

## Porous Properties of Silica Prepared by Selective Acid Leaching of Heat-Treated Vermiculite

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### Abstract

The porous properties of silica prepared from heat-treated Transvaal vermiculite (South Africa) by acid leaching were determined. The effect of temperature on the destruction of the crystal structure of the vermiculite was determined, leading to the adoption of heating conditions of 600 °C for 2 h which produce a fully amorphous sample. The heat-treated samples were leached with 2 M hydrochloric acid at 80 °C for 0.5, 2 and 8 h and their porous properties were characterized by measuring their specific surface areas and pore volumes. The highest surface area and pore volume (559 m<sup>2</sup>/g and 0.51 ml/g) was obtained for the sample leached for 8 h. Thermal amorphisation of vermiculite exerts a negative influence on the porous properties of the mineral.

**Keywords:** vermiculite, acid leaching, mesoporous silica, heating

### INTRODUCTION

Selective leaching of clay minerals with acid is a simple technique for the preparation of porous silica for applications such as gas adsorbents, catalyst supports and cracking catalysts. There are many examples of the use of this technique to prepare amorphous silica from metakaolinite [1], montmorillonite [2, 3], sepiolite [4], antigorite [5], phlogopite [6] and vermiculite [7, 8]. To facilitate the acid-leaching process, the clay is first activated by heating to about 550 °C to remove the structural hydroxyl groups. Alternatively, activation can be carried out by high-energy grinding (mechanical activation) which degrades the crystal structure, reduces the particle size, and, as with thermal activation, lowers the coordination number of any Al present. On the other hand, the present authors have shown that vermiculite which has not undergone preliminary calcination or mechanical activation can be acid-

leached to produce silica with a very high surface area >600 m<sup>2</sup>/g and total pore volume of 0.44 ml/g [8]. Vermiculite is known to contain different hydration states according to the number of water layers in the interlaminar spaces between the silicate sheets [9]. Therefore, it might be expected that leaching might be facilitated by removal of this water, producing an X-ray amorphous starting material.

In this study we have investigated the porous properties of silica produced by selective leaching of vermiculite after calcining at a temperature sufficient to render it amorphous.

### EXPERIMENTAL

#### Materials

The raw material was a commercial vermiculite from Transvaal, South Africa (Berumitech Co.), described in detail elsewhere [8]. The loss on ignition of this mineral was 11.16 %, and its

structural formula is  $(\text{Ca}_{0.17}\text{K}_{0.53})(\text{Mg}_{2.73}\text{Fe}_{0.18}\text{Ti}_{0.05})(\text{Si}_{2.89}\text{Al}_{0.84}\text{Fe}_{0.27})\text{O}_{10}(\text{OH})_2$ . Samples were calcined in a laboratory furnace at 400, 600, 800 and 1000 °C for 2 h. The sample heated at 600 °C proved to be X-ray amorphous, and was subjected to leaching with 2 M HCl as follows: 5 g of sample were reacted with 200 ml of acid at 80 °C for 0.5, 2 and 8 h. After leaching, 100 ml of cold distilled water was added and the sample was allowed to cool for 30 min. The suspension was filtered and dried at 110 °C overnight.

### Characterization

XRD measurements were carried out using monochromated  $\text{CuK}\alpha$  radiation with a computer controlled Shimadzu LabX XRD-6100 diffractometer. The chemical compositions were determined by X-ray fluorescence using a Rigaku RIX2000 spectrometer.

Nitrogen gas adsorption-desorption isotherms were measured at 77 K using a Quanta Chrome Autosorb-1 instrument. The sample was outgassed at 180 °C for 6 h in vacuum. The specific surface area ( $S_{\text{BET}}$ ) was calculated by the BET method and the pore size distributions was calculated by the BJH method using the desorption isotherms. The total pore volume was obtained from the maximum amount of nitrogen gas adsorbed at partial pressure  $(P/P_0) = 0.999$ . The infrared spectra were measured with a Shimadzu FTIR 8120 spectrometer using the KBr disc technique. Solid state  $^{29}\text{Si}$  MAS NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and Doty probe spun at 10–12 kHz. The  $^{29}\text{Si}$  spectra were acquired using a 90° pulse of 60 ms and recycle time of 100 s, and were referenced to tetramethylsilane (TMS).

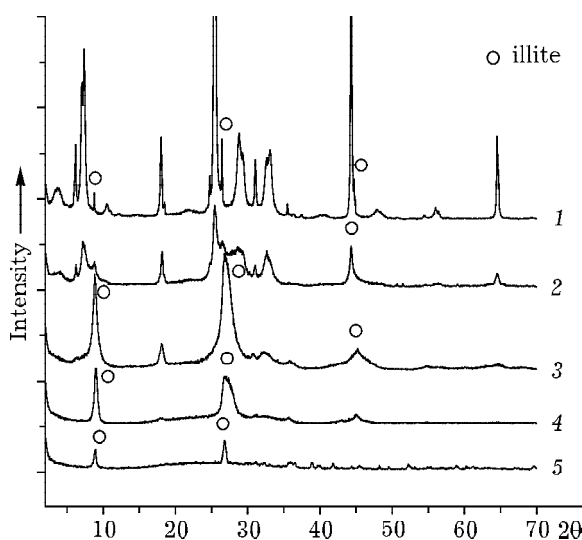


Fig. 1. XRD patterns of raw (1) and calcined (2–5) vermiculite. Calcination temperature, °C: 400 (2), 600 (3), 800 (4), and 1000 (5).

### RESULTS AND DISCUSSION

The XRD patterns of the samples calcined at various temperatures (Fig. 1) show that calcination at 400 °C greatly reduces the crystallinity of the vermiculite and after heating at 600 °C the vermiculite peaks have almost disappeared.

However, the peaks of the illite impurity are still present at 1000 °C, reflecting its greater thermal stability. As previously noted, the leaching of clay minerals occurs more readily when they are in an amorphised state. The amorphous sample prepared by heating at 600 °C was therefore chosen for the subsequent leaching experiments.

Table 1 shows the chemical compositions and porous properties of the raw and leached vermiculites. All the leached samples were heated at 600 °C prior to leaching.

TABLE 1

Chemical composition and porous properties of the raw and amorphised vermiculite

Sample	Surface area, $\text{m}^2/\text{g}$	Pore volume, $\text{ml}/\text{g}$	Chemical composition, mass %						
			$\text{SiO}_2$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{TiO}_2$
Raw	1.4	0.01	43.2	27.4	10.7	8.88	6.22	2.45	1.05
600 °C, 0.5 h	269	0.17	67.51	15.1	6.41	6.01	3.49	0.52	0.96
600 °C, 2 h	547	0.42	93.81	1.98	0.97	1.74	0.66	0.28	0.56
600 °C, 8 h	559	0.51	99.61	0.078	0.09	0.23	–	–	–

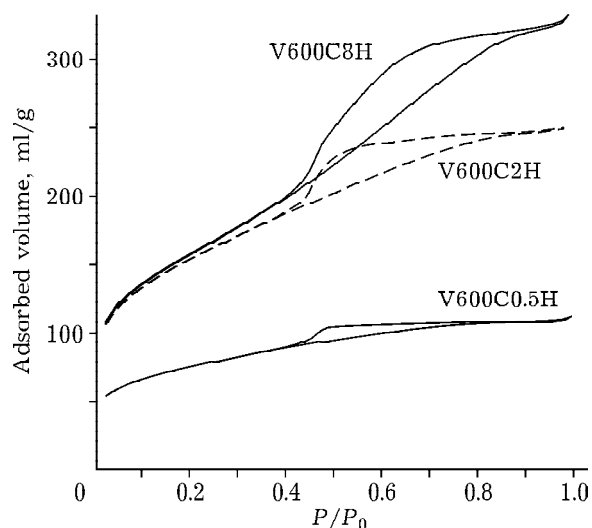


Fig. 2. Nitrogen adsorption isotherms of the calcined and leached sample.

The  $\text{SiO}_2$  content of the samples is increased by leaching, becoming virtually pure  $\text{SiO}_2$  after 8 h treatment. The maximum value of  $S_{\text{BET}}$  was also recorded for this sample, but very little change in the porous properties is found in samples leached for 2–8 h. However, the surface area is smaller than the value previously reported for leached non-amorphised vermiculite [8]. Figure 2 shows the nitrogen adsorption isotherms of the leached samples. The nitrogen adsorption-desorption isotherms of the leached products indicate a type I isotherm, characteristic of microporous materials, but showing hysteresis corresponding to the presence of mesopores [10].

The hysteresis loops of the samples leached for 0.5 and 2 h resemble a type H4 loop, corresponding to narrow slit-like pores. After leaching for 8 h, the shape of the hysteresis loop changes to type H2, corresponding to ink bottle shaped pores. The increase in the number of mesopores is responsible for the increase in pore volume (see Table 1). The pore size distribution (PSD) curves of the leached samples determined from the desorption isotherms (Fig. 3) are also in agreement with the nitrogen adsorption isotherm and pore volume values.

The shape of the PSD in the sample leached for 8 h suggests the formation of mesopores, possibly by condensation of micropores. A sharp peak at 1.8 nm usually appears when nitrogen gas is used as the adsorbate, militating against its use as the sole determinant of the pore size distribution

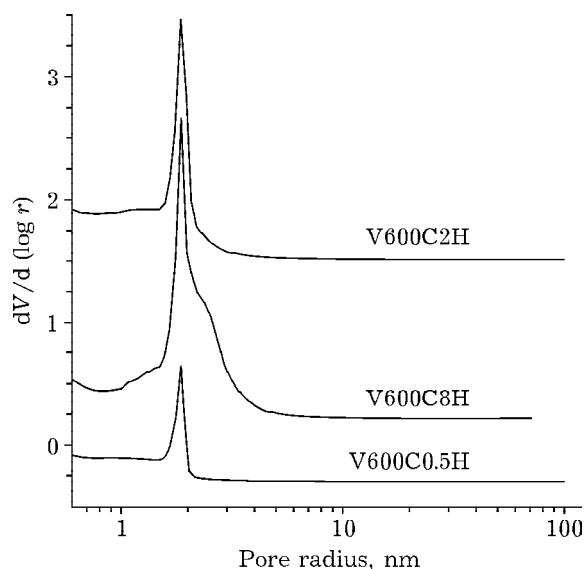


Fig. 3. Desorption pore size distribution curves of the leached samples.

values. The PSD curves indicate that longer leaching increases the number of mesopores.

Figure 4 shows the XRD patterns of the leached samples, indicating a decrease in the intensity of the crystalline peaks with leaching time.

The XRD pattern of the sample leached for 8 h shows only a halo at about  $2\theta = 20\text{--}25^\circ$  arising from amorphous silica. By contrast with untreated vermiculite leached for 2 h, illite peaks are still present. Since such illite peaks were present only in the 30 min leached unheated vermiculite samples [8], it can be concluded that calcining the vermiculite at

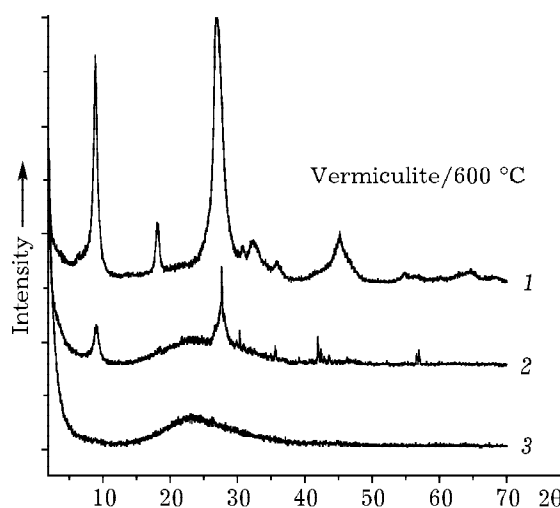


Fig. 4. XRD patterns of the leached products. Leaching time, h: calcined, 600 °C (1), 2 (2), and 4 (3).

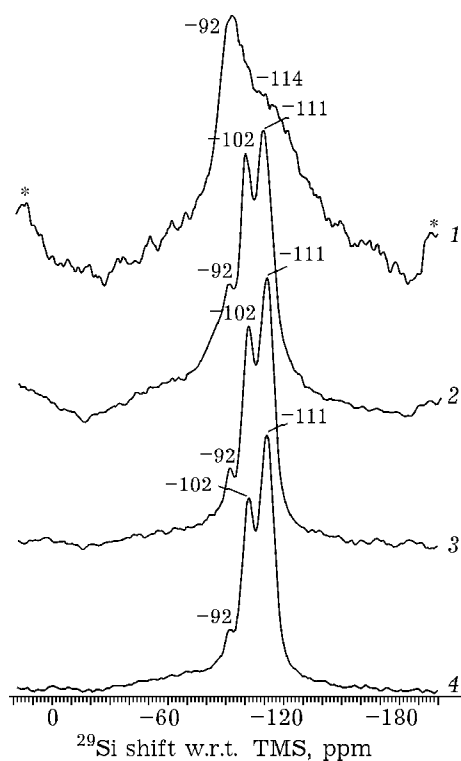


Fig. 5.  $^{29}\text{Si}$  MAS NMR spectra of amorphised vermiculite (1) and leached products (2-4). Leaching time, h: 0.5 (2), 2 (3), and 8 (4).

600 °C reduces the leaching tendency of the illite impurity.

Figure 5 shows the  $^{29}\text{Si}$  MAS NMR spectra of the calcined vermiculite and leached products. The  $^{29}\text{Si}$  MAS NMR spectrum of vermiculite heated at 600 °C shows broad peaks at -92 ppm (fitted area  $\approx 49\%$ ) and -114 ppm (fitted area  $\approx 51\%$ ). The relative peak areas quoted here were obtained by a curve-fitting procedure. The peak at -92 ppm arises from the layered silicate structure and that at -114 ppm is due to an amorphous silica constituent [11].

All the leached samples show three sharp peaks at about -92 ppm (probably related to an impurity phase), -102 ppm (corresponding to the  $\text{Q}^3$  layer structural unit) and -111 ppm (assigned to the  $\text{Q}^4$  framework silica structural unit) [8]. The relative intensity of the impurity phase at -92 ppm decreases sharply with leaching time, from 22% after 30 min to about 4% after 8 h leaching. The relative intensity of the -102 ppm resonance (34-37%) is relatively independent of leaching time, while the intensity of the  $\text{Q}^4$  resonance at -111 ppm progressively increases, from 44% after 30 min to 62% after leaching for 8 h. This observation

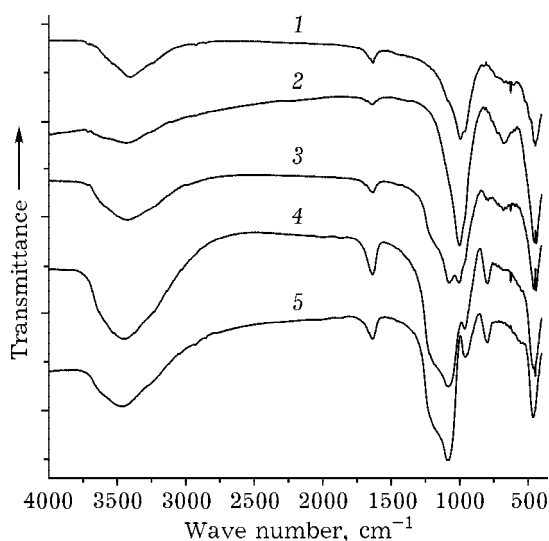


Fig. 6. FTIR spectra of raw and heated vermiculite and the leached products; 1 - raw, 2 - calcined, 600 °C; 3-5 - leached (3 - 0.5 h, 4 - 2 h, 5 - 8 h).

is in agreement with the pore size distribution results and suggests that the porous silica consists of layered regions containing the micropores and framework regions in which mesopores are formed by condensation of the micropores.

The FTIR spectra of the raw, heated and leached samples are shown in Fig. 6.

Calcination reduces the number of water and hydroxyl groups of the raw vermiculite, evidenced by the IR intensity decrease in the  $3500\text{ cm}^{-1}$  region.

The spectra of the samples leached for 2 and 8 h become similar to that of amorphous silica, showing the absorption bands at 1080, 810 and  $460\text{ cm}^{-1}$  arising from the stretching and bending vibrations of  $\text{SiO}_4$  tetrahedral [12]. However, the 30 min leached sample retains absorption bands of the vermiculite structure, suggesting that thermal amorphisation of the vermiculite does not facilitate the formation of porous silica. The spectra of the 2 and 8 h leached samples also show the absorption band at  $950\text{ cm}^{-1}$  assigned to silanol groups in the silica structure [8]. Longer leaching also increases the number of silanol groups in the product, as evidenced by the increase in intensity of this band.

The structure of vermiculite consists of silicate layers separated by double sheets of water molecules carrying exchangeable cations. It is possible that heat treatment may reduce the mobility of these cations and make structure more rigid. Thus, thermal amorphisation prior

to leaching may not be beneficial to the production of silica from vermiculite.

### CONCLUSIONS

Porous silica was prepared by leaching vermiculite thermally amorphised at 600 °C. The maximum specific surface area achieved by leaching was about 550 m<sup>2</sup>/g with a pore volume 0.51 ml/g. The leached sample contains both micro and mesopores. However, it appears that preliminary thermal amorphisation is not beneficial for the formation of porous silica from vermiculite.

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