

MECHANISM OF ACID ACTIVATION OF MAGNESIC PALYGORSKITE

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Abstract—This paper compares the texture of palygorskite after acid leaching with that of the product after extraction silica is removed. These effects were evaluated on the basis of nitrogen adsorption-desorption and mercury penetration porosimetry. Acid leaching at reflux temperature with 2 N HCl resulted in an increase in surface area from 138 to 399 m²/g, due to a partial (~50%) dissolution of the octahedral sheet and the creation of microporosity. This microporosity disappeared if the silica generated by the leaching was removed. The surface area also decreased from 399 to 214 m²/g, and the pore volume decreased from 0.538 to 0.507 cm³/g. The microporosity must therefore have been due to texture development in the generated silica.

Key Words—Acid leaching, Palygorskite, Porosity, Silica, Surface area.

INTRODUCTION

Palygorskite is an aluminum-magnesium silicate (Bradley, 1940) and has a fibrous morphology. Its resulting physico-chemical characteristics (e.g., high surface area and porosity, thermal resistance, chemical inertness) make it a potentially attractive adsorbent. Its adsorption capacity can be increased by modifying its texture by means of chemical and/or thermal treatments, without loss of any other physico-chemical properties (Nathan, 1968; Makki and Flicoteaux, 1976; Corma *et al.*, 1987).

González Martínez (1988) showed that the textural variations of palygorskite subjected to progressive acid leaching are due, on the one hand, to modifications in the undestroyed silicate fractions and, on the other hand, to the silica fragments created during the partial dissolution of the octahedral sheet of the sample. To quantify the contribution of these two effects to the final texture of the samples, a comparative study of the texture before and after silica extraction was carried out.

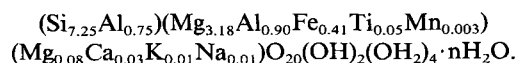
EXPERIMENTAL

The palygorskite used was from Sacramenia-Segovia, Spain, and had the following chemical composition (Martín Pozas *et al.*, 1983):

SiO₂, 53.61; Al₂O₃, 9.29; Fe₂O₃, 3.10; TiO₂, 0.39;
MgO, 13.20; MnO, 0.02; CaO, 0.20; Na₂O, 0.04;
K₂O, 0.75; H₂O, 19.80 wt. %.

Our analyses gave a cation-exchange capacity of 25.8 meq/100 g and a mineralogical composition of 85% palygorskite, 10% quartz, and 5% mica. The structural

formula deduced from these data can be written as follows:



Thus, the mineral was a trioctahedral magnesian palygorskite, having a low cation-exchange capacity. The textural parameters were as follows: fiber length = 0.03–0.30 μm; S_{BET} = 138 m²/g; C_{BET} = 196; pore volume = 0.34 cm³/g (P/P₀ = 0.98).

After mechanical grinding and separation of the ≤0.40-mm-size fraction, acid leaching was carried out by placing the sample in contact with HCl of increasing concentrations (1, 2, 3, 4, and 6 N), with constant stirring and reflux heating for 1 hr. The liquid/solid ratio was 500 cm³/5 g. The slurry was cooled, stirred for another 2 hr, and allowed to settle for 48 hr. It was then filtered, washed Cl⁻ free, and dried at 100°C. Products were denoted P, P-1N, P-2N, etc., where 1N, 2N . . . refer to the concentrations of the HCl solution. Another sample, denoted P-6N-24h, was treated with 6 N HCl for a longer time (24 hr).

The silica produced by acid leaching was dissolved by digestion with warm 5% sodium carbonate solution (Ross and Hendricks, 1945). The extraction operation was repeated until the percentage of extracted silica was negligible. Samples from which silica was extracted are denoted in the same way as the acid-treated products, but with the addition of an asterisk, P*-1N, etc.

Nitrogen isotherms of the samples were obtained in a conventional volumetric adsorption apparatus using N₂ (N-39) as the adsorbent and He (N-45) for the calibrations. Mercury penetration porosimetry measure-

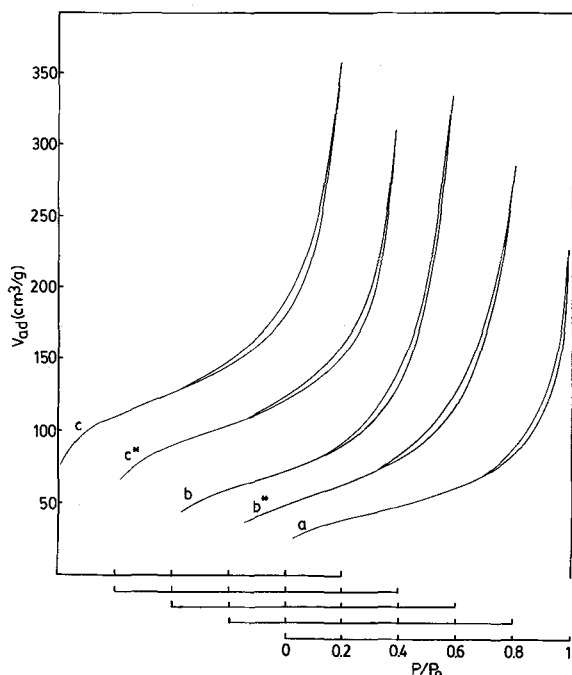


Figure 1. Nitrogen adsorption-desorption isotherms: (a) natural sample, P; (b), (c) acid-treated samples, P-1N and P-2N, respectively; (b*), (c*) after extracted silica, P*-1N and P*-2N, respectively.

ments were carried out in a Micromeritics 9300 apparatus, which reached pressures as high as 30,000 psi, covering the radius interval between 30 and 90,000 Å.

For analysis of the isotherms the criteria of Brockhoff and De Boer (1967) were followed to obtain parameters S_{BET} (specific surface area, calculated from the BET equation), C_{BET} (energetic constant of BET theory), and V_{ad} (pore volume as calculated with the liquid adsorptive at $P/P_0 = 0.98$). The distribution of the pore size in the mesopore range was obtained by the method of Pierce (1953). The microporosity of the samples was analyzed using the t-method of Lippens and De Boer (1965). The curve proposed by Lecloux and Pirard (1979) for values of C_{BET} between 100 and 300 was chosen as the standard.

The volume and distribution of the macropores were obtained from the mercury-intrusion porosimetry data.

RESULTS AND DISCUSSION

The isotherms of some of the samples are shown in Figure 1. Acid leaching did not modify the shape of the isotherms, and only an increase in initial uptake is apparent. The hysteresis loops are a combination of the types H1 and H3 in all the samples (Gregg and Sing, 1982).

The textural parameters resulting from the analysis of these isotherms are given in Table 1. Because of their asymptotic character, the volumes of liquid corresponding to the gas adsorbed at the saturation pressure of $P/P_0 = 0.98$ are taken as pore volumes.

A continuous change in the specific surface was observed with increasing intensity of the acid attack. It reached a maximum, 399 m^2/g , three times that of the original sample after attack with 2 N HCl and decreased smoothly with increasing acid concentration until, at 6 N HCl for 24 hr, a drastic decrease of the specific surface, 197 m^2/g , was observed. C_{BET} changed in a similar way, and values >300 were obtained. For sample P-6N-24h, C_{BET} was similar to that given in the literature for silica (Lecloux and Pirard, 1979). The total volume of adsorbed N_2 , V_{ad} , increased to 0.538 cm^3/g after the acid attack until the concentration reached 2 N HCl and remained constant with more severe acid treatment. The mean pore radius, \bar{R}_p , decreased with the intensity of acid attack, suggesting the appearance of a new pore system having smaller pore size.

The accumulated surface area, S_{acum} , and accumulated pore volume, V_{acum} , determined by the Pierce method are given in Table 2. This method excludes the porosity <20 Å. The values of S_{acum} and V_{acum} increased with acid treatment, but not proportionally to the values of the S_{BET} and V_{ad} , respectively. Thus, the ratio $V_{\text{acum}}/V_{\text{ad}}$ (Table 2) indicates that the acid treatment created a microporous system in the material, which increased continuously with the acid concentration up to 2 N. This microporosity is confirmed by the t-plots of the original and acid-treated samples

Table 1. Textural characteristics from isotherms of acid-treated palygorskite samples before (after) silica extraction.

Sample ¹	P	P-1N	P-2N	P-3N	P-4N	P-6N	P-6N-24h
S_{BET} (m^2/g)	138 (130)	326 (180)	399 (214)	378 (212)	371 —	365 —	197 —
C_{BET}	196 (117)	283 (89)	328 (199)	306 (180)	264 —	270 —	126 —
V_{ad} (cm^3/g)	0.340 (0.330)	0.451 (0.424)	0.538 (0.507)	0.530 (0.510)	0.534 —	0.544 —	0.569 —
\bar{R}_p (Å)	49 (51)	28 (47)	27 (47)	28 (48)	29 —	30 —	58 —

¹ See text for sample treatment designations. S_{BET} = specific surface area; C_{BET} = energetic constant of BET theory; V_{ad} = pore volume as calculated with the liquid adsorptive at $P/P_0 = 0.98$; \bar{R}_p = mean pore radius.

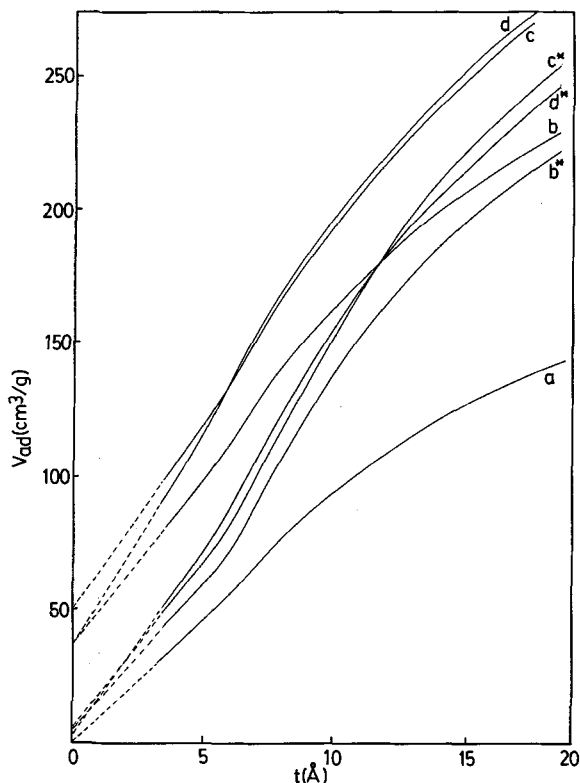


Figure 2. *t*-plots: (a) natural sample, P; (b), (c), (d) acid-treated samples, P-1N, P-2N, and P-3N, respectively; (b*), (c*), (d*) after extracted silica, P*-1N, P*-2N, and P*-3N, respectively.

shown in Figure 2. The plot of natural palygorskite passes through the origin, indicating a lack of microporosity; in contrast, the acid-activated samples have non-zero intercepts, indicative of microporosity. S_t values are shown in Table 2. The mesoporosity, expressed by the values of S_{acum} , increased with the acid concentration to 3 N HCl and remained constant for higher concentrations.

Macroporosity data obtained by mercury penetration for pore areas of 200 to 100,000 Å are listed in

Table 3. Mercury porosimetry values for acid-treated palygorskite samples.

Sample ¹	$V_p (>200 \text{ \AA})$ (cm ³ /g)	$S_{\text{Hg}} (>200 \text{ \AA})$ (m ² /g)	$S_{\text{Hg}} (<200 \text{ \AA})$ (m ² /g)
P	0.430	8	113
P-1N	0.868	18	113
P-2N	0.682	14	110
P-3N	0.479	10	101
P-4N	0.413	14	164
P-6N-24h	0.005	0	73

¹ See text for sample treatment designations. V_p = accumulated pore volume from mercury porosimetry; S_{Hg} = accumulated surface area from mercury porosimetry.

Table 3. No measurable effect of the acid treatment was noted, except for the sample treated with 6 N HCl for 24 hr. Here, all porosity >200 Å disappeared.

Silica losses for the original and acid-treated samples subjected to the silica extraction operation are shown in Table 4. The percentage of silica extracted from the original sample was zero, indicating no attack on the Si of the silicate. The percentages of cations extracted by the acid treatment are also reported in this table; no additional extraction took place by acid concentrations >3 N, and a 24-hr treatment was necessary to produce almost total destruction of the sample.

No noticeable textural changes were produced in the natural sample when it was subjected to the silica-extraction treatment. Thus, the variations observed in the acid-treated samples must have been due to the acid leaching and not to the extraction treatment itself. The N_2 adsorption-desorption isotherms (Figure 1) have the same shape as those measured before extraction of silica, indicating that the texture of the mineral was preserved during this latter treatment. Textural data are shown in Tables 1 and 2.

Sharp reductions of about 50% in S_{BET} and 10% in pore volume values were observed for P*-N samples, compared with P-N samples (Table 1). The ratio $V_{\text{acum}}/V_{\text{ad}}$ was almost 1, and *t*-plots pass through the origin (Figure 2), indicating a loss microporosity due to the acid leaching. From the pore distribution and accu-

Table 2. Pore distribution and accumulation using the Pierce method and *t*-plots of acid-treated palygorskite samples before (after) silica extraction.

Sample ¹	P	P-1N	P-2N	P-3N	P-4N	P-6N	P-6N-24h
S_{acum} (m ² /g)	135 (140)	196 (208)	206 (220)	254 (218)	253 —	255 —	196 —
V_{acum} (cm ³ /g)	0.323 (0.318)	0.378 (0.424)	0.434 (0.487)	0.454 (0.505)	0.461 —	0.474 —	0.546 —
$V_{\text{acum}}/V_{\text{ad}}$	0.95 (0.96)	0.84 (1.00)	0.81 (0.98)	0.86 (0.99)	0.86 —	0.87 —	0.96 —
S_t (m ² /g)	139 (135)	192 (173)	219 (196)	252 (209)	249 —	247 —	199 —

¹ See text for sample treatment designations. S_{acum} = accumulated surface area by the Pierce method; V_{acum} = accumulated pore volume by the Pierce method; S_t = surface area calculated from *t*-plot.

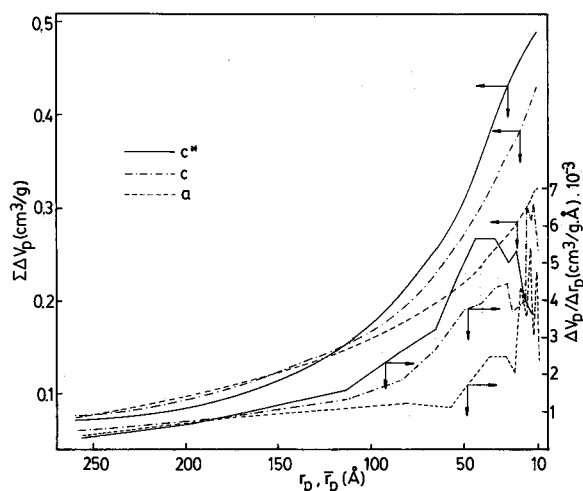


Figure 3. Pore distribution and accumulation. (a) natural sample, P; (c) acid-treated sample, P-2N; (c*) after extracted silica, P*-2N.

mulation curves (Figure 3) a reduction in the amount of small pores for the silica-free sample is apparent. Therefore, the microporous system created by acid leaching disappeared if the silica generated was removed. The microporosity must therefore have been due to texture development in the generated silica. Additionally, the increase of S_{accum} with the severity of the acid treatment, both before and after the silica extraction, must have been due to the development of the mesoporosity produced by the disaggregation of the fiber bundles.

The preceding results suggest the following mechanism for the acid leaching of the sample: The acid attack produced a progressive dissolution of the octahedral sheet, creating microporosity between the tetrahedral silicate sheets. These silicate sheets maintained the skeleton of the mineral and contained silanol groups, generated by the acid hydrolysis reaction (Figure 4). As a result of this process, both surface area and pore volume increased. The generated silica surrounded and protected the undestroyed silicate fractions, which largely retained their fibrous morphology. With increasing acid concentration and reaction time,

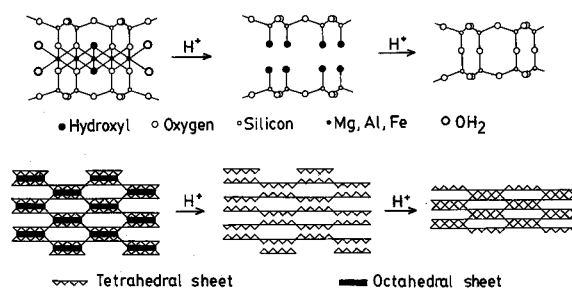


Figure 4. Proposed mechanism of acid leaching of magnesian palygorskite.

the condensation of the silanol groups increased and, thus, the microporosity and the surface area decreased.

If the sample was treated with 6 N HCl for 24 hr, the palygorskite was totally destroyed. The isotherm of the P-6N-24h sample had the same shape as the original fibrous material, confirming the proposed mechanism.

CONCLUSIONS

A product having a surface area more than three times that of the original sample was prepared by an acid treatment of natural magnesian palygorskite. Initially, fibrous bundles disaggregated, which increased mesoporosity. As the acid attack progressed, the octahedral sheet increasingly dissolved, creating microporosity between the tetrahedral silicate sheets. In a third stage, increasing acid concentration and/or reaction time condensed silanol groups, and the microporosity decreased. The microporosity disappeared from the activated samples after silica extraction.

The fibrous morphology of the samples was preserved throughout the acid treatment, both before and after silica extraction.

REFERENCES

- Bradley, W. F. (1940) The structural scheme of attapulgite: *Amer. Mineral.* **25**, 405–410.
 Broekhoff, J. C. P. and De Boer, J. H. (1967) Studies on pore systems in catalysts: *J. Cat.* **9**, 8–14.
 Corma, A., Mifsud, A., and Sanz, E. (1987) Influence of the chemical composition and textural characteristic of paly-

Table 4. Weight percentage of extracted cations of acid-treated palygorskite samples.

Sample ¹	P	P-1N	P-2N	P-3N	P-4N	P-6N	P-6N-24h
SiO ₂		0.3	0.3	0.1	0.1	0.0	0.0
Al ₂ O ₃		31.7	51.3	58.6	59.4	60.0	73.4
Fe ₂ O ₃		30.4	48.9	58.1	61.8	63.1	80.3
MgO		34.5	52.7	57.2	57.8	59.2	89.7
SiO ₂ (extracted) ²	0	27	40	43	43	42	87

¹ See text for sample treatment designations. Cations dissolved in the liquid phase during acid leaching.

² Silica remaining in the solid phase after acid leaching and which was then extracted with Na₂CO₃ (see text).

- gorskite on the acid leaching of octahedral cations: *Clay Miner.* **22**, 225–232.
- González Martínez, F. (1988) Palygorskitas españolas. Aplicabilidad en adsorción y catálisis: Ph.D. thesis, University of Oviedo, Oviedo, Spain, 250 pp.
- Gregg, S. J. and Sing, K. S. W. (1982) *Adsorption Surface Area and Porosity*: Academic Press, London, 303 pp.
- Lecloux, A. and Pirard, J. P. (1979) The importance of standard isotherms in the analysis of adsorption isotherms for determining the porous texture of solids: *J. Colloid Interface Sci.* **70**, 265–281.
- Lippens, B. C. and De Boer, J. H. (1965) Studies on pore systems in catalysts. V. The t method: *J. Cat.* **4**, 319–323.
- Makki, M. B. and Flicoteaux, C. (1976) Activation des argiles: *Bull. Soc. Chim. Fr.* **1**, 15–22.
- Martín Pozas, J. M., Martín-Vivaldi, J., and Sanchez Camazano, M. (1983) El yacimiento de Sepiolita-Paligorskita de Sacramenia, Segovia: *Bol. Geol. Min.* **94-2**, 113–120.
- Nathan, Y. (1968) Dissolution of palygorskite by hydrochloric acid: *Israel J. Chem.* **6**, 275–283.
- Pierce, C. (1953) Computation of pore sizes from physical adsorption data: *J. Phys. Chem.* **57**, 149–152.
- Ross, C. S. and Hendricks, S. B. (1945) Minerals of the montmorillonite group; their origin and relation to soils and clays: *U.S. Geol. Surv. Prof. Pap.* **205-B**, 23–79.

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