INTERNAL SURFACE AREA OF WYOMING BENTONITE FROM SWELLING RELATIONSHIPS

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Abstract—The internal surface area of Na–Wyoming bentonite was determined for linearly swelling pastes, using a physically based equation which describes such swelling. Information required is simply the linear relationship between interplatelet spacing, determined by X-ray powder diffraction, vs total water content determined gravimetrically. However, before the three-unknown parameter equation can be so applied, that portion of external-pore water, which normally increases linearly commensurately as interstitial water increases, must be decreased to zero. This was accomplished by adding dilute quantities of NaCl salt to the clay-paste system to decrease the attractive forces between positive-edge and negative-face sites, and stirring vigorously to further destroy the card-house structure and align the clay platelets.

INTRODUCTION

Internal surface areas of expandable three-layer clays normally are not determined *per se*, but are calculated indirectly as the difference between the total and external surface areas. Total surface area commonly is determined by adsorption of a polar gas, which intercalates interlamellar regions and adsorbs on external surfaces. External area is determined from adsorption isotherms, using either non-polar molecules, which adsorb on external surfaces only (i.e., do not penetrate interstitially) or using polar molecules, after first irreversibly collapsing the expandable clay by heating or charge reduction.

A few methods have been proposed for direct determination of internal surface area. The planar area of 2:1 type clays, which approximates the internal area, may be calculated for mineralogically defined pure-specimen types from crystallographic data and chemical analysis (Jackson, 1956). Mehra and Jackson (1959) determined the interlayer surface area of smectite with glycerol by measuring duo- vs mono-layer adsorption at 35 and 110°C, respectively. Schofield and Talibuddin (1948) theoretically related anion-exclusion to internal surface area.

Different surface area methods often give unexplainably different results suggesting that the associated assumptions may not apply rigidly to all adsorbate–adsorbent situations. A new approach for determining the internal surface area of smectites, which is based on a physical interpretation of the osmotic swelling of the clay, is presented here.

THEORY

The interlayer swelling of Na and Li-smectites due to osmotic imbibition of salt-free water has been shown by several researchers (Fink and Nakayama, 1972) to be a linear function of the total water content. Fink and Nakayama developed a linear equation to describe this swelling:

$$d = [9.4 - \mu a/S_i] + [\mu(1 - b)/S_i] W_t, \qquad (1)$$

where d is the average repeat spacing of the expanded platelets and W_t is the total liquid water present in the system (in g H_2O/g clay). Thus, plots of d vs W_t are linear with intercepts of $[9.4 - \mu a/S_i]$ and slopes of $[\mu(1 - b)/S_i]$.

The thickness of an individual platelet is 9.4 Å; μ is a combined constant and units conversion factor equal to 2×10^4 Å m^2/g which accounts for the internal water being associated with the two adjacent smectite surfaces and assumes the water has unit density. The constant a (in g H_2O/g clay) is theorized (Fink and Nakayama, 1972) to be that quantity of hydration water that maximizes at low W_t levels, then remains constant as total water in the system increases [e.g., water associated with internal surfaces of limited swelling clay components, like vermiculite or attapulgite, or possibly the initial hydration layers on edge and external (non-paired) planar surfaces]. The constant b is theorized to be the proportion of water in the osmotic swelling region which hydrates external positions $(0 < b < 1)$. The term bW_t thus provides for a linear increase in the external-pore water of hydration, as the total water in the system increases. Of course, S_i (in m^2/g clay) is the internal planar surface area of the osmotic-swelling clay.

Equation (1) contains three unknown parameters: a, b, and S_i. If one of the three terms is known by an independent method, equation (1) permits evaluation of the other two. Fink and Nakayama (1972) determined a and b values for all known published swelling data of mineralogically characterized smectites, for which theoretical planar surface areas S_i

could be calculated. They thought that the normally small b values observed might relate to undetectable residual traces of electrolyte in the systems which caused a slight suppression of intracrystalline, forcing the extra water into external positions.

The objective of this experiment was to ascertain if the internal surface area (S_i) of Wyoming bentonite could be determined by applying the theoretical linear swelling equation [equation (1)], where the slope is obtained at various salt concentrations. It was thought that extrapolating to zero salt content should give a reproducible b, which then could be used to define S_i.

METHOD

Wyoming bentonite (Volclay)* was purified by removing carbonates and free iron oxides, fractionating to $<2\,\mu m$, Na-saturating with four washes of N NaCl, and removing excess salt by centrifugation and pressure-membrane extraction ($AgNO_3$ test). After salt removal, the clay was resuspended and passed through a Na-exchange resin as added assurance against hydrolysis. The clay was dewatered, dried over P_2O_5, and divided into four subsamples.

Each subsample was rehydrated to 1 g H_2O/g clay using one of four NaCl solutions: 0.001, 0.010, 0.100, or 0.300 N. The samples were thoroughly mixed in vials, stoppered, and stored for 2 weeks with occasional mixing. Then the four samples were further subdivided, and each subsample diluted with increasing amounts of deionized water as usual to cover the range of 1 to approximately 3 g H_2O/g clay. Again, these subsamples were mixed, stoppered, and equilibrated for 2 weeks with occasional mixing. The d-spacing of these clay pastes was determined using the low-angle, X-ray powder diffraction techniques of Fink and Thomas (1963), which included correction of the diffractograms for the Lorentz and polarization factors of oriented specimens (MacEwan et al., 1961). Total water content was determined gravimetrically on material dried at 300°C.

RESULTS AND DISCUSSION

The results were serendipitous. Of course, as expected, the d-spacing of the swelling bentonite pastes was a linear function of the total water content W_t–at least for the 0.001, 0.01, and 0.1 N salt-concentration series (Figure 1). But contrary to expectation, the b values, determined with equation (1), using the theoretical planar surface area (Jackson, 1956), of 746 m^2/g, were essentially zero for the two most dilute salt content series (0.001 and 0.01 N). Thus, these two systems had practically no linearly increasing portion of external-pore water. In other words, except for an
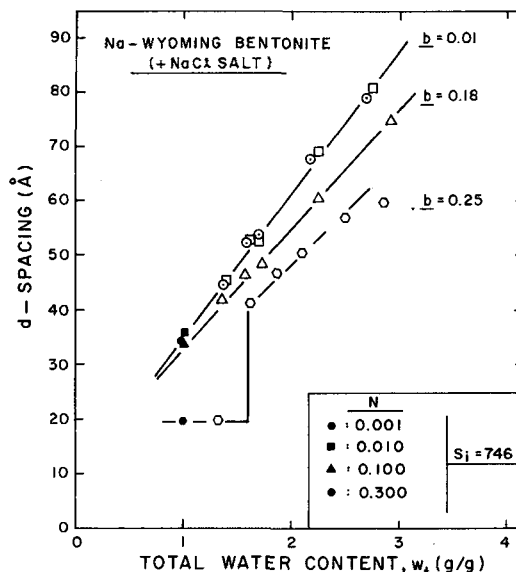
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* Trade names and company names are included for the benefit of the reader and do not infer any endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture.

Figure 1. Osmotic-swelling of Na–Wyoming bentonite in NaCl salt solutions. Solid symbols denote starting salt concentrations; open symbols denote increasing dilutions of original samples with deionized water.

initial, small, constant portion of external-surface water [i.e., the a values from equation (1); see Table 1], almost all the water from the incremental dilutions went interstitially where it could be accounted for by regular intraplatelet expansion. The significance of this is that if b can be so controlled at zero for smectite systems, whether they be pure minerals or clay mixtures, then the internal surface area S_i can be determined directly from the slope of plots of d vs W_t using equation (1) (i.e., as $b \rightarrow 0$, $S_i \rightarrow \mu$/slope).

Increasing the salt content of the original solution phase to 0.1 N decreased the swelling as originally expected. The plot of d vs W_t was linear and b equalled 0.18 (Figure 1), indicating that both external-pore and internal water were increasing linearly as total water W_t increased. Also, as expected, (e.g., Norrish and Russell-Colom, 1963) the plate spacing collapsed to 19.6 Å in the concentrated 0.3 N NaCl system, but jumped to the osmotic swelling region (40 Å) when diluted to about 0.2 N. A b value of 0.25 was estimated for this swelling system, even though the plot was curvilinear throughout the swelling range tested.

Based on b values for Na-Wyoming bentonite determined in this study and from those found in the literature (Table 1), apparently b has a finite value (normally about 0.1–0.15) in salt-free systems, decreases to almost zero for systems containing small amounts of residual salt, and then increases again as residual salt content increases above 0.01 N, until finally the plates collapse to about 20 Å (Figure 2). The b value seems to maximize between 0.2 to 0.3, when the salt concentration in the solution phase exceeds 0.2–0.3 N. At higher salt concentrations where the plates collapse, or where plots of d vs W_t are not linear, equation (1) does not apply. Equation (1),

Table 1. Values of fixed external water (a) and proportionality factor of linearly increasing external-pore water (b) for osmotically-swelling Na–Wyoming bentonites

Reference	Treatment	External water constants	
		Fixed (a) g H_2O/g Clay	Proportionality (b)
Hight et al. (1962)	salt free	0.00	0.47
Norrish (1954)	salt free	0.09	0.17
Foster et al. (1954)	salt free	0.20	0.10
Fink et al. (1968)	salt free	0.12	0.10
Fink et al. (1968)	+90% kaolinite	0.05	0.02
Fink et al. (1968)	+70% kaolinite	0.25	−0.14*
Fink et al. (1968)	+50% kaolinite	0.12	−0.01
Fink et al. (1968)	+30% kaolinite	0.12	0.02
This study	starting concentration		
This study	0.001 N NaCl	0.03	0.01
This study	0.010 N NaCl	0.03	0.01
This study	0.100 N NaCl	−0.10	0.18
This study	0.300 N NaCl	−†	0.25‡

* unexplainable large negative value.
† a-value meaningless.
‡ estimated b-value.

for example, may not even accurately describe the 0.1 N system: the b value of 0.18 seems reasonable enough, but it is difficult to rationalize a negative a value (−0.10, Table 1). The negative a value suggests a slight skewing of the swelling plot to smaller slopes which disproportionately increases the d-axis intercept, thus falsely decreasing a.

External-pore water and card-house structure

Double-layer theory predicts that salt in the system should decrease swelling pressures, partially collapse the plates, decrease interlayer swelling, and force the water into the external-pore regions. The two clay pastes, containing the greater amounts of salt, did

Figure 2. Proportionality factor (b) of linearly increasing external-pore water vs starting salt concentration of osmotic-swelling Na–Wyoming bentonite: solid circles denote literature values for salt-free systems, open circles denote values from this study. Triangles denote the initial Bingham yield stress vs salt concentration of Na–Wyoming bentonite soils (data of van Olphen, 1951).

partially collapse, as expected, but the two dilute systems expanded beyond that noted for salt-free systems. Why? Several credible explanations for such a behavior are possible. Certainly, the potential for additional swelling exists. The half-distance between the clay plates (particularly for the two most dilute systems) was considerably less than the potential extent of the double layer. Thus, water could have been forcefully drawn interstitially if some other forces had not prevented it. But such an explanation applies even more to salt-free systems—yet b values for them (Table 1) ranged from 0.1 to 0.47. [The 0.47 value of Hight et al. (1962) seems incongruous but the two b values of 0.1 and one of 0.17, while substantial, are reasonable]. These positive b values in the salt-free swelling systems probably represent a retarding hysteresis in swelling caused by the card-house effect resulting from bonding interactions between the positive-edge and the negative-face sites. Rowell (1965) theorized that such edge-face links cause a frictional resistance to swelling, and even tend to pull the tactoid structure of the clay apart upon hydration, creating even more pore space.

The card-house effect can be substantially decreased by chemically covering the positive edge sites. Rowell (1965) found that addition of Na-hexametaphosphate to swelling clay neutralized edge-face bonds, and increased swelling. Norrish and Rausell-Colom (1963) reported similar results. Emerson (1963) who examined total swelling of Na–Wyoming bentonite flakes in continuously diluted salt solutions, as I did here, observed that swelling was increased when pyrophosphate was added to the system. He attributed this increased swelling to a removal of Al-ions from the clay external surfaces with subsequent decrease in edge-face bonding. Results sited here indicate that the card-house effect retards interlayer swelling and increases external-pore water in salt-free Na–bentonite systems.
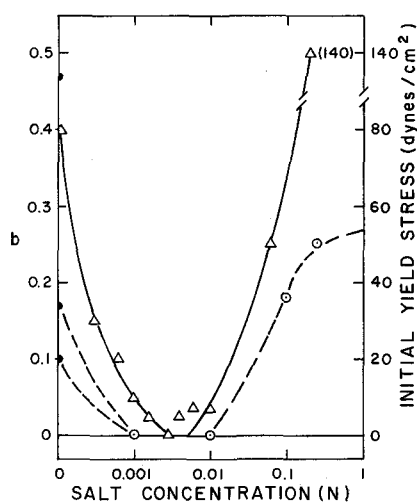
But is there any evidence that residual salt alone can reduce the card-house effect? Van Olphen (1951), using viscosity techniques, showed that a slight amount of salt in such swelling systems markedly decreased the Bingham yield stress. He found that the yield stress, indeed, passed through a minimum value at salt contents in the same range within which I obtain my near-zero *b* values (Figure 2). He related this decrease in yield stress to a slight compression of the double-layer, which shifts part of the counter ions to the Stern layer, thus decreasing the effective surface charge. Such results, he believed, were more pronounced at attractive positive-edge and negative-face sites. Aylmore and Quirk (1960) also showed that dilute salt solutions caused a relaxation of structural strains within the clay matrix, which resulted in an increase in solution uptake in compressed clay cores.

The card-house effect also may be decreased by mechanical action on the system, which breaks some of these edge-face bonds, aligns the plates, and allows water to move interstitially. Warkentin *et al.* (1957) compressed Na–Wyoming bentonite suspensions to 20 atm, which aligned the plates so that subsequent swelling pressures measured during compression and decompression were reversible and followed double-layer theoretical values. The compression to 20 atm essentially eliminated voids in the system which previously had held up to 30% of the water. My samples were stirred vigorously which also should have aligned the plates and eliminated pore water. The zero *b* values support this conclusion.

Additional support for the high degree of plate alignment comes from the low *a* values (0.03 g/g) of the two low-salt clay-paste systems. If a normal external surface area of 50 m²/g is assumed, these clays would have had only 2–2.5 layers of external water. However, Greene-Kelly (1964) found that sedimented films of Na–Wyoming bentonite had specific surfaces of less than 5 m²/g. If stirring my systems likewise reduced external areas, then the number of water layers would be 20–26. These are reasonable values that certainly are compatible with interlayer separations up to the approximately 70 Å obtained with this study.

More evidence that decreasing the card-house structure concomitantly decreases the external pore-water is the low *b* values that Fink *et al.* (1968) obtained with bentonite–kaolinite mixtures (Table 1). It is postulated that the kaolinite adsorbed on the positively-charged edges of the bentonite, thus allowing the plates to more readily slip past each other.

These documented research findings support the hypotheses that the osmotic-swelling of the salt-free Na–Wyoming bentonites was affected by electrostatic bonding between the positive-edge and negative-face sites, which resulted in a card-house clay-platelet arrangement. This in turn resulted in a linearly increasing proportion of external-pore water as the total amount of water in the clay-paste systems increased. The evidence suggests that if this card-house structure

is destroyed, and the clay platelets become perfectly aligned, then this linearly increasing portion of external pore water can be decreased to essentially zero; i.e., after adsorption of a relatively fixed portion of hydrating water on the external surfaces, all additional water goes interstitially to regularly swell the clay platelets.

In the experiment reported here, this destruction of the card-house structure is attributed to the combination of a low, residual, salt content, which negated the bonding between platelet edges and faces, and mechanical action, which further aligned the clay platelets.

CONCLUSIONS

The internal surface area of smectites (whether specimen type or as clay type mixtures) can be determined for osmotically-swelling systems using the physically-based equation presented here. Small additions of NaCl salt in the systems, in combination with vigorous stirring, apparently effectively destroyed the clay card-house structure to permit near-perfect platelet alignment. Such alignment decreases the linearly increasing portion of external-pore water to zero, permitting all water added in the linear swelling range to be accountable by intraplatelet expansion. This decreases the swelling equation to two unknowns, permitting determination of internal surface area from slopes of linear regression analyses of *d*-spacing vs total water content of such linearly swelling smectites.

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