups or Domains

The existence of turbostatic groups or domains and the formation of gel structures are extremely important with respect to the interpretation of the film thickness developed by clay particles and the cause of hysteresis in a two-phase system such as clay and water.

Condensation into domains (Aylmore and Quirk, 1959) is not readily reversible so that each point on the virgin consolidation curve has a different basic pore (capillary) volume; this leads to the series of reversible hysteresis loops since the pores which have not collapsed at a given terminal pressure will continue to function as pores. These remaining pores, however, will show some contraction and expansion and this would not be expected to be completely reversible and hence provides a probable explanation of hysteresis in two-phase systems at relatively low suctions (<5 atm). The series of hysteresis loops enables the same water content (voids ratio) to be obtained with quite different structural arrangements within the clay mass and must of necessity result in appreciable differences in the strength of the soil structure depending on the ratio of the water held in pores to that held within the domains.

The swelling of these domain units for divalent ion systems and also for monovalent ion systems at high electrolyte concentration is controlled by a potential barrier and, since the plates at full swelling are separated by less than 60 \AA of water, it seems reasonable to attribute the potential barrier to coulombic attractive forces as discussed by MacEwan (1948, 1954), or to the presence of positive charges on the clay crystals.

The strength of clay materials is clearly dependent on the degree of development and the strength of domain particles since in many circumstances these particles rather than the individual clay crystals are functional.

(c) Applicability of Diffuse Double Layer Concepts

Much consideration has been given by many workers to the applicability of diffuse double layer formation to the swelling of clay-water systems. However, it should be remembered that such theories deal exclusively with repulsions and the film thicknesses predicted take no account of possible attractive forces arising from the presence of an opposing surface. MacEwan (1948, 1954) has suggested that electrostatic attractive forces will extend to at least 30 \AA . From Norrish's results for the intercrystalline swelling of montmorillonite it appears that these electrostatic attractions extend to separations in excess of 100 \AA . Consequently, although diffuse double layer repulsions may exist, the magnitude of the spacings developed may be appreciably lower than those predicted by this theory.

For the monovalent systems it seems likely that once the potential barrier within a domain has been overcome, the development of diffuse

layers as envisaged by the Gouy–Chapman theory plays a significant part in determining the solution uptake. Its applicability in a qualitative way is indicated by the marked effect of electrolyte concentration on the solution content of the sodium cores on wetting from the dry state (Figs. 9 and 11). This sensitivity to electrolyte concentration is far less evident on drying from the suspension state, as shown by the large solution contents retained in molar chloride solution (Quirk and Aylmore, 1960). This seems to indicate that although diffuse double layers are present, their collapse with increasing electrolyte concentration takes place within the gel structure formed and hence does not give rise to an equivalent shrinkage. As diffuse double layer theory in a general way implies an equivalence between mechanical and osmotic components of the free energy, the existence of these gel structures is strongly supported by the sensitivity of the gels to increased mechanical pressure which induces particle rearrangement.

For divalent systems, however, the magnitude of the film thickness developed on wetting from the dry state, and its insensitivity to variations in electrolyte concentrations less than molar, lead to the conclusion that swelling resulting from the formation of diffuse double layers does not become significantly operative in these circumstances. This is presumably because the strong electrostatic attractions prevent the expansion of the domain over the potential barrier. Where surfaces are not directly opposed it is possible that diffuse double layers do form, but such formation appears to be of little significance in regard to divalent clay swelling. It might be argued that the lack of sensitivity to electrolyte concentration at the much higher solution contents obtained on drying from the suspension state could be attributed to the accommodation of diffuse double layers within the gel structure as for the sodium clays. However, there is at present no evidence to substantiate this suggestion and the low values reported for chloride exclusion by calcium systems (Quirk, 1957) indicate that diffuse double layer formation seems unlikely. Further experiments are necessary to establish this point but it is clear that the diffuse double layer theory cannot be used to describe the swelling of calcium clay systems.

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