SURFACE AREAS OF CLAY MINERALS AS DERIVED FROM MEASUREMENTS OF GLYCEROL RETENTION

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ABSTRACT

The use of glycerol retention measurements to calculate surface areas of clay minerals is described. Assuming that the glycerol retained on external surfaces is monomolecular in thickness, and that both this layer and the monomolecular glycerol layers adsorbed on internal surfaces of montmorillonite, vermiculite, and halloysite are of the density of liquid glycerol, it is calculated that each percentage of glycerol retained corresponds to an area of 17.6 square meters per gram on external surfaces and 35.3 on internal surfaces. The corresponding figures for ethylene glycol retention under these conditions are 22.3 and 44.6, respectively. For nonexpanding clays, surface areas calculated from glycerol retention values agree well with published figures derived from Brunauer, Emmett, and Teller (B.E.T.) gas adsorption measurements. For montmorillonites, surface areas agree reasonably well with published determinations based on B.E.T. treatment using polar adsorbates. Values of surface area are also presented for samples of vermiculite and endellite and for the nonexpanding clay minerals—illite, kaolinite, halloysite, and allophane.

Calculations of the surface area as a function of particle size for montmorillonites of hypothetically uniform particle sizes show that montmorillonites dispersed into very thin flakes must have an appreciable external surface. The ratio of internal to total surface is shown to furnish an estimate of the thickness of the individual montmorillonite flakes. Glycerol retention data for a Wyoming bentonite saturated with a number of different cations are interpreted as indicating particle thicknesses varying from 3 unit cells (about 30A) for Na^+ saturation to about 20 unit cells for saturation with a number of polyvalent cations.

INTRODUCTION

The most widely used method for the measurement of surface areas of very fine materials involves the adsorption of nitrogen (or similar gases) at low temperatures. When the "adsorption isotherm" data obtained are analyzed according to the theory of multimolecular adsorption developed by Brunauer, Emmett, and Teller (1938), they yield a value for the volume or weight of a monomolecular layer of the gas on the external surface of the sample. With a suitable value for the cross-sectional area of the gas molecule, this "monolayer capacity" can be converted to surface area.

A difficulty arises in measuring surface areas of clays containing montmorillonite, vermiculite, and endellite, since these have, in addition to the external surfaces of the individual particles, a large area of so-called "internal surface" which is not accessible to nitrogen. Recently, however, gas adsorption measurements on montmorillonites have been carried out with polar gases, notably water vapor and ammonia, and interpretation of the results according to the B.E.T. equation has given values for combined internal and external surfaces of the same order of magnitude as the theoretical value of about 760 m^2/g predicted from dimensions of the lattice structure.

As reported in a concurrent paper (Kinter and Diamond, 1958), a method was developed for measuring glycerol retention of clays. Glycerol-treated clays are heated at 110°C in the presence of free glycerol vapor, rapidly losing excess glycerol and arriving at a weight equilibrium. At equilibrium, montmorillonites, vermiculite, and endellite were found to retain a monomolecular layer of glycerol on their internal surfaces. It was also shown that there is a definite retention of glycerol on the external surfaces of these and other clay minerals, presumably as a monomolecular layer. It is the purpose of the present paper to derive appropriate factors to convert glycerol retention data to values of surface area, to compare computed surface area values for a number of clays with published values for the same or similar clays, and to interpret some of these values in terms of the dimensions of individual particles of montmorillonites.

CONVERSION OF GLYCEROL RETENTION DATA TO VALUES OF SURFACE AREA

The volume of a gram of glycerol at normal density (1.26 g/cm^3) is 0.794 cm^3. Assuming that glycerol retained on the internal surfaces of montmorillonite at equilibrium is in the form of a monomolecular layer at this density and with a thickness of 4.5A (as indicated by x-ray diffraction results discussed below), the area of the glycerol film may be computed as follows:

$$\text{Area of glycerol layer} = \frac{\text{Volume}}{\text{Thickness}} = \frac{0.794\ \text{cm}^3}{4.5 \times 10^{-8}\ \text{cm}} = 1765\ \text{m}^2$$

per gram of glycerol retained. Thus a glycerol retention of 1 percent would be equivalent to a monolayer area of 17.65 m^2/g; however, since the layer of glycerol is between two basal surfaces of the clay, the *internal clay surface* covered by the monolayer is twice the area of the monolayer itself, or 35.3 m^2/g. If it is further assumed that a monomolecular layer of glycerol is similarly retained on the *external* surfaces of the clay particles, the *external surface area* covered for each percent of glycerol retained is 17.65 m^2. These calculations correspond to a cross-sectional area of 26.9A^2 per *molecule* of glycerol.

The values assumed for the density and thickness of the glycerol layer are open to some question. The density at 20°C is used above, whereas the actual determination of retention is made at 110°C. The density of glycerol at 110°C calculated from the formula in the International Critical Tables is 1.20, about 5 percent less than that at 20°C. As to the thickness of the monolayer, x-ray diffraction data were obtained in our own laboratory on the basal spacings of several montmorillonites in three conditions: the monolayer glycerol complex, the two-layer complex, and collapsed by heat treatment. Spacings for the monolayer complex ranged from 13.8A to 14.54A, the average being about 14.1A; for the two-layer complex, spacings ranged from 17.7A to about 18.4A, averaging about 18.0A; and for collapsed montmorillonites, spacings were close to 9.6A in all cases. The ranges in the spacings of the two complexes indicate that small but real differences exist between different montmorillonites; small differences were also noted for the same montmorillonites saturated with different cations. From the spacing data cited, a value of 4.5A was taken as the thickness of the monolayer, noting, however, that 8.4A was obtained for the two-layer complex, in close agreement with the 8.3A value cited by MacEwan (1948).

The true thickness of a corresponding monolayer of glycerol in vermiculite is difficult to determine. Although x-ray measurements of glycerated vermiculite and vermiculite collapsed by heating indicate a difference in spacing of approximately 5A (14.2 – 9.2A), there is doubt that this difference represents the actual thickness of the glycerol monolayer. There appears to be no essential difference between the spacings of glycerated and glycolated vermiculites, both being about 14.1-14.3A, in sharp contrast to the real differences between glycerated and glycolated montmorillonites. As Walker (1950) has pointed out, this spacing in vermiculites is essentially the same as that set by the hydrated interlayer cation (Mg^{2+}) previous to treatment with the polyalcohol. Although this spacing is thus retained after treatment with the polyalcohol, it may well be that the monolayer does not fully occupy the space. In view of this uncertainty, it is felt that the monolayer thickness derived from measurements of montmorillonite complexes would be a reasonable approximation for the thickness of the corresponding monolayer in vermiculite.

As described in a concurrent paper (Kinter and Diamond, 1958), the original spacing of 10.1A for an endellite (Chattooga Co., Georgia) was increased to 11.2A upon glyceration. The thickness of the glycerol monolayer would thus be 4.0A, which is in reasonable agreement with the 3.8A figure given by MacEwan (1948) for a glycerol monolayer in endellite. The cross-sectional area per glycerol molecule corresponding to a 4.0A monolayer thickness (at liquid density) would be about $30A^2$, as compared to $27A^2$ computed from the 4.5A thickness for monolayer of montmorillonite complexes. Despite the 10 percent difference, the latter factor will be used in calculating the surface area of endellite from glycerol retention data.

Corresponding figures for the retention of ethylene glycol on montmorillonite under similar circumstances can be computed in the same manner. Assuming the density as that of liquid glycol, and the thickness of the molecule as 3.9A (from x-ray diffraction evidence), the retention of each 0.01 g of glycol corresponds to an area of 22.3 m^2 on external surfaces and twice this, or 44.6 m^2, on internal surfaces; this corresponds to a cross-sectional area of $23.0A^2$ per molecule, which contrasts strongly with the $33A^2$ figure suggested by Dyal and Hendricks (1950) for ethylene glycol on montmorillonite.

Published Determinations of Surface Areas of Montmorillonite Clays

Dyal and Hendricks (1950) computed the theoretical basal-face surface area of *pure* montmorillonite as 810 m^2/g; Mooney, Keenan, and Wood

(1952) and Quirk (1955) computed values of about 760 m^2/g. A number of authors have listed experimental values of surface area for several montmorillonites, determined by (1) low-temperature adsorption methods employing nitrogen or other nonpolar gases for external surfaces and (2) adsorption of ammonia or water vapor for total surface. Several have reported ethylene glycol retention values determined according to the method of Dyal and Hendricks (1950), from which surface areas can be computed by using the factor proposed by Dyal and Hendricks, corresponding to an area of $33A^2$ per molecule, or the factor suggested above, corresponding to an area of $23A^2$ for the ethylene glycol molecule.

In general, the reported values of *external* surface area range from about 15 to about 100 m^2/g (Brooks, 1955; Zettlemoyer, Young, and Chessick, 1955; Lopez-Gonzalez and Deitz, 1952; Mooney, Keenan, and Wood, 1952, 1952a; Dyal and Hendricks, 1950; Nelson and Hendricks, 1943). A number of factors seemingly contribute to the variation, including the type and purity of the montmorillonite, the saturating cation, the outgassing temperature, and in general the preparatory treatment received by the sample.

The values of *total* surface area generally reported for measurements with polar gases range from about half to somewhat above the calculated theoretical surface area of 760 to about 800 m^2/g (Orchiston, 1954, 1955; Zettlemoyer, Young, and Chessick, 1955; Mortland, 1955; Mooney, Keenan, and Wood, 1952, 1952a). Cation saturation apparently has considerable influence on the surface areas indicated. There is a discrepancy in that certain authors calculate surface areas after doubling that portion of the monolayer capacity due to internal surfaces, while others do not. In fact, the general validity of calculating total surface areas from water vapor adsorption data is open to some question (Quirk, 1955).

Surface Areas of Montmorillonites Derived from Glycerol Retention Data

In Table 1 are presented glycerol retention data and calculated surface areas for minus 0.2-micron fractions of several montmorillonites of the A.P.I. reference series. The predominant cation in all cases is considered to be Na^+, since sodium metaphosphate was used in the initial dispersion of all samples. External surface area was calculated by multiplying the "external glycerol retention" by the factor 17.65. The difference between total and external glycerol retention represents the internal retention, from which the internal surface area was obtained by multiplying by the factor 35.3.

Two of the montmorillonites, H-25 and H-28, as indicated by high retention values after 600°C treatment, were not irreversibly collapsed, and the average of the external retention values of the other montmorillonites was used in calculating surface areas of these two materials. Generally speaking, the external surface areas indicated are relatively small, ranging from 16 to 35 m^2/g. Internal surfaces are about 20 times as great, ranging from about 600 to more than

Table 1.—Glycerol Retention Values and Computed Surface Areas of -0.2μ Fractions of Some A.P.I. Series Reference Montmorillonites (Na^+ Predominant Cation)

			Retention, Percent			Surface Area, m^2/g		
No.	Type	Source	Total	External (After 600°C Heating)	Internal	External	Internal	Total
H-19	Montmorillonite	Polkville, Miss.	19.3	1.8	17.5	32	618	650
H-23	Montmorillonite	Chambers, Ariz.	18.9	0.9	18.0	16	636	652
H-24	Montmorillonite	Otay, Calif.	22.2	2.0	20.2	35	714	749
H-25	Montmorillonite	Upton, Wyo.	18.1	11.0[1]				
				(1.6)[2]	(16.5)	(28)	(583)	(611)
H-28	Montmorillonite	Little Rock, Ark.	18.4	11.4[1]				
				(1.6)[2]	(16.8)	(28)	(594)	(622)
H-33a	Nontronite	Garfield, Wash.	14.2	1.4	12.8	25	452	477

[1] 600°C heating insufficient to inhibit retention of glycerol on internal surfaces.

[2] Average figure for external retention of montmorillonites; surface areas computed using this figure are enclosed in parentheses.

700 m^2/g, near the maximum expected for pure montmorillonite. The maximum total surface area indicated is that for the H-24 montmorillonite, 749 m^2/g. The nontronite sample, H-33a, has the same order of external area as the montmorillonites but a somewhat lower internal area, probably due largely to a high content of iron oxide impurities in this very fine fraction, but partly also to the effect of substitution of the relatively heavy iron ion for the much lighter magnesium in the crystal lattice. This would increase the weight of the unit cell and correspondingly reduce the surface area per gram.

In Table 2 are presented similar data for a bentonite (Volclay, American Colloid Co.) saturated with several different cations by treatment with ion-exchange resins. The clay material (passing the 200-mesh sieve) was not fractionated or otherwise purified. Accordingly, the sample was not particularly pure, x-ray diffraction data showing the presence of about 10 percent quartz; it is likely that other impurities, such as volcanic glass, were also present. As expected, for K^+ and NH_4^+ saturation the values of internal surface area are low since these cations are known to collapse some of the expanding layers irreversibly on drying to 110°C. Na^+ saturation gave an unusually high value for external surface and a correspondingly low value for internal surface; qualitatively this could have resulted from an extreme dispersion of the Na^+-saturated clay into very thin particles, a possibility that is further developed later in the report. The relatively lower external surface areas and higher internal surface areas obtained for saturation with the polyvalent cations are noteworthy; values for the divalent cations Ca^{2+} and Fe^{2+} appear to be similar, while Mg^{2+} yields a somewhat higher value of internal surface, similar to the values obtained for saturation with the trivalent cations Fe^{3+} and Al^{3+}.

The relative order of total surface areas of montmorillonites saturated with various cations found from this work is quite similar to that reported by Orchiston (1955) for results of water vapor sorption on an Arizona montmorillonite and for surface areas calculated from Bower and Gschwend's (1952) data on glycol retention of different saturations of a Wyoming bentonite. There is general agreement in the relative orders, with the notable exception that the ranking of Mg^{2+} is considerably higher in the series determined by glycerol retention.

TABLE 2.—SURFACE AREA OF VOLCLAY BENTONITE (<200-MESH) SATURATED WITH VARIOUS CATIONS, AS CALCULATED FROM GLYCEROL RETENTION DATA (KINTER AND DIAMOND, 1958)

Cation	Surface Area, m^2/g		
	External	Internal	Total
Li^+	65	403	468
Na^+	116	258	374
H^+	74	364	438
NH_4^+	79	244	323
K^+	44	265	309
Ca^{2+}	49	396	445
Mg^{2+}	35	508	543
Fe^{2+}	48	417	465
Fe^{3+}	49	466	515
Al^{3+}	49	516	565

SURFACE AREAS OF OTHER CLAYS

Illite

Surface areas of 91 and 76 m^2/g were calculated from glycerol retention values of a minus 2-micron fraction of illite (H-35, Fithian, Illinois) and an unfractionated sample of H-36, Morris, Illinois. These figures compare with published measurements ranging from 67 to about 100 m^2/g for illites derived from Illinois shale by B.E.T. determinations using nitrogen and ethane (Brooks, 1955; Dyal and Hendricks, 1950; Nelson and Hendricks, 1943). Water vapor sorption measurements on similar materials by Orchiston (1955) lead to surface area figures of 78 to 86 m^2/g. With due allowance for possible differences in purity and particle size of the materials, the glycerol retention surface areas agree well with published values.

Kaolinites

Surface areas of 23 and 14 m^2/g were calculated from glycerol retention data for minus 2-micron fractions of two A.P.I. kaolinites (H-1, Murfreesboro, Arkansas, and H-5, Bath, South Carolina). Values reported for surface areas of various kaolinites by nitrogen and ethane adsorption range from about 7 to about 30 m^2/g (Brooks, 1955; Keenan, Mooney, and Wood, 1952; Dyal and Hendricks, 1950; Nelson and Hendricks, 1943). Surface areas of kaolinites within this range were also indicated by adsorption of the polar gases, water and ammonia (Orchiston, 1954; Mortland, 1955).

Glycerol retention of a minus 2-micron fraction of an English china clay indicated a surface area of 25 m^2/g; Dyal and Hendricks (1950) report a surface area of 28.2 m^2/g for a similar size fraction of an English china clay.

Vermiculite

Surface areas were also calculated for the vermiculite described in a companion paper (Kinter and Diamond, 1958). Glycerol retention data on coarse flakes (retained on a 200-mesh sieve) of this seemingly pure vermiculite indicate a total surface of 275 m^2/g. When the flakes were mechanically reduced in size to minus 2 microns, a much higher value of 685 m^2/g was obtained, neglecting in the calculation the minor portion of glycerol retention on external surfaces. The latter value compares closely with those of montmorillonites, and indicates a virtually complete penetration of glycerol into the interlayer spaces, in contrast with the apparently reduced penetration of the larger flakes. A range of 100 to 300 m^2/g (by water adsorption) for total surface area and a value of 0.5 m^2/g (by nitrogen adsorption) for external surface area have been reported for coarse commercial vermiculite before exfoliation (Zonolite Co., 1954).

Halloysite

In general, the surface areas of halloysites by gas adsorption are somewhat higher than those of kaolinites, most published values being about 45 m^2/g (Brooks, 1955; Dyal and Hendricks, 1950; Nelson and Hendricks, 1943). Values calculated from glycerol retention data for two unfractionated A.P.I. reference halloysites (H-12b, Bedford, Indiana, and H-13, Eureka, Utah) are 76 and 102 m^2/g respectively. The Bedford sample is reported as containing about 10 percent allophane (Main, Kerr, and Hamilton, 1950), which may explain the relatively high value found for it. However, though the Eureka sample has a seemingly greater surface area than the Bedford, these authors did not report it to contain allophane. The discrepancy is not attributable to endellite layers in the halloysite, since in determining the glycerol retention value the sample was predried at 110°C, and any endellite layers would have been collapsed.

Endellite

A total surface area of 430 m^2/g was obtained for a sample of endellite from Chattooga Co., Georgia, from glycerol retention data for material preserved in the natural moist state; retention on a portion of this material predried at 110°C indicated an "external" surface of only 27 m^2/g. Both values are based on an assumed area of $26.9A^2$ per molecule of glycerol, as derived from data on montmorillonite-glycerol complexes. As previously discussed, the values may be about 10 percent too low.

Allophane

A total surface area of approximately 260 m^2/g for a soil allophane was derived from retention data on the minus 2-micron fraction of an Ando soil from Japan. The D.T.A. curve of this material and its complete lack of crystallinity, as shown by x-ray diffraction, indicate that it may be described as essentially pure allophane. The surface area was calculated from the glycerol retention data on the assumption that all the glycerol was retained on "external" surfaces. This surface-area figure for the Ando soil allophane is in good agreement with surface areas determined by nitrogen adsorption for some allophane soil-clay fractions from New Zealand, which average about 300 m^2/g (Birrell and Gradwell, 1956).

GLYCEROL RETENTION OF NON-CLAY MATERIALS

An attempt was made to determine the applicability of the glycerol retention method to the measurement of surface areas of various materials other than clay minerals. Samples of several such materials of known surface area (as measured by nitrogen adsorption) were kindly supplied by Dr. V. R. Deitz of the Bone-Char Research Project, Inc., National Bureau of Standards. These samples included a silica material derived from open-hearth furnace operation, a silica-alumina cracking catalyst, a bone-char (chemically identical to hydroxyapatite), and a pure sample of anatase (TiO_2). Nitrogen surface areas ranged from 10 m^2/g for the anatase to about 550 m^2/g for the cracking catalyst. There was a definite equilibrium in the retention of glycerol by all these materials except the anatase; but when the retention values were converted to surface area by the factor previously derived for clay minerals (17.65 m^2/g per percent retention) the indicated surface areas were only about 50 percent of the nitrogen adsorption figures.

Although there is a definite retention of glycerol on the surfaces of most of these materials under the experimental conditions involved, the nature of the packing of the molecules on their surfaces is not necessarily the same as it is on clays. Pores having surfaces accessible to nitrogen but not to glycerol could also account for the low values obtained.

SURFACE AREAS OF MONTMORILLONITE IN TERMS OF PARTICLE DIMENSIONS

One possible explanation of the rather pronounced variation in surface-area measurements of a montmorillonite saturated with different cations is that the cations may cause differences in the degree of dispersion of the montmorillonite particles and the effective particle size. Brooks (1955) concluded that for sodium Wyoming bentonite, the effective particle size in an aqueous suspension was appreciably smaller than the particle-aggregate accessible to nitrogen after drying. Measurements involving internal surfaces must employ polar molecules; in a previously dried sample, the extent to which these polar molecules penetrate between the unit-cell surfaces and also the extent to which the penetration disrupts the particle-aggregates and alters the effective particle size may depend on the particular cation present.

It seems reasonable that if sodium, a dispersing cation, were present, the disruption of particles would be greater than with a polyvalent, flocculating cation. The glycerol-retention technique specifically involves addition of glycerol and water to a dried clay, with only such dispersion as can be achieved by moderate shaking; while this has been shown to result in essentially complete penetration of the glycerol throughout the interlayer surfaces, the effect of the treatment on the breadth and thickness of the resulting montmorillonite "particles" is likely to vary with the nature of the saturating cation.

If this possibility is allowed, it becomes of interest to attempt to calculate the internal and external surface areas of montmorillonite as functions of particle dimensions. For this purpose, the following dimensions may be used for the unit cell of montmorillonite: $a = 5.1\text{A}$; $b = 8.8\text{A}$; $c = 9.6\text{A}$. The composition of the unit cell is taken as

$$2\ [(\mathrm{Al}_{1.67})(\mathrm{Mg}_{0.33})\mathrm{Si}_4\mathrm{O}_{10}(\mathrm{OH})_2]$$

with 718 atomic units, neglecting the exchangeable cation. For simplicity, a montmorillonite particle can be considered as a rectangular solid L, M, and N unit cells thick in the a, b, and c dimensions, respectively. Weak bonding in the c direction permits the entrance of polar molecules and thus all unit-cell surfaces normal to the c direction (except the top and bottom of the particle) are "internal surfaces," the top and bottom of the particle and the edge and end surfaces constituting the external surfaces.

A further simplification can be made by assuming that the particle contains roughly the same number of unit cells in the "a" and the "b" directions, thus requiring only two parameters for surface area calculations: L, the width of the particle in unit cells in the a and b directions; and N, the height of the particle in unit cells in the c direction. A diagrammatic representation of a montmorillonite particle according to this concept is provided in Figure 1.

The external surface area per gram of particles of a given size is the product of the external surface per particle and the number of particles per gram. It can be shown that employing these simplifications the external surface area of a montmorillonite of uniform particle size can be expressed as:

$$\text{External surface (m}^2\text{/g)} = \frac{2241\ (N) + 754\ (L)}{LN}$$

This external surface can be apportioned into *face surface*, given by $754/N$

(which is independent of particle width), and *edge surface*, given by $2241/L$ (which is independent of particle thickness).

The *internal surface* of this hypothetical montmorillonite can be expressed as:

$$\text{Internal surface } (\text{m}^2/\text{g}) = \frac{754\,(N-1)}{N}$$

(which is independent of particle width).

The *total surface* is the sum of the internal and external surfaces and is given by:

$$\text{Total surface } (\text{m}^2/\text{g}) = \frac{2241}{L} + 754$$

Thus the total surface is independent of the thickness of the particles. Indeed, for wide enough particles (about 100 unit cells in width) the edge contribution becomes small, and the total surface area is essentially a constant. Montmorillonites composed of particles of lesser width should have progressively larger total surface areas as progressively greater amounts of edge surface are exposed.

If attention is confined to particles of sufficient width that edge surface does not become appreciable (and presumably most real montmorillonites are made

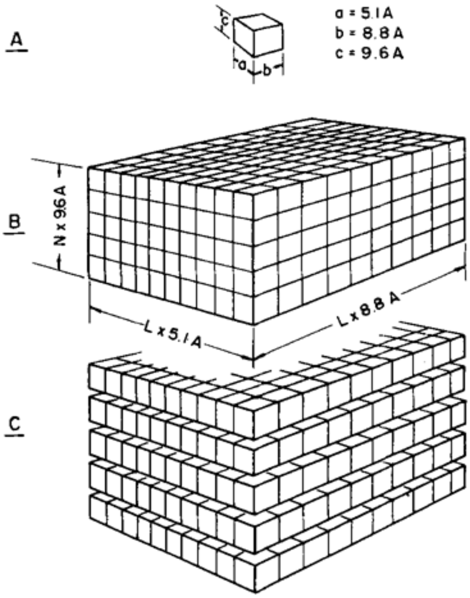

FIGURE 1. — Diagrammatic model of a montmorillonite particle. A, Unit cell outline. B, Collapsed particle exhibiting only external surface. C, Expanded particle exhibiting external and internal surface.

up of such particles), the total surface is essentially a constant. Since the amount of internal surface depends on particle thickness, the relative proportion of internal to total surface should provide an indication of the thickness of the particles. Figure 2 presents the calculated ratio of internal to total surface area vs. particle thickness for various particle widths. If particle widths above 100 unit cells are assumed, the narrow band above $L = 100$ can be used as a "calibration curve" giving an estimate of particle thickness as a function of the internal to total surface area ratio.

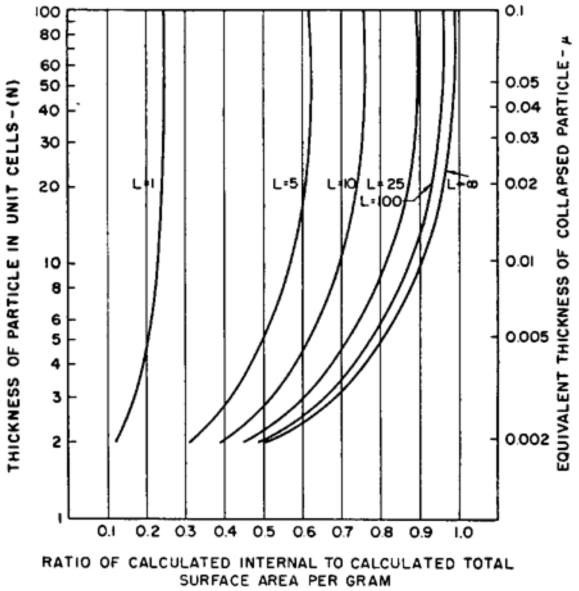

FIGURE 2. — Ratio of calculated internal to calculated total surface area per gram of hypothetical montmorillonite particles as a function of particle thickness (N) for various particle widths (L).

It must be borne in mind that the model employed represents a montmorillonite particle as a rectangular solid with smooth surfaces and is thus a gross simplification; real montmorillonite particles are of course irregular in outline, as seen in electron micrographs, and are of varying thicknesses and often curled, crumpled, or otherwise distorted, if indeed individual particles can be observed at all. Furthermore the simple mathematical derivation is for a material having particles all of the same size; real montmorillonites are polydisperse, and the surface area would be affected by the nature of the particle size distribution.

Consideration must also be given to the reduction in internal surface caused by partial irreversible collapse of the interlayer spaces after saturation with certain cations (notably K^+ and NH_4^+), the presence of impurities, and other complicating factors.

The computed ratios of internal to total surface areas determined by glycerol retention for the various cation saturations of the Volclay montmorillonite (Table 2) can be compared with Figure 2, even though the measured total surface areas are not the same for the different cation saturations. If particle width is assumed to be in excess of 100 unit cells, a thickness of 3 to 4 unit cells is indicated for the Na^+-saturated montmorillonite, 6 to 7 unit cells for the saturation with H^+, and about 20 unit cells for saturations with the various polyvalent cations.

Similar experimentally determined ratios can be calculated from the surface area data for the 0.2-micron fractions of several A.P.I. series montmorillonites as listed in Table 1. In all these samples Na^+ is considered to be the predominant cation, since dispersion was accomplished with sodium metaphosphate. Despite this fact, the external surface areas reported for these fine fractions are low, the highest being only 35 m^2/g; and the ratios of internal to total surface are all over 95 percent. This would indicate, according to the previous interpretation, that the individual particles were 30 or more unit cells in thickness, contrasting strongly with the 3 to 4 unit cell thickness previously indicated for Na^+-saturated Volclay.

Since experimental confirmation of these deductions is completely lacking, the estimate provided should not be considered as direct evidence that the particle thickness is actually as indicated. Indeed, such experimental confirmation is difficult to procure, since the montmorillonite particles existing, for example, in an electron microscope preparation may be quite different in size from the particles comprising a glycerol retention specimen at equilibrium. Evidence exists that small variations in dispersion, drying, grinding, or other preparatory treatments produce considerable variations in the resulting external surface areas of montmorllonites, and thus in their apparent particle sizes (Brooks, 1955; Zettlemoyer, Young, and Chessick, 1955; Mooney, Keenan, and Wood, 1952a). The particles thus observed or measured by any particular experimental procedure are those that happen to exist after the necessary sample preparations that are involved.

CONCLUSIONS

The following conclusions are drawn from the work described in this paper:

1. Glycerol retention may be employed to provide a relatively simple and rapid method of measuring surface areas of both expanding and nonexpanding clays. A separate determination of the glycerol retained on external surfaces is required for computation of the total surface of expanding clays. Surface areas of clays composed of mixtures of montmorillonite and vermiculite may be determined without reference to the relative amounts of each present.

2. Calculations of surface areas of nonexpanding clay minerals from glycerol retention data are in good agreement with published values for the same or similar materials derived from gas-adsorption methods.

3. Calculations of external surface areas of montmorillonite clays from glycerol-retention data of heated montmorillonites are in approximate agreement with reported measurements by *nonpolar* gas-adsorption methods, especially when the variations in external surfaces produced by differences in pretreatments are considered.

4. Calculations of *total* surface areas of montmorillonite clays are in reasonable agreement with those reported for similar materials by adsorption of *polar* gases, notably NH_3. The values are somewhat lower than certain published values derived from water-vapor desorption isotherms; however, the correctness of the latter values has been questioned.

5. It is suggested that the factor proposed by Dyal and Hendricks to convert ethylene glycol retention data to surface area is about one-third too high. A factor is proposed that is consistent with a liquidlike packing and the observed thickness of the glycol films by x-ray diffraction measurements.

6. The relations between the internal and the external surface areas and the particle thickness and width have been worked out for montmorillonite on the basis of a simplified model of a montmorillonite particle. It is shown that the ratio of "internal" to "total" surface may provide an estimate of particle thickness for a given montmorillonite.

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