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EXTERNAL SPECIFIC SURFACE AREA OF VERMICULITE¹K. V. RAMAN AND M. M. MORTLAND, *Department of Soil Science,
Michigan State University, East Lansing, Michigan.*

INTRODUCTION

The physical and chemical properties of soils and sediments are largely dependent upon the specific surface of the mineral fraction. Measurement of surface area using low temperature adsorption isotherms, usually nitrogen, by the Brunauer, Emmett and Teller (B.E.T.) method has been reported for soils and clays (Emmett *et al.*, 1938; Nelson and Hendricks, 1943) and is reviewed by Mortland and Kemper (1965). The interlayer surface of montmorillonite and vermiculite is not measured at the low temperature and pressure employed, and the method gives the external surface values only.

In the phenomenon of nitrogen adsorption, the gas molecules occupy not only the geometric or outer surface, but also penetrate into the capillaries, crevices and cracks, and measure their surface as well. Electron microscopic observations by Raman and Jackson (1964) indicate that vermiculite surfaces, unlike mica surfaces, contain micromorphological structural variations such as small humps and discontinuity of layers, the terminal layer edges forming scrolls. Presence of such scrolls and innumerable terminal layer edges could influence the surface area measured by this technique. It was therefore considered worthwhile investigating in detail the surface area of various size fractions of vermiculite and the effect of different interlayer cations on the measured specific external surface.

MATERIALS AND METHODS

The following samples were used in the study:

Vermiculite from Libby, Montana and from S. Africa (supplied by Ward's); kaolinite from Bath, S. Carolina (Ward's); biotite from Spruce Pine, N. Carolina (Ward's); muscovite from Ontario, Canada (Ward's).

Muscovite, biotite, and vermiculite samples had to be ground in order to obtain the smaller size fractions. A Waring blender was employed for this purpose. The samples were suspended in water overnight and the supernatant was discarded. This removed any soluble salts present and favored easy dispersion. The samples were then ground in the blender and fractionated by gravity or centrifugal sedimentation (Jackson, 1956)

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after dispersion with an ultrasonic dispersion unit. Homoionic samples were prepared by washing them with the respective chloride salts and rendering them salt-free. The samples were then freeze dried. Kaolinite and mica samples were used in the study to check the agreement between the observed external surface values and the calculated external surface, as electron micrographs of these minerals show relatively smooth surface morphology (Raman and Jackson, 1965).

Surface area was determined by nitrogen adsorption with a Perkin-Elmer Shell Model 212B Sorptometer, using helium as a carrier gas and liquid nitrogen as coolant. The samples were degassed by heating them in sample tubes for 8 hours at 80° C. in a slow stream of helium. The area of the desorption peak was used for the calculation of the surface area

TABLE 1. CHANGES IN THE THEORETICAL SURFACE AREA OF PLATY PARTICLES WITH CHANGES IN WIDTH:HEIGHT RATIO (M²/G)

Particle Size microns	Width:height ratio		
	10:1	20:1	50:1
50	0.08	0.12	0.20
20	0.20	0.29	0.51
5	0.80	1.17	2.03
2	2.01	2.93	5.08
1	4.01	5.87	10.17
0.1	40.08	58.64	101.68

and four points were obtained for the B.E.T. plot. The plot was linear in all cases and passed through the origin for most samples.

Pilot experiments with a number of different samples showed that the measurements could be duplicated within 3 to 5%. Details of the method are given by Nelson and Eggertsen (1958). The calibration of the instrument was checked by Miner, Ellis, and Parfitt (1965), who found a good agreement between the measured values and those determined by the classical B.E.T. method.

RESULTS

Calculation of the theoretical external specific surface of the particles of varying sizes is carried out by geometrical formulas. Kunkel (1948) has shown that platy particles have a lower settling velocity than spherical particles and so the effective equivalent spherical diameter of platy particles is greater. The equivalent spherical diameter is increased 20% to compensate for their slower settling rate. Details of the calculation procedure is discussed by Jackson (1956).

The width:height ratio of the particles is another consideration which

affects the value of the calculated surface area. For the common clay minerals this is taken as 10:1 (Jackson, 1956). However, in coarser particles and in minerals like mica which have a perfect (001) cleavage, this ratio may not hold. Table 1 gives the changes in the calculated surface area caused by changes in width:height ratio. As discussed later in the text, for kaolinite, a close agreement exists between the measured surface area and the calculated surface area based on a width:height ratio of 10:1; for micas, with good basal cleavage, a wider ratio is indicated.

Table 2 gives the surface area for kaolinite, muscovite, biotite, and vermiculite of different homoionic systems. The measured surface area of muscovite and biotite is about 50 to 100% more than that of kaolinite for fractions of the same size range except for the finest fraction (0.1 to 1 μ). The measured surface area of kaolinite is in good agreement with

TABLE 2. SURFACE AREA MEASURED BY NITROGEN ADSORPTION (M^2/G)

Size Range microns	Kao- linite	Mus- covite	Biotite	Vermiculite							
				From South Africa	From Libby, Montana	Ca ¹	Mg	Li	Na	K	NH ₃ gas
20-50	ND	0.85	0.74	2.21	1.95	1.79	2.17	2.21	1.91	1.32	1.27
5-20	0.94	1.87	1.90	3.79	3.31	3.29	3.67	3.52	3.46	2.36	2.21
2-5	2.43	4.57	3.89	9.41	8.23	8.18	8.94	8.11	8.20	6.34	6.18
1-2	4.01	7.12	6.89	16.21	15.24	13.82	17.23	19.26	17.94	10.97	11.42
0.1-1	29.00	29.46	24.28	56.28	49.24	46.74	51.32	50.61	48.79	38.27	36.79

¹ For homoionic saturations, vermiculite from Libby, Montana was used.

the calculated surface area range for the particular fraction, when the particles are assumed to be 10 times as wide as high. For the micas, however, this value is too low and the measured values indicate that the particles are 20 to 50 times as wide as high. Since micas have a good basal cleavage, mechanical rupture causes the particles to cleave more readily in the (001) plane, thus maintaining a high width:height ratio. However, below a certain critical particle size, the particles could break laterally almost as readily as they cleave.

Vermiculite, on the other hand, has a surface area of almost twice that of corresponding mica. Of the two vermiculites studied, the sample from South Africa has a slightly higher surface area than that from Libby, Montana. It is to be admitted, however, that both samples contain varying quantities of unweathered mica. In the natural state, the samples have both magnesium and sodium in their exchange complex. Conversion of this natural material to homoionic systems of Ca, Li, Na or Mg did not significantly alter their surface area, though Mg saturated systems had a tendency to exhibit a higher surface area than other systems. On

K saturation or treatment of the natural sample with NH_3 gas, the surface area decreased to the extent of 23 to 33% of the original. On a percentage basis, the loss in surface area was more in the coarser fractions than in the finer fractions.

The fact that vermiculite possesses an external surface area considerably more than that of mica and that part of this external surface area could be lost by treatment of the sample with K or NH_3 gas raises some interesting questions on the nature of these surfaces. Raman and Jackson (1964) observed that vermiculite surfaces possess innumerable terminal layers scrolled at the edges. On K or NH_4 saturation, such scrolled layers unscrolled on the surface leaving a smooth morphology, comparable to that of K micas. They also observed that such unscrolling was not perfect in some areas possibly because of the relatively large displacements which had occurred in these areas during the scrolling process.

The increased surface areas of vermiculites are supposed to arise from the presence of scrolls, a surface phenomenon characteristic of vermiculite and weathered micas. Hydrated alkali or alkaline earth ions produce or enhance these surface scrolls. Gas adsorption techniques such as the one used here would measure the scrolls produced here as well as that of the cracks and crevices present as a consequence. K or NH_4 saturation causes the unscrolling of such scrolls and consequently the measured surface area is lower. It is interesting to note that though the surface area is reduced by about 30%, the measured area is still higher than that of the micas, which agrees with the electron microscopic observation of Raman and Jackson (1964), that K or NH_4 caused considerable but not complete unscrolling.

If the desorption is carried out under identical conditions, the shape of the desorption curves could give an indication of the ease of release of the adsorbed gas. A water bath of uniform temperature ($60^\circ \pm 1^\circ \text{C.}$) was applied to the sample tube immediately on withdrawal of the liquid nitrogen bath, in order to hasten the desorption process. The curves (Fig. 1) were symmetrical for kaolinite and muscovite; a tailing of the peak is noticed in all samples of vermiculite. Part of the desorbed nitrogen is not released spontaneously indicating that this nitrogen may be released from scrolls, cracks or crevices, a desorption process which may take a more tortuous path.

Treatment of the sample with NH_3 gas produces the same amount of reduction in surface area as saturation with K salt. Mortland *et al.* (1963) presented infrared spectroscopic evidence to show that NH_3 gas adsorbed on air-dry montmorillonitic or vermiculitic clays changed to NH_4^+ ion by interaction with the proton of residual water molecules as-

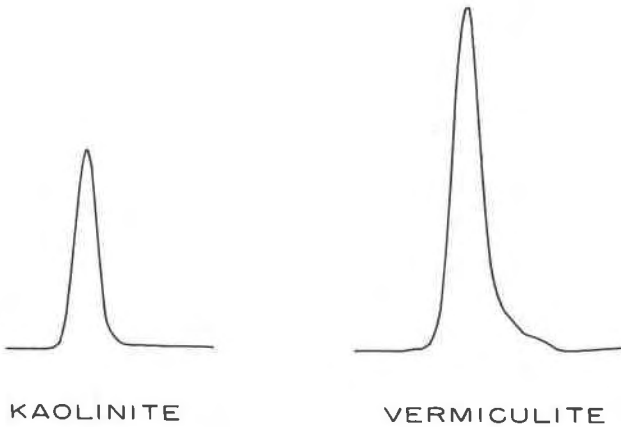


FIG. 1. Typical desorption curves of kaolinite and vermiculite. Time is represented in x -axis and thermal conductivity in y -axis. The tailing of the peak in vermiculite indicates delayed release of nitrogen, possibly from scrolls, cracks and crevices.

sociated with the interlayer cation. Treatment with NH_3 gas, in effect, thus has the same effect as saturation with NH_4 salt.

Evidence for the presence of cracks and crevices of the type discussed here in vermiculite also comes from other chemical work. Mortland *et al.* (1963) found that a dehydrated vermiculite, whether saturated with calcium or sodium, would not expand in the presence of ammonia even after several increments of ammonia pressure. The c axis spacings remained rational, indicating little, if any, interstratification with expanded and nonexpanded layers. However, it was found that, after degassing, the vermiculite had retained considerable ammonium of the order of one-third to one-half the cation exchange capacity. Retention of ammonia at the peripheral edges of particles cannot account for such large quantities. Diffusion of ammonia through the cracks and crevices, unscrolling of terminal layer edges and the consequent partial sealing of tortuous diffusion paths, could account for such high retention.

SUMMARY

The external specific surface area of a number of carefully fractionated size ranges of natural vermiculite from several different sources and of kaolinite, muscovite and biotite was determined using a nitrogen absorption technique with a B.E.T. plot. The results were compared with the external surface area values calculated for the particular size range using geometrical formulas for shape and thickness. There was a reasonably close agreement between the calculated and the measured values for all

size ranges of kaolinite and the $<5\mu$ fractions of muscovite and biotite. The disagreement between measured and calculated values for the coarser fractions of micas may arise from certain basic assumptions on width and thickness of particles, implied in the calculated values, which may not hold for thicker particles.

For vermiculite, however, the measured external surface values were higher than the calculated values for the size range and was nearly twice the surface area of micas of corresponding size ranges. Saturation with Ca, Mg, Li or Na did not significantly influence the measured external surface area values, whereas K or NH_4 saturation or treatment with NH_3 gas decreased the surface area by about 30%. Such higher values in natural and other homoionic vermiculites is attributed to the presence of scrolled layer edges, and to capillaries, cracks and crevices in the mineral; the unscrolling of scrolled surfaces on K or NH_4 saturation causes a decrease in measured surface areas.

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