Clays and Clay Minerals, Vol. 28, No. 2, pp. 135–141, 1980.

SWELLING COMPONENTS OF COMPACTED Ca-MONTMORILLONITE

J. C. PARKER, L. W. ZELAZNY, AND D. F. AMOS

Department of Agronomy, Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract—Intracrystalline water adsorption of Ca-montmorillonite was calculated as the product of one-half the interlayer spacing from X-ray powder diffraction analysis and the difference between the desorption surface area determined with ethylene glycol-monoethyl ether and BET surface area determined by N_2 adsorption. Osmotic adsorption was calculated as the product of the N_2 surface area and theoretical double layer thickness. Measured water adsorption of P_2O_5-dry clay, compacted to initial densities (γ_0) from 0.52 to 1.59 g/cm^3 and submerged in 0.01 N $CaCl_2$ was 2.4 to 4.2 times greater than intracrystalline plus osmotic adsorption due to the occurrence of pores exceeding double layer dimensions. The increase in expansion caused by reducing electrolyte concentration to 0.001 N was equal to the predicted increase in double layer volume, verifying the existence of an osmotic component to swelling.

Measured expansion following submersion in 0.01 N $CaCl_2$ increased continuously with γ_0 from 0.53 cm^3/g at γ_0 = 0.52 g/cm^3 to 1.17 cm^3/g at γ_0 = 1.59 g/cm^3, while estimated osmotic plus intracrystalline expansion was constant at 0.30 cm^3/g. This discrepancy is attributed to swelling caused by gas pressures developing ahead of advancing wetting fronts. The effect of compaction on expansion is explained by reductions in pore size, as measured by N_2 desorption, which accompany compaction. Reduced pore size should increase entrapped air pressures, whereas gradual wetting should favor their dissipation. Accordingly, slow wetting reduced the expansion of a sample where γ_0 = 1.06 g/cm^3 from 0.77 to 0.37 cm^3/g. Swelling due to entrapped air pressures produced a large increase in the number of pores $>10^4$ Å in diameter, as determined by Hg intrusion porosimetry.

Key Words—Compaction, Double layer theory, Montmorillonite, Pore-size distribution, Swelling, Water adsorption.

INTRODUCTION

Water adsorption by clay minerals has been described in terms of an initial crystalline phase and a later osmotic phase (Norrish, 1972). The former concerns the adsorption of the first few "layers" of water on mineral surfaces driven by surface and cation hydration energies (Sposito and Babcock, 1966; Kittrick, 1969). Further adsorption has been termed osmotic since it has been considered to be due to chemical potential gradients between free and adsorbed water (Verwey and Overbeek, 1946; Bolt and Peech, 1953; Norrish, 1972).

A quantitative treatment of osmotic swelling was first made by Schofield (1946) based on the Gouy-Chapman double layer theory. While this theory has limitations due to a number of simplifying assumptions (Bolt and Peech, 1953; Bolt, 1955; Low, 1959; Rosenquist, 1962), predicted osmotic pressures have corresponded fairly well with swelling pressures developed by Na-montmorillonite, at least below 50 atm and following an initial compression (Bolt and Miller, 1955; Warkentin *et al.*, 1957; Norrish and Rausell-Colom, 1963; Barclay and Ottewill, 1970; Walker, 1975).

Measured swelling pressures of Ca-montmorillonite, however, fall well below values predicted in a similar manner (Warkentin *et al.*, 1957). Clearly, attractive forces of a much greater magnitude exist between montmorillonite platelets saturated with Ca than with Na. X-ray powder diffraction studies suggest that Ca-montmorillonite exhibits an energy minimum deep enough to restrict expansion beyond an interlayer spacing of ~10 Å following initial platelet collapse (Keren and Shainberg, 1975). The resulting structures, composed of oriented platelets which undergo limited interlayer expansion, have been variously described as packets, domains, turbostratic groups, tactoids, and quasicrystals (Aylmore and Quirk, 1960; Blackmore and Miller, 1961; O'Conner and Kemper, 1969). By hypothesizing the existence of quasicrystals composed of neatly stacked platelets which develop diffuse double layers on exterior surfaces only, Blackmore and Miller (1961) achieved more reasonable agreement between measured swelling pressures of Ca-montmorillonite and pressures calculated from double layer theory.

In systems exhibiting quasicrystalline structure, two components of swelling may be distinguished. One is due to adsorption on intracrystalline surfaces and is restricted to a few water "layers" by cation-surface and surface-surface interactions. The second is due to diffuse double layer development on external surfaces which are unconstrained by planar surface interactions. The amount of intracrystalline swelling will depend upon surface charge characteristics, exchange complex composition, and water vapor pressure (Kittrick, 1969;

Copyright © 1980, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

Keren and Shainberg, 1975), as well as on intracrystalline surface area. The amount of external, osmotic adsorption will be governed by surface charge characteristics, exchange complex and bulk solution composition, and external surface area.

There is considerable disagreement in the literature regarding the relative contributions of osmotic and intracrystalline water adsorption to total adsorption and swelling in soils. Van Olphen (1975) suggested that over the normal moisture range the osmotic component is the predominant cause of soil swelling. In a statistical study, Greene-Kelly (1974) concluded that intracrystalline shrinkage accounted for only a fraction of the total shrinkage from pF 6 to 4. Contrary to this, Aylmore and Quirk (1962) postulated that diffuse double layer formation is of little significance in systems with divalent exchangeable cations, and Quirk (1978) suggested that swelling in such systems is largely a capillary phenomenon. Schafer and Singer (1976) reported fair success with a model which assumes that all soil swelling results from intracrystalline adsorption.

Blackmore and Miller (1961) demonstrated that precompression of Ca-montmorillonite pastes increased intracrystalline surface area at the expense of external surface area. It has also been shown that potential swelling increases with increasing initial density (Holtz and Gibbs, 1959). Whether the effect of compaction on swelling is related to changes in osmotic and intracrystalline water adsorption or to other mechanisms is not clear.

The purpose of this paper is to elucidate the mechanisms of water adsorption and swelling and to evaluate the effects of compaction on their relative contributions to total water adsorption and expansion of Ca-montmorillonite.

METHODS AND MATERIALS

Theoretical

Osmotic and intracrystalline water adsorption by compacted Ca-montmorillonite was calculated by assuming the existence of discrete quasicrystals which develop fully extended, diffuse double layers on external surfaces, but exhibit limited intracrystalline expansion. From geometrical considerations, intracrystalline adsorption by such a system will be given by the product of internal surface area and one-half the interlayer separation. Osmotic adsorption will equal the product of external surface area and double layer thickness.

The low temperature BET surface area determined by N_2 adsorption was taken as a measure of external surface area (Van Olphen, 1975). Internal surface area was taken as the difference between the total surface area measured by ethylene glycol-monoethyl ether (EGME) and the N_2 surface area. Interlayer spacing was computed as the difference between c-axis spacing from X-ray powder diffraction analysis (XRD) and the solid crystal thickness taken as 9.6 Å. Double layer thickness (D) was calculated as:

$$D = \delta + 1/\kappa \quad (1)$$

where δ is the Stern layer thickness taken to be 5 Å (approximately two water layers) and $1/\kappa$ is the Gouy layer thickness. In the general case:

$$1/\kappa = (\epsilon\kappa T/e^2 \sum_i n_i z_i^2)^{1/2} \quad (2)$$

where ϵ is the permittivity of the medium, k is Boltzmann's constant, T is the absolute temperature, e is the electronic charge, and n_i and z_i are the concentration in ions/cm^3 and charge, respectively, of ions in bulk solution. Permittivity is the product of relative permittivity taken as 80 and the permittivity of a vacuum.

Experimental

Wyoming montmorillonite (The Clay Minerals Society Source Clay Repository SWy–1) was Ca-saturated by washing three times with 1 N $CaCl_2$ followed each time by centrifugation and decantation. Excess salts were removed with distilled water washes followed by 1:1 water-methanol and acetone washes until a negative $AgNO_3$ test was obtained. The 80°C-dried clay was gently ground with mortar and pestle and stored in a desiccator over P_2O_5.

A total surface area of 810 m^2/g was determined by desorption of EGME over a $CaCl_2$–EGME slurry (Carter *et al.*, 1965), assuming that 2.86×10^{-4} g EGME covers 1 m^2 of surface. A c-axis spacing of 13.3 Å was found for P_2O_5-dry, Ca-saturated clay by XRD of an oriented sample in a closed goniometer chamber containing P_2O_5. The c-spacing in a 100% relative humidity chamber was 19.4 Å. The specific gravity of 105°C-dry clay was found to be 2.70 g/cm^3 by water displacement.

Cores measuring 36 mm in diameter and 10 mm in height were prepared by static compaction of P_2O_5-dry Ca-montmorillonite in 38 mm high stainless steel rings by means of a hydraulic press. The bottom of each ring was secured to a 6-mm thick porous stone. Quantities of clay in each ring were adjusted to yield cores with densities from 0.52 to 1.59 g/cm^3. Densities were expressed on a 105°C-dry basis by correcting for the moisture content of P_2O_5-dry clay which was found to be 0.08 g/g. A 0.5–1.0-g subsample from each core was carefully chipped loose so as to minimize disturbance of the clay structure and saved for N_2 gas adsorption measurements. The holes in the cores were refilled with the same quantity of clay that was removed. Porous stones of 35-mm diameter were placed inside each ring on top of the core, and initial height readings were made to the nearest 0.001 inch with a tripod-mounted strain gauge.

Cores having initial densities of 0.52, 0.75, 1.06, 1.37, and 1.59 g/cm^3 were submerged in 0.01 N $CaCl_2$. A sec-

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

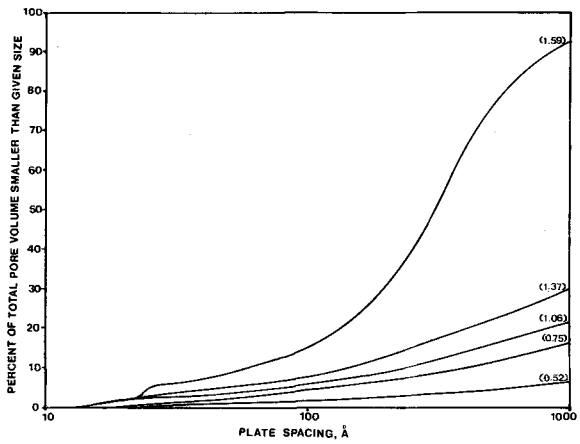


Figure 1. Effects of compaction on N_2 desorption pore-size distributions of Ca-montmorillonite prior to wetting. Intial densities in g/cm³ given in parentheses above each curve.

ond core of density 1.06 g/cm³ was submerged in 0.001 N $CaCl_2$ and a third in 0.01 N $Ca(H_2PO_4)_2$. A fourth core was allowed to equilibrate with water vapor in a desiccator containing distilled water. Weight and height readings were recorded until they stabilized in 5 weeks, after which 0.01 N $CaCl_2$ was added to the sample a few drops each day for several weeks until free solution was evident on the top porous stone.

At the completion of each test, height readings of each sample were taken from which final volumes were calculated. Specific volume change was calculated as the change in volume per unit mass of sample. Total water adsorption was assumed to be equal to the final void volume, computed as the difference between total final volume and the calculated volume of solids. Portions of each core were freeze-dried following immersion in liquid N_2 and saved for surface area and pore-size distribution analyses.

Nitrogen gas adsorption measurements were performed with a Micromeritics Model 2100-D gas adsorption apparatus. Samples were degassed overnight at 200°C to a pressure of <2 μm Hg. Isotherms were determined at liquid N_2 temperatures which were measured to the nearest 0.01°C. Surface areas were calculated by applying the BET equation to adsorption data in the range 0.05 to 0.30 p/p_0 assuming a surface area for N_2 of 16.2 Å² per molecule. Complete adsorption and desorption isotherms were determined for samples taken from cores prior to wetting. The distribution of pores in the range 10–1000 Å were calculated from N_2 desorption data by employing the Kelvin equation and assuming a pore geometry consisting of parallel slits (Aylmore, 1974). The contact angle between N_2 and the clay surface was assumed to be zero. Plate separation distances used in the Kelvin equation were corrected for film thickness not attributable to capillary condensation using a Halsey-type expression:

$$t = 3.54(-2.58/\ln p/p_0)^{0.45} \quad (3)$$

where t is film thickness and p/p_0 is the relative pressure. Eq. (3) was derived from data compiled by Adamson (1976) for N_2 adsorption by various nonporous solids.

Pore size distributions were also determined for several samples by Hg intrusion through the courtesy of Quantachrome Corporation. Pore size was calculated from the Young-Laplace equation:

$$d = P/2\gamma_{Hg} \cos \theta \quad (4)$$

where d is the plate separation, P is the pressure, γ_{Hg} is the surface tension of Hg, and θ is the contact angle between Hg and clay which was assumed to be 140°.

RESULTS AND DISCUSSION

Effects of initial density

Pore-size distributions by N_2 desorption of Ca-montmorillonite samples prior to wetting are shown in Figure 1. A gradual increase in the fraction of pores $<10^3$ Å is evident as density increases from 0.52 to 1.37 g/cm³ followed by a dramatic increase for the highest density sample. Mercury intrusion analyses on the 0.52- and 1.06-g/cm³ samples agreed with N_2 data within a few percent for the volume of pores $<10^3$ Å in diameter and indicated that the volume of pores $<10^4$ Å in diameter was 79 and 98%, respectively.

Dry static compaction had little effect on N_2 BET surface areas. Initial samples of density 0.52–1.37 g/cm³ had N_2 surface areas of 21–23 m²/g. The ratio of total surface area to N_2 surface area suggests a statistical quasicrystalline thickness of 35–39 platelets. Compaction to 1.59 g/cm³ increased the N_2 surface area to 28 m²/g indicating a disruption of structural units due perhaps to intracrystalline shear. Pressures generated during wetting apparently reversed this process, since final N_2 surface areas for all treatments were 20–22 m²/g. Final N_2 surface areas were used to calculate osmotic and intracrystalline adsorption.

The measured variations in N_2 surface area resulted in only small differences in predicted osmotic plus intracrystalline adsorption in 0.01 N $CaCl_2$ as a function of initial density. However, as seen in Figure 2, measured water adsorption varied greatly with initial density. The difference between measured and predicted adsorption represents the volume of water present external to non-overlapping double layers. The decrease in this "occluded water" as density increased from 0.52 to 1.37 g/cm³ is readily explained by the observed reduction in the initial volume of pores which exceed double layer dimensions (Figure 1). The increase in "occluded water" for the highest density sample, however, indicates that additional factors must be considered. Evidently, expansion beyond double layer dimensions can take place.

What could cause this enhanced expansion? On immersion, a wetting front will move inward drawn by

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

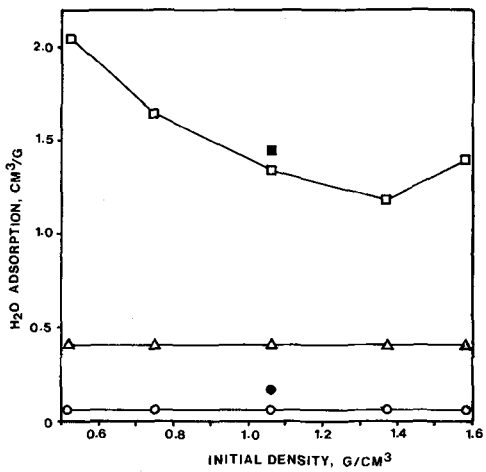


Figure 2. Effects of compaction on water adsorption of P_2O_5-dry cores. (□) measured total adsorption after submersion in 0.01 N $CaCl_2$; (■) measured total adsorption after submersion in 0.001 N $CaCl_2$; (○) predicted osmotic adsorption in 0.01 N $CaCl_2$; (●) predicted osmotic adsorption in 0.001 N $CaCl_2$; (△) predicted intracrystalline adsorption.

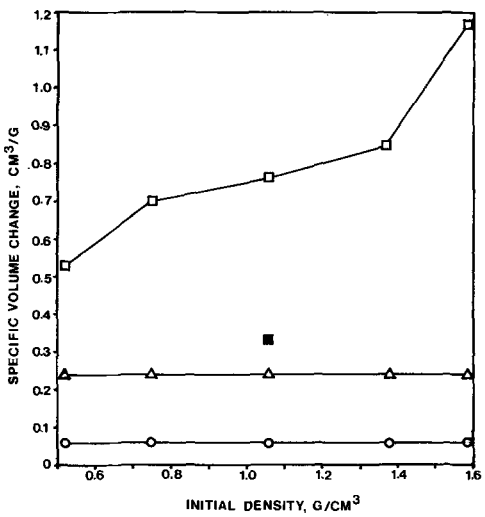


Figure 3. Effects of compaction on expansion of P_2O_5-dry cores. (□) measured total expansion after submersion in 0.01 N $CaCl_2$; (■) measured total expansion following slow wetting with 0.01 N $CaCl_2$ preceded by vapor wetting; (○) estimated osmotic swelling in 0.01 N $CaCl_2$; (△) estimated intracrystalline swelling.

capillarity. If air diffusion is limited, gas pressures will develop which may induce expansion. The magnitude of these entrapped air pressures should vary inversely with pore size in accordance with the Laplace equation:

$$P = 2\gamma_w/d \qquad (5)$$

where P is the pressure, γ_w is the surface tension of water, and d is the plate separation. The observed reduction in pore size during compaction will then have two opposing effects: (1) a reduction in the initial pore volume exceeding double layer dimensions, and (2) an increase in entrapped air pressures. It is significant that the increase in "occluded water" for the highest density sample (Figure 2) is associated with the most pronounced reduction in pore size (Figure 1).

As a first approximation, the change in intracrystalline volume can be equated with the contribution of intracrystalline swelling to total expansion; osmotic adsorption is assumed to be equal to the contribution of osmotic swelling. Intracrystalline and osmotic swelling, thus estimated, are shown in Figure 3 along with measured specific volume changes after submersion in 0.01 N $CaCl_2$. Estimated osmotic and intracrystalline expansion remained virtually constant, yet measured expansion increased continuously with increasing initial density. These increases in expansion closely follow the observed reductions in pore size (Figure 1) reflecting the increase in entrapped air pressures predicted by Eq. (5). The greatest increase in expansion occurred between 1.37 and 1.59 g/cm³ density, corresponding again to the most marked reduction in initial pore size. Roughly 50 to 75% of the total expansion following submersion in 0.01 N $CaCl_2$ is attributable to swelling caused by entrapped air pressures depending on initial density. Of the remainder, about 75% is estimated to be due to intracrystalline swelling and about 25% to osmotic swelling (Figure 3).

Effects of electrolyte

Reducing the concentration of $CaCl_2$ from 0.01 to 0.001 N should increase osmotic adsorption by 0.11 cm³/g as double layer thickness increases from ~30 to 83 Å, but it should have no effect on intracrystalline adsorption. Measured total adsorption was found to be 1.34 and 1.45 cm³/g for submersion of 1.06-g/cm³ initial density samples in 0.01 and 0.001 N $CaCl_2$, respectively. Their respective specific volume changes were 0.77 and 0.88 cm³/g. These increases in water adsorption and expansion caused by reducing electrolyte concentration are equal to the predicted increase in osmotic adsorption. The existence of an osmotic component to water adsorption and swelling appears to be confirmed.

Double layer theory does not predict a difference in H_2O adsorption for surfaces in contact with $CaCl_2$ or $Ca(H_2PO_4)_2$ solutions of the same concentration. Measured specific expansion and adsorption, however, increased by 0.15 cm³/g when 1.06-g/cm³ initial density samples were submerged in 0.01 N $Ca(H_2PO_4)_2$ rather than in 0.01 N $CaCl_2$. Specific adsorption of phosphate on mineral edges would be expected to reduce edge-to-face interactions. The importance of edge-to-face bonds in limiting expansion has been noted by other authors (Norrish and Rausell-Colom, 1963; Rowell, 1965).

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

Table 1. Pore size distributions of 1.06 g/cm³ initial density samples by Hg intrusion before wetting and after slow and fast wetting.

Sample treatment	Pore volumes in cm³/g for various pore sizes			
	20–100 Å	10^2–10^3 Å	10^3–10^4 Å	$>10^4$ Å
Before wetting	0.03	0.09	0.35	0.01
After slow wetting	0.03	0.03	0.63	0.09
After fast wetting	0.06	0.02	0.21	1.18

Effects of rate of wetting

Vapor H_2O adsorption by the 1.06-g/cm³ initial density sample plateaued at a water content of 0.30 g/g and a specific volume change of 0.17 cm³/g. Following gradual wetting with 0.01 N $CaCl_2$, water adsorption increased to 0.90 cm³/g resulting in an additional 0.20 cm³/g expansion. Total expansion was thus reduced from 0.77 cm³/g for immediate submersion in 0.01 N $CaCl_2$ to 0.33 cm³/g for the slow wetting procedure. The estimated intracrystalline plus osmotic swelling was 0.30 cm³/g. This leaves only an expansion of 0.03 cm³/g unaccounted for during slow wetting as opposed to 0.47 cm³/g during rapid wetting.

The close agreement between estimated and measured swelling for slow wetting may be fortuitous to some extent, but the dramatic effect of rate of wetting further confirms the importance of swelling caused by entrapped air. During wetting from the vapor state, no capillary pressures will develop in response to the advance of a wetting front, because no true wetting front exists. The gradual addition of liquid water or dilute electrolyte favors the dissipation of entrapped air because of the localized nature of the wetting front. Thus, swelling due to entrapped air is greatly reduced during slow wetting. This interpretation is supported by results of Emerson (1964) who reported that sample evacuation prior to submersion also reduced swelling.

The foregoing scenario is supported by the changes in pore size distribution observed following slow and fast wetting given in Table 1. Slow wetting produced a 0.28-cm³/g increase in the volume of pores 10^3–10^4 Å in diameter and a 0.08-cm³/g increase in pores $>10^4$ Å in diameter, while rapid wetting resulted in a 0.14-cm³/g decrease in pores 10^3–10^4 Å in diameter and a 1.17 cm³/g increase in pores $>10^4$ Å in diameter. This pronounced expansion of 10^3–10^4-Å pores during rapid wetting cannot be accounted for by the extension of double layers which are less than 100 Å in thickness.

SUMMARY AND CONCLUSIONS

Dry static compaction had little effect on predicted osmotic or intracrystalline water adsorption. In 0.01 N $CaCl_2$, estimated intracrystalline expansion was about 4 times greater than estimated osmotic expansion, but in 0.001 N $CaCl_2$ it was about 1.5 times greater. The existence of an osmotic component to swelling was confirmed by determining that the measured increase in swelling caused by decreasing electrolyte concentration was equal to the predicted increase in double layer volume. Edge-to-face bonds were found to reduce expansion significantly.

From about 50 to 75% of the total swelling which followed submersion of Ca-montmorillonite in 0.01 N $CaCl_2$ was attributed to expansion caused by gas pressures which develop ahead of advancing wetting fronts. These pressures should increase with decreasing pore size in keeping with the Laplace equation. Accordingly, compaction increased swelling caused by entrapped air pressures as pore size was diminished. Slow wetting ameliorated this expansion by allowing dissipation of entrapped air.

REFERENCES

Adamson, A. W. (1976) *Physical Chemistry of Surfaces:* 3rd ed., John Wiley & Sons, New York, p. 585.

Aylmore, L. A. G. (1974) Hysteresis in gas sorption isotherms: *J. Colloid Interface Sci.* **46,** 410–416.

Aylmore, L. A. G. and Quirk, J. P. (1960) Domain or turbostratic structure of clays: *Nature* **187,** 1046–1048.

Aylmore, L. A. G. and Quirk, J. P. (1962) The structural status of clay systems: *Clays & Clay Minerals* **9,** 104–130.

Barclay, L. M. and Ottewill, R. H. (1970) Measurement of forces between colloidal particles: *Special Discussions Faraday Society* **1,** 138–147.

Blackmore, A. V. and Miller, R. D. (1961) Tactoid size and osmotic swelling in Ca montmorillonite: *Soil Sci. Soc. Amer. Proc.* **25,** 169–173.

Bolt, G. H. (1955) Analysis of the validity of the Gouy-Chapman theory of the electric double layer: *J. Coll. Sci.* **10,** 206–218.

Bolt, G. H. and Miller, R. D. (1955) Compression studies of illite suspensions: *Soil Sci. Soc. Amer. Proc.* **19,** 285–288.

Bolt, G. H. and Peech, M. (1953) The application of the Gouy theory to soil-water systems: *Soil Sci. Soc. Amer. Proc.* **17,** 210–213.

Carter, D. L., Heilman, M. D., and Gonzolez, G. L. (1965) Ethylene glycol monoethyl ether for determining surface area of silicate minerals: *Soil Sci.* **100,** 356–360.

Emerson, W. W. (1964) The slaking of soil crumbs as influenced by clay mineral composition: *Aust. J. Soil Res.* **2,** 211–217.

Greene-Kelly, R. (1974) Shrinkage of clay soils: a statistical correlation with other soil properties: *Geoderma* **11,** 243–257.

Holtz, W. G. and Gibbs, H. J. (1959) Expansive clay—properties and problems: *Quart. Colo. Sch. Mines* **54,** 89–117.

Keren, R. and Shainberg, I. (1975) Water vapor isotherms and heat of immersion of Na/Ca-montmorillonite systems—I: Homoionic clay: *Clays & Clay Minerals* **23,** 193–200.

Kittrick, J. A. (1969) Interlayer forces in montmorillonite and vermiculite: *Soil Sci. Soc. Amer. Proc.* **33,** 217–222.

Low, P. F. (1959) Discussion of physico-chemical properties of soils: ion exchange phenomena: *J. Soil Mech. Found. Div., Proc. Amer. Soc. Civil Eng. No. SM2* **85,** 79–89.

Norrish, K. (1972) Forces between clay particles: *Proc. Int. Clay Conf.*, Madrid, Spain, 375–382.

Norrish, K. and Rausell-Colom, J. A. (1963) Low angle X-ray diffraction studies of the swelling of motmorillonite and vermiculite: *Clays & Clay Minerals* **10,** 123–149.

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

O'Connor, G. A. and Kemper, W. D. (1969) Quasi-crystals in Na-Ca systems: *Soil Sci. Soc. Amer. Proc.* **33,** 464–469.
Quirk, J. P. (1978) Some physico-chemical aspects of soil structural stability—a review: in *Modification of Soil Structure,* W. W. Emerson, R. D. Bond, and A. R. Dexter, eds., John Wiley & Sons, New York, 3–16.
Rosenquist, I. Th. (1962) The influence of physico-chemical factors upon the mechanical properties of clays: *Clays & Clay Minerals* **9,** 12–27.
Rowell, D. L. (1965) Influence of positive charge on the inter- and intracrystalline swelling of oriented aggregates of Na montmorillonite in NaCl solutions: *Soil Sci.* **100,** 340–347.
Schafer, W. M. and Singer, M. J. (1976) Influence of physical and mineralogical properties on swelling of soils in Yolo County, California: *Soil Sci. Soc. Amer. J.* **40,** 557–562.
Schofield, R. K. (1946) Ionic forces in thick films of liquid between charged surfaces: *Trans. Faraday Soc.* **42,** 219–225.
Sposito, G. and Babcock, K. L. (1966) Equilibrium theory of the kaolinite-water system at low moisture contents, with some remarks concerning adsorption hysteresis: Clays & Clay Minerals **14,** 133–147.
van Olphen, H. (1975) Water in soils: in *Soil Components, Vol. 2,* J. E. Giesking, ed., Springer-Verlag, New York, 497–527.
Verwey, E. J. W. and Overbeek, J. Th. G. (1946) Long distance forces acting between colloidal particles: *Trans. Faraday Soc.* **42,** 117–123.
Walker, F. G. (1975) Vermiculites: in *Soil Components, Vol. 2,* J. E. Giesking, ed., Springer-Verlag, New York, 155–189.
Warkentin, B. P., Bolt, G. H., and Miller, R. D. (1957) Swelling pressure of montmorillonite: *Soil Sci. Soc. Amer. Proc.* **21,** 495–497.

(Received 26 August 1979; accepted 23 October 1979)

Резюме—Была высчитана адсорбция внутрикристаллиьеской воды Са-монтмориллонитом, как произведение половины межслойного промежутка, по ланным порошкового метода рентгеноструктурного анализа, и разницы между площадью десорбционной поверхности, найденной с помощью этиленгликсол-моноэтилэфира и площадью поверхности BET, найденной адсорбцией N_2. Осмотическая адсорбция была высчитана как произведение площади поверхности N_2 и теоретической толщины двойного слоя. Измеренная адсорбция воды P_2O_5-сухой глиной, сжатой до первоначальных плотностей (γ_0) от 0,52 до 1,59 г/см^3 и погруженной в 0,01 N $CaCl_2$, быра в 2, 4ло 4,2 раз борьше, чем внутрикристаллическая плюс осмотическая адсорбция, благодаря наличию пор, превышающих размеры двойного слоя. Увеличение расширения, вызванное понижением концентрации электролита до 0,001 N, было равно предсказанному повышению объема двойного слоя, что подтверждает сушествование осмотического компонента разбухания.

Измеренное расширение после погружения в 0,01 N $CaCl_2$ непрерывно возрастало с увеличением γ_0 от 0,53 см^3/г при γ_0 = 0,52 г/см^3 до 1,17 см^3/г при γ_0 = 1,59 г/см^3, в то время как подсчитанное осмотическое плюс внутрикристаллическое расширение было постоянным и равнялось 0,30 см^3/г. Это противоречие обусловлено разбуханием, вызванным давлениями газа, возникающими перед наступающими фронтами смачивания. Воздействие уплотнения на расширение объясняется уменьшением размера пор, как было замерено десорбцией N_2, которая сопровождала уплотнение. Уменьшенный размер пор должен увеличить давление захваченного воздуха, в то время как постепенное смачивание должно способствовать понижению давления. Следовательно, медленное смачивание уменьшило расширение образца, где γ_0 = 1,06 г/см^3, от 0,77 до 0,37 см^3/г. Разбухание из-за давления захваченного воздуха привело к большому увеличению числа пор $>10^4$ Å в диаметре, как показало измерение пор методом внедрения Hg. [N. R.]

Resümee—Die interkristalline Wasseradsorption von Ca-Montmorillonit wurde als das Produkt aus einem halben Schichtabstand, aus der Röntgendiffraktometeranalyse, und der Differenz zwischen der Desorptionsoberfläche, bestimmt mit Ethylenglycol-Monoetyläther, und der BET-Oberfläche, bestimmt durch N_2-Adsorption, berechnet. Die osmotische Adsorption wurde als das Produkt aus der N_2-Adsorptionsoberfläche und der theoretischen doppelten Schichtdicke berechnet. Die gemessene Wasseradsorption von mit P_2O_5-getrocknetem Ton, der auf ursprüngliche Dichten (γ_0) von 0,52 bis 1,59 g/cm^3 komprimiert und in 0,01 N $CaCl_2$ getränkt wurde, war um das 2,4- bis 4,2-fache größer als die interkristalline plus osmotische Adsorption. Die Ursache ist das Auftreten von Poren, die größer sind als der Abstand zwischen den Doppelschichten. Die Zunahme in der Ausdehnung bei Reduktion der Elektrolytkonzentration auf 0,001 N war gleich der vorausgesagten Zunahme im doppelten Schichtvolumen und bestätigte somit eine osmotische Komponente beim Quellen.

Die gemessene Ausdehnung, die nach dem Tränken in 0,01 N $CaCl_2$ festgestellt wurde, nahm kontinuierlich zu mit γ_0 von 0,53 cm^3/g bei γ_0 = 0,52 g/cm^3 auf 1,17 cm^3/g bei γ_0 = 1,59 g/cm^3, während die geschätzte osmotische plus interkristalline Ausdehnung bei 0,30 cm^3/g konstant war. Diese Diskrepanz wird dem Quellen zugeschrieben, das durch die Gasdrücke verursacht wird, die sich vor der vorschreitenden Feuchtigkeitsfront ausbilden. Der Effekt der Verdichtung auf die Ausdehnung wird durch die Reduktion der Porengröße erklärt, wie sie bei der N_2-Desorption gemessen wurde, die die Verdichtung begleitet. Eine reduzierte Porengröße sollte die eingefangenen Luftdrücke erhöhen, während allmähliches Befeuchten ihr Verschwinden begünstigen sollte. Demgemäß reduzierte allmähliches Befeuchten die Ausdehnung einer Probe mit γ_0 = 1,06 g/cm^3 von 0,77 auf 0,37 cm^3/g. Das Quellen, das auf eingefangene Luftdrücke zurückgeht, erzeugte eine große Zunahme in der Porenzahl, $>10^4$ Å im Durchmesser, wie durch Hg-Intrusionsporosimetrie festgestellt wurde. [U.W.]

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press

Résumé—L'adsorption intracristalline d'eau de montmorillonite-Ca a été calculée comme étant le produit de la moitié de l'espacement intercouche de l'analyse de diffraction poudrée aux rayons-X et de la différence entre la surface de désorption déterminée à l'éther éthylèneglycol-monoéthyl et la surface BET déterminée à l'adsorption N_2. L'adsorption osmotique a été calculée comme étant le produit de la surface N_2 et de l'épaisseur de couche double théorique. L'adsorption mesurée d'eau par l'argile sèche P_2O_5, compactée à sa densité initiale (γ_0) de 0,52 à 1,59 g/cm^3 et submergée dans 0,01 N $CaCl_2$ était de 2,4 à 4,2 fois plus importante que l'adsorption intracristalline et osmotique à cause de la présence de pores excédant les dimensions de couche double. L'accroissement de l'expansion causé par la réduction de l'électrolyte à 0,001 N était égal à l'accroissement prédit du volume de couche double, verifiant l'existence d'un composant osmotique dans le gonflement.

L'expansion mesurée après submersion dans 0,001 N $CaCl_2$ a augmenté continuellement avec la valeur γ_0, de 0,53 cm^3/g à γ_0 = 0,52 g/cm^3, à 1,17 cm^3/g à γ_0 = 1,59 g/cm^3, tandis que l'expansion osmotique et intracristalline estimée était constante à 0,30 cm^3/g. Ce désaccord est attribué au gonflement causé par les pressions des gaz se developant devant les fronts mouillants. L'effet de la compaction sur l'expansion est expliquée par des réductions de la taille des pores, mesurées par désorption N_2 qui accompagnent la compaction. Des tailles de pores réduites devraient accroitre les pressions des gaz emprisonnés, tandis qu'un mouillage graduel devrait favoriser leur dissipation. Ainsi, un mouillage lent a réduit l'expansion d'un échantillon où γ_0 = 1,06 g/cm^3 de 0,77 à 0,37 cm^3/g. Le gonflement dû à des pressions d'air emprisonné a produit une grande augmentation, déterminée par la porosimétrie d'intrusion Hg, des nombres de pores 10^4 Å de diamètre. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280210 Published online by Cambridge University Press