

# SURFACE AREA CHANGES OF A VERMICULITE BY ACID AND THERMAL TREATMENT

*by*

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## ABSTRACT

A vermiculite from Beni-Uxera, North Africa, was refluxed with HCl solutions of various concentrations to determine the effect of such a treatment on its surface area. The treated vermiculite was analyzed for "free" SiO<sub>2</sub> and by x-ray diffraction, and the refluxing solutions were analyzed for the cations removed from the vermiculite. Surface areas were determined by means of adsorption isotherms of *n*-butane at 0°C.

The surface area of the acid-treated vermiculite increases with increase in concentration of the acid. Heating of the acid-treated samples or the natural samples decreases the surface area.

The increase in surface area by acid treatment is due to destruction of the vermiculite and its conversion to a "free" form of SiO<sub>2</sub> which possesses a large surface area. x-Ray analysis indicated that this "free" SiO<sub>2</sub> was not present in the interlayer positions of the crystal lattice of vermiculite.

## I. INTRODUCTION

Travers (1933), Nutting (1935), Mills, Holmes and Cornelius (1950), Gutierrez-Rios and Lopez-Gonzalez (1952), and Lopez-Gonzalez and Deitz (1952) have found that the surface area of several clay minerals is modified as a result of acid treatment. Furthermore, the changes in surface area were found to be correlated with changes in crystal structure of these clay minerals.

Since the crystal structure of vermiculite is similar to that of montmorillonite it was felt that a study of vermiculite might shed additional light on the effect of acid treatment on the silicate minerals as a whole. The present report is a result of such a study.

## II. MATERIAL AND EXPERIMENTAL PROCEDURES

The material used in the present work was a vermiculite from Beni-Uxera, North Africa (Hoyos de Castro, Gonzalez-Garcia and Martin-Vivaldi, 1950). The samples were ground and passed through a 100 mesh/cm<sup>2</sup> sieve. On the sieved material the following determinations were made: chemical analysis, cumulative dehydration curve, and x-ray powder diffraction photographs using a Philips 57.3 mm diam. camera, with Cu K<sub>α</sub> radiation.

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The acid treatment of the vermiculite was conducted in the following way: several 50 g samples of ground vermiculite were refluxed for 30 min with 500 cm<sup>3</sup> of HCl solutions of various concentrations, ranging from 0.1 N to 2.5 N. The acid-treated samples were washed with distilled water until the wash water was free from chloride ions. Finally, the samples were dried at room temperature. The components removed by acid treatment were determined in the filtrate.

As a consequence of removal of cations from the crystal lattice of the silicate by the acid solution process, some silica is liberated and remains in the acid-treated samples because of its low solubility. This "free" SiO<sub>2</sub> was determined by boiling a small portion of the samples for five minutes in a 5 percent solution of sodium carbonate.

Surface areas of the original and acid-treated vermiculite were calculated from the adsorption isotherms of *n*-butane at 0°C by the B.E.T. method (Brunauer, Emmett and Teller, 1938). All the samples were outgassed in the adsorption chamber for 4 hr before the first aliquot of *n*-butane to be adsorbed was added. The butane, provided by The Matheson Co., Inc., had a purity no less than 99.5 percent.

### III. EXPERIMENTAL RESULTS

The results of the chemical analysis of the original vermiculite are shown in Table 1.

TABLE 1.—CHEMICAL COMPOSITION OF THE VERMICULITE<sup>1</sup>

	Percent	
SiO <sub>2</sub>	..	39.99
Al <sub>2</sub> O <sub>3</sub>	..	13.83
Fe <sub>2</sub> O <sub>3</sub>	..	10.65
MgO	..	24.80
CaO	..	0.84
H <sub>2</sub> O	..	9.30
Total		99.41

<sup>1</sup> Sample dried to constant weight at 110°C. The water loss of the original sample at this temperature was 8.8 percent.

The loss of water at different temperatures was determined and the results obtained are shown in the cumulative dehydration curve of Fig. 1, which closely resembles Walker's (1951, p. 211) cumulative dehydration curve of vermiculite.

The components removed by acid treatment of the vermiculite are expressed in Table 2.

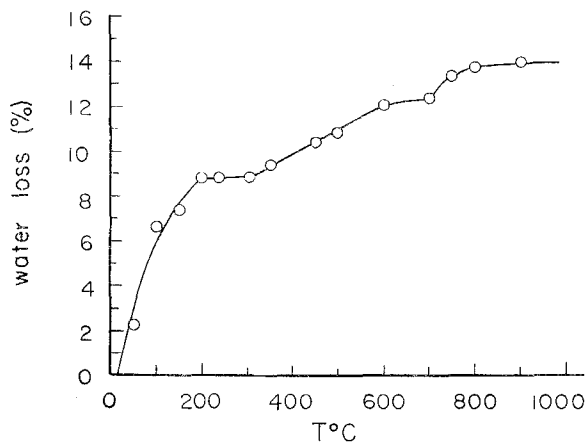


FIGURE 1.—Cumulative dehydration curve for vermiculite.

TABLE 2.—PERCENT COMPONENTS REMOVED BY TREATMENT OF VERMICULITE WITH HCl<sup>1</sup>

Component Removed	Concentration of HCl				
	0.1 N	0.5 N	1.0 N	1.25 N	2.5 N
SiO <sub>2</sub>	1.00	0.48	3.33	3.43	3.03
Al <sub>2</sub> O <sub>3</sub>	0.18	4.66	5.25		11.41
Fe <sub>2</sub> O <sub>3</sub>	0.25	3.58	6.10	13.18	9.06
MgO	1.42	8.97	12.60		14.56
Total Removed (%)	2.85	17.69	27.28	31.17	48.40

<sup>1</sup> Data refer to samples at equilibrium at 110°C. Because of the small content of calcium in the original vermiculite, calcium was not determined in the filtrate.

Table 3 shows the percent of the total R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub> plus Fe<sub>2</sub>O<sub>3</sub>) that has been removed from the crystal lattice by acid solutions of various concentrations.

Table 4 shows the percent of "free" SiO<sub>2</sub> in the acid treated samples.

The 001 x-ray diffraction spacings of the vermiculite before and after acid treatment, after thermal treatment at 650°C for 4 hr, and after removing the "free" SiO<sub>2</sub> produced by the acid are shown in Table 5.

Some of the data obtained from adsorption of *n*-butane at 0°C on the original and acid treated vermiculite are shown in Fig. 2, plotted according to the B.E.T. method.

Table 6 shows the surface areas that have been calculated from Fig. 2, assuming that the cross-sectional area of the adsorbed *n*-butane molecule at 0°C is 32 Å<sup>2</sup> (Davis and DeWitt, 1948).

TABLE 3.—PERCENT  $R_2O_3$  REMOVED FROM THE ORIGINAL VERMICULITE CRYSTAL LATTICE BY HCl<sup>1</sup>

Concentration of HCl	Percent $R_2O_3$ Removed
0.10 N	1.8
0.50 N	33.6
1.00 N	46.3
1.25 N	56.4
2.50 N	83.6

<sup>1</sup> In a sample of vermiculite treated with HCl 5 N the total amount of  $R_2O_3$  removed was 100 percent, which corresponds to total destruction of the silicate lattice.

TABLE 4.—PERCENT "FREE"  $SiO_2$  IN THE ACID-TREATED VERMICULITE (Samples at equilibrium at 110°C)

Concentration of HCl	Percent "Free" $SiO_2$
0.10 N	2.1
1.00 N	15.7
1.25 N	16.8
2.50 N	74.3

TABLE 5.—001 SPACINGS OF VERMICULITE BEFORE AND AFTER ACID TREATMENT

Material	No Thermal Treatment	Heated 4 hr at 650°C
Original	14.2	9.1
Treated with N HCl	14.0	9.3
Treated with N HCl (without "free" $SiO_2$ )	..	9.3

TABLE 6.—SURFACE AREA OF THE SAMPLES OF VERMICULITE

Material	Temperatures				"Free" $SiO_2$
	110°C	275°C	400°C	650°C	
Original	84	11	14	11	..
0.10 N . HCl	103	10	11	..	2.1
1.00 N . HCl	125	96	86	59	15.7
1.25 N . HCl	128	117	96	68	16.8
2.50 N . HCl	510	418	336	268	74.3

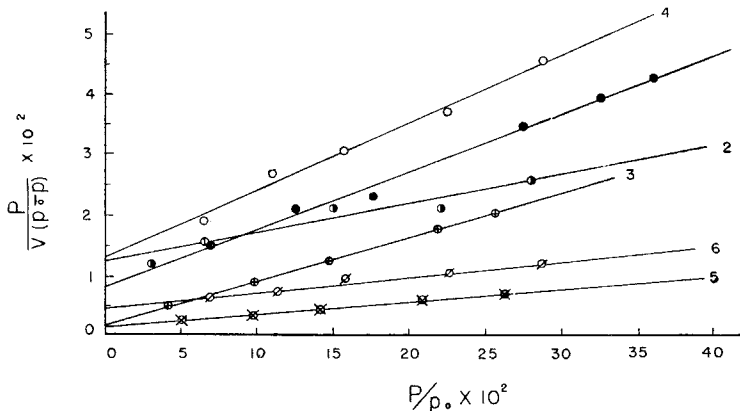


FIGURE 2.—Adsorption of *n*-butane on vermiculite at 0°C. Data are plotted according to the B.E.T. equation. (1) Original vermiculite. (2) Treated with 1.25 N HCl. (3) Treated with 1.25 N HCl and outgassed at 275°C, 4 hr. (4) Treated with 1.25 N HCl and heated at 650°C, 4 hr. (5) Treated with 2.50 N HCl and outgassed at 400°C, 4 hr. (6) Treated with 2.5 N HCl and heated at 650°C, 4 hr. The outgassing temperature and time for samples, 1, 2, 4 and 6 were 110°C, 4 hr.

#### IV. DISCUSSION AND CONCLUDING REMARKS

Tables 2 and 3 show that the removal of cations from the vermiculite lattice increases with concentration of acid. Under the conditions used in the present work (50 g of ground material, boiling for 30 min in 500 cm<sup>3</sup> of HCl solution) the structure of the vermiculite was destroyed completely when the concentration of the HCl was 5 N.

Removal of cations from the crystal lattice of vermiculite by acid treatment produces a corresponding amount of "free" SiO<sub>2</sub>; practically all this silica remains in the acid-treated samples because of its low solubility in acid solution (Table 4).

x-Ray powder diffraction patterns show (Table 5) that the 001 spacings for the original vermiculite (14.2 Å) and after treatment for 4 hr at 650°C (9.1 Å) (the difference being due to the loss of "unbonded" and "bonded" water) are practically equal to the corresponding spacings for the acid-treated vermiculite before (14.0 Å) and after similar thermal treatment (9.0 Å). This fact shows that the "free" SiO<sub>2</sub> produced during acid treatment is not situated between the silicate layers of the acid-treated product. In order to present additional evidence, a sample of the acid-treated vermiculite was boiled in a solution of 5 percent sodium carbonate (which removed the "free" SiO<sub>2</sub>) and then washed and dried. x-Ray patterns of this sample also showed a basal spacing of 9.3 Å (Table 5). Consequently, the "free" SiO<sub>2</sub> either must be situated at the edges of the remaining crystal layers or form independent nuclei. In a montmorillonite, the basal spacing for an acid-treated sample was found to be 1.4 Å greater than that of the original sample (Lopez-Gonzalez and Gonzalez-Garcia, 1954). It is suggested that the swelling of

montmorillonite permitted the acid to act extensively between the layers and that some of the "free"  $\text{SiO}_2$  formed could remain there and thus could be responsible for the increase in basal spacing.

The surface area of the original vermiculite outgassed at  $110^\circ\text{C}$ , available to *n*-butane, is  $84 \text{ m}^2/\text{g}$  (Table 6 and Fig. 3). Determination of surface area on montmorillonite (outgassed at  $110^\circ\text{C}$ ) from the adsorption isotherms of

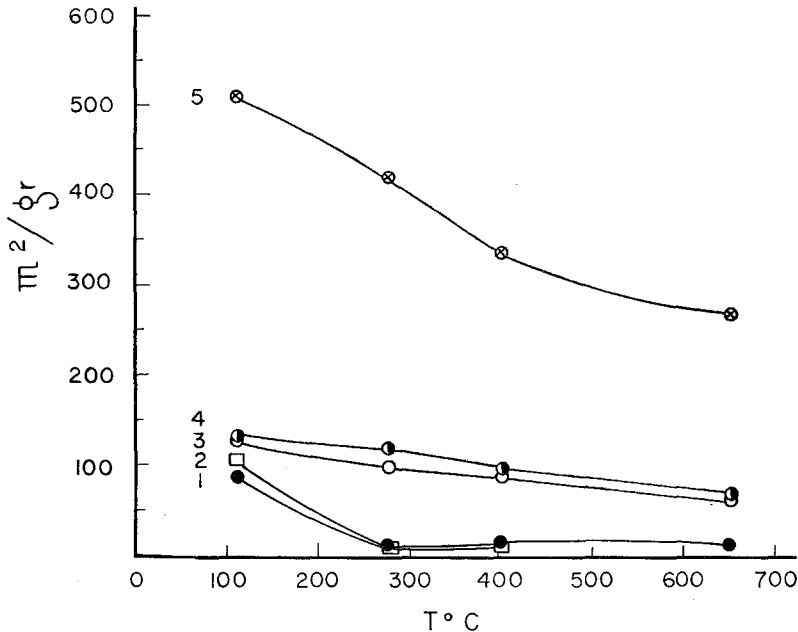


FIGURE 3.—Surface area changes of vermiculite as a function of acid and thermal treatment. (1) Original vermiculite. (2) Treated with 0.10 N HCl. (3) Treated with 1.00 N HCl. (4) Treated with 1.25 N HCl. (5) Treated with 2.50 N HCl.

nitrogen at  $-195^\circ\text{C}$ , also gives values close to  $80 \text{ m}^2/\text{g}$  (Escard, 1950; Lopez-Gonzalez and Deitz, 1952). These and other facts indicate that the surface of montmorillonite available to nitrogen is only the external (nonswelling) surface, which has been calculated, from a theoretical basis, to be of the order of  $80 \text{ m}^2/\text{g}$  (Dyal and Hendricks, 1950). From the value obtained in this work for the surface area of vermiculite ( $84 \text{ m}^2/\text{g}$ ), and taking into account its nonswelling behavior, we can assume that the surface area available to *n*-butane in the above-mentioned conditions is only the external surface. However, the possibility of availability of some of the internal surface of vermiculite to *n*-butane under our experimental conditions can not be completely disregarded.

When the original vermiculite is outgassed at higher temperatures ( $275^\circ\text{C}$ ) the surface area decreases to  $11 \text{ m}^2/\text{g}$  and this value remains practically

constant up to 650°C (Fig. 3). This decrease of the surface area can be explained by a regrouping of the small particles of vermiculite, which will give, consequently, aggregates of greater external order and smaller surface area. Determinations of surface area in samples heated at temperatures higher than 650°C have not been made since at 700°C the crystal structure of vermiculite is destroyed (Fig. 1).

In acid-treated vermiculite the surface area increases greatly with increase in SiO<sub>2</sub>. The "free" SiO<sub>2</sub> produced in the acid treatment seems to be responsible for the increase in surface area. When temperature increases, the collapse of "free" SiO<sub>2</sub> may account for the decrease of surface area in the heated, acid-treated samples (Fig. 3).

The surface area of the acid-treated vermiculite is not much lower than that of the silica gels and silica-alumina gels (Adams and Voge, 1957; Schlaffer, Morgan and Wilson, 1957) whose preparation requires long and careful processes. The fact that a relatively small amount of HCl, acting during a short period of time (i.e. 30 min) on samples of vermiculite, gives a product of a very high surface area is to be considered of technical importance.

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