

STRUCTURAL AND TEXTURAL MODIFICATIONS OF Palygorskite AND Sepiolite under Acid Treatment

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Abstract—Sepiolite from Mara (Zaragoza, Spain) and palygorskite from Attapulugus (Georgia, USA) were activated by treatment at different concentrations with solutions of boiling HCl under reflux conditions. The natural and treated solids were characterized by mineralogical, chemical and textural analyses.

Acid attack resulted in a progressive dissolution of the octahedral layer of these silicates. Silica contents increased and octahedral cations (Al, Mg and Fe) decreased with the intensity of the acid attack. In both cases, fibrous free silica was obtained.

The sepiolite was destroyed more rapidly than palygorskite under the conditions used because of its magnesian composition and the larger size of its structural microchannels. The maximum increase in specific surface area was obtained for sepiolite at 3 N and for palygorskite at 9 N. Cleaning and disaggregation of the particles and the increase in the number of micropores were responsible for this increase in specific surface area.

Key Words—Acid Attack, Activation of Clays, Fibrous Silica, Palygorskite, Sepiolite.

INTRODUCTION

Sepiolite and palygorskite form the fibrous clay minerals group. Both minerals have microchannels in their structure and different types of molecules of water: absorbed and zeolitic water, bonded and hydroxyl groups. The theoretical formula of sepiolite is $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$ and that of palygorskite is $\text{Si}_8\text{O}_{20}\text{Al}_2\text{Mg}_2(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$.

The adsorptive and catalytic behavior of many solids is strongly influenced by the extent and nature of the external surface. Appropriate acid treatments of clay minerals modify their surface area and/or the number of acid sites by disaggregation of clay particles, elimination of mineral impurities, removal of metal-exchange cations and proton exchange. Both natural silicates and the solids obtained after their acid activation are used as adsorbents, decontaminants, deodorants and catalysts or catalyst supports (Campelo et al. 1987; Corma and Pérez-Pariente 1987; Herrero et al. 1991; Sugiura et al. 1991).

The behavior of sepiolite when treated with acid solutions has been studied from different points of view (Bonilla et al. 1981; Corma et al. 1986; Cetisli and Gedikbey 1990; Vicente et al. 1994). However, the literature contains few references to acid treatment of palygorskite as compared with other clays (Singer 1976; Corma et al. 1987; González et al. 1989; Corma et al. 1990; Suárez et al. 1995). One paper has reported the treatment of sepiolite and palygorskite under the same experimental conditions, but only a chemical study was performed (Abdul-Latif and Weaver 1969). These authors indicate that sepiolite is less stable under chemical weathering than palygorskite. They propose a continuous reaction model, which would be

similar over the whole of the surface of the solids because of the solids' very porous structure, but would change from one point to another. Corma et al. (1986) found difficulties when considering proton diffusion to the pores of palygorskite. These authors reported that the removal of Mg(II) and Fe(II) is easier than that of Al(III), the latter occupying the center of the ribbons and hence being more difficult to remove. This is in agreement with Güven (1992), who found that the edges of the octahedral ribbons are occupied exclusively by Mg.

Here, the progress of acid attack of palygorskite and sepiolite by hydrochloric acid at different concentrations is studied together with the textural modifications occurring in the solids obtained.

EXPERIMENTAL

Palygorskite from the Engelhard Minerals & Chemical Corporation Mine supplied by Minerals Unlimited (Georgia) (sample called PA), and sepiolite from Mara (Zaragoza, Spain) supplied by Mineralogía y Tecnología de Arcillas S.A. (MYTA) (sample SE) were used in this work. The mineralogical study was performed by X-ray diffraction (XRD) of powdered samples using the original sample and the $<2 \mu\text{m}$ fraction obtained by aqueous decantation and studied as oriented aggregates under ambient conditions, after solvation with ethylene glycol and heating to 550 °C. A Siemens D-500 XRD diffractometer with a Cu anticathode and graphite monochromator was employed. The semi-quantification of the samples was performed using the "method of reflecting strengths or reference intensities" by taking into account the area of the diagnostic peaks of the different minerals and their reflecting

strength. The reflecting strengths used are those of Martín-Pozas (1975) and Galán and Espinosa (1978).

Natural samples were subjected to progressive acid treatment with hydrochloric acid; the only variable was the concentration of acid used. A 5-g sample of ground clay was treated under mechanical stirring with 50 mL of 0.5, 1, 3, 5, 7 and 9 *N* HCl solutions at boiling temperature under reflux for 1 h. After this, heating was stopped and the sample was maintained for 4 h in acid solution at room temperature. After the treatments, the resulting solids were washed until no chloride anions could be detected, dried at 50 °C and kept over H₂SO₄ solutions.

Elemental analyses were carried out by plasma emission spectroscopy, using a Perkin-Elmer Model plasma II emission spectrometer. In their preparation for analysis, solids were digested in a mixture of nitric and hydrofluoric acids.

Fourier transform infrared (FTIR) spectra were obtained in the 4000–500 cm⁻¹ region on a Perkin-Elmer 1730 FTIR spectrometer using the KBr pellet technique.

Nitrogen adsorption-desorption isotherms at 77 K of the original and treated samples were obtained with a Micromeritics ASAP 2000 analyzer after outgassing the samples at 110 °C for 8 h with a residual pressure of 10 mm Hg.

Micromorphologic analyses were carried out on a Zeiss TM 902 transmission electron microscope with an acceleration voltage of 80 kV on a sample dispersed in water and deposited on a grid.

RESULTS AND DISCUSSION

Mineralogy

The mineralogical compositions of the raw samples were determined from X-ray diffractograms (Figure 1). The following mineral phases were identified: palygorskite (86%), quartz (3%), smectite (7%), illite (1%) and feldspars (3%) for the PA sample and sepiolite (70%), illite (12%), quartz (10%), dolomite (7%) and feldspars (1%) for the SE sample.

The powder XRD patterns for the PA and SE samples and the series treated with HCl are given in Figure 1. When the concentration of HCl was increased, the intensity of the peaks of the fibrous clays decreased. In the PA series, the intensity of characteristic peaks at 10.4, 6.5, and 5.3 Å decreased progressively and disappeared when the sample was treated with 9 *N* HCl. At the same time, an increase in insoluble impurities in the sample was observed, and the main reflections corresponding to quartz and feldspar were found to become more intense as the attack intensity progressed. In the PA9*N* sample, a small peak was seen at 10 Å, corresponding to micas, and hence this mineral seemed to be resistant to the treatment.

The peaks corresponding to sepiolite disappeared in the SE3*N* sample and only reflections corresponding to micas, quartz and feldspars were observed when the severity of the attack was increased. Concomitantly, as shown by the appearance of an increase in the broad characteristic band of free silica situated between $2\theta = 16\text{--}30^\circ$, the amount of this compound increased with the acid concentration in both series of samples.

Chemical Analyses

The chemical compositions of the natural clays and solids resulting from the treatment are given in Table 1. It has not been possible to calculate the structural formula of sepiolite and palygorskite due to the impurities present in the sample.

The solids obtained after acid treatment showed a progressive decrease in Al, Mg and Fe (octahedral cations) and an enrichment in SiO₂ coming from the tetrahedral layer of palygorskite and sepiolite. The enrichment in SiO₂ in samples treated is a relative increase due to the remobilization of the octahedral cations. The octahedral cations pass into the solution while silica, owing to its insolubility in acid solution, remains in the solids obtained.

In the PA series of samples, the comparison between the samples treated is carried out with the natural sample. When palygorskite was treated with 7 *N* HCl, 83% of the Al₂O₃, 94% of the Fe₂O₃ and 91% of the MgO were removed from the palygorskite sample. When 9 *N* HCl was used, 15% of Al₂O₃ remained in the solid obtained and a third of the K₂O was dissolved by partial alteration of micas and feldspar (which remained as partially insoluble impurities). In the PA9*N* sample, 96.31% of the SiO₂ was found. This silica comes from the tetrahedral layer of the palygorskite, mainly as amorphous silica and from the impurities of insoluble silicates (quartz, feldspar and mica) that are also concentrated. Dissolution of Ca was also observed, Ca being an exchangeable cation. These results are in accordance with those of Suárez et al. (1995), obtained treating Bercimuel palygorskite. This palygorskite is completely destroyed at 7 *N* HCl, a lower concentration than for the PA sample, due to the higher Fe content of the former.

Chemical analysis of the SE sample revealed a high content of impurities, specially dolomite. This mineral is responsible for the large amounts of CaO in the sample. CaO is completely removed with weak acid attack. As with the palygorskite series, dissolution of the octahedral cations and the formation of amorphous silica can be observed in the evolution in the contents of the different oxides. The most weakly treated sample, SE0.5*N*, is used to compare with treated samples because it has no dolomite (which contributes Mg and Ca that are dissolved by the weakest acid attack). The percentages of Al₂O₃, Fe₂O₃ and MgO decreased (with respect to the SE0.5*N* sample). With more intense at-

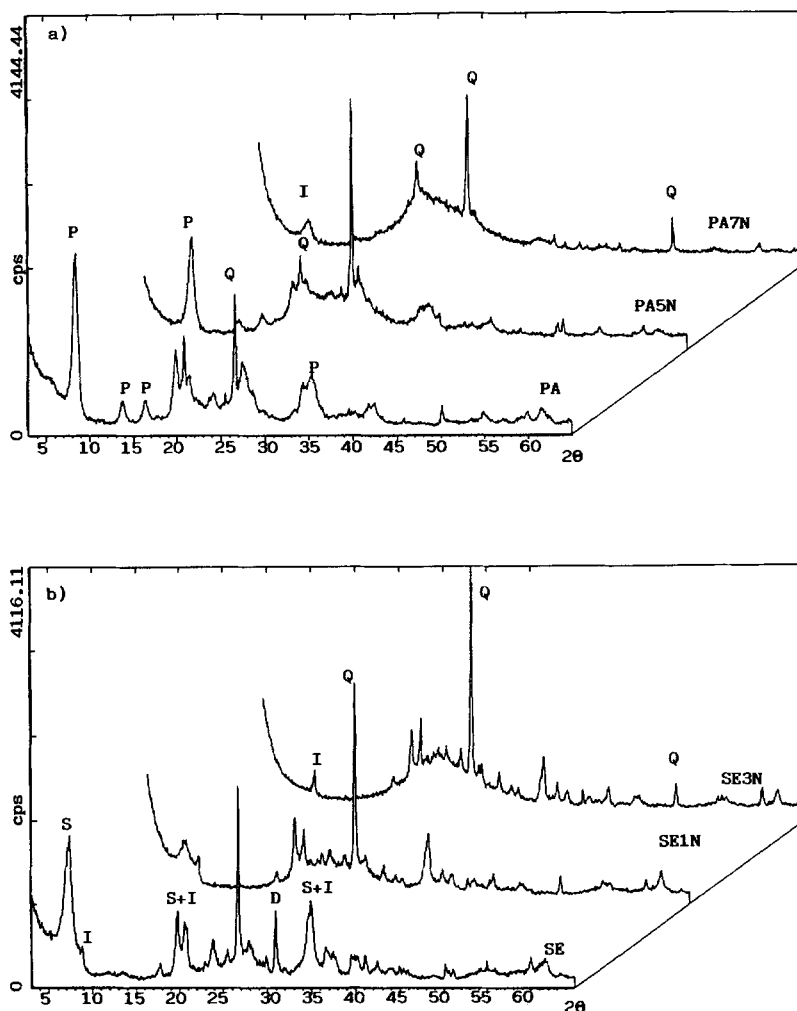


Figure 1. X-ray diffractograms for PA and SE samples: a) nontreated (PA), treated with 5 N HCl (PA5N) and treated with 9 N HCl (PA9N) and b) nontreated (SE), treated with 1 N HCl (SE1N) and treated with 3 N HCl (SE3N).

Table 1. Total chemical analyses of the natural and treated samples.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
PA	69.01	12.37	3.90	0.02	10.43	1.81	0.06	0.98	0.47	0.94
PA1N	76.60	9.96	3.25	0.01	8.46	0.06	0.06	0.84	0.65	0.09
PA3N	85.53	6.13	1.40	0.01	5.46	0.04	0.06	0.67	0.65	0.05
PA5N	90.33	4.27	0.77	—	3.45	0.02	0.06	0.55	0.52	0.02
PA7N	95.43	2.11	0.23	—	0.97	0.04	0.08	0.60	0.49	0.05
PA9N	96.31	1.83	0.15	—	0.41	0.05	0.09	0.66	0.47	0.03
SE	69.03	8.58	3.06	0.02	13.45	2.57	0.14	2.73	0.33	0.07
SE0.5N	70.47	10.89	4.09	0.02	10.94	0.16	0.17	2.91	0.27	0.06
SE1N	79.94	9.62	2.99	0.01	3.75	0.07	0.12	2.89	0.51	0.08
SE3N	87.58	7.96	0.63	—	0.44	0.04	0.11	2.62	0.58	0.01
SE5N	90.63	5.94	0.43	—	0.27	0.02	0.13	2.01	0.55	—
SE7N	91.79	5.34	0.37	—	0.23	0.02	0.08	1.72	0.41	0.01

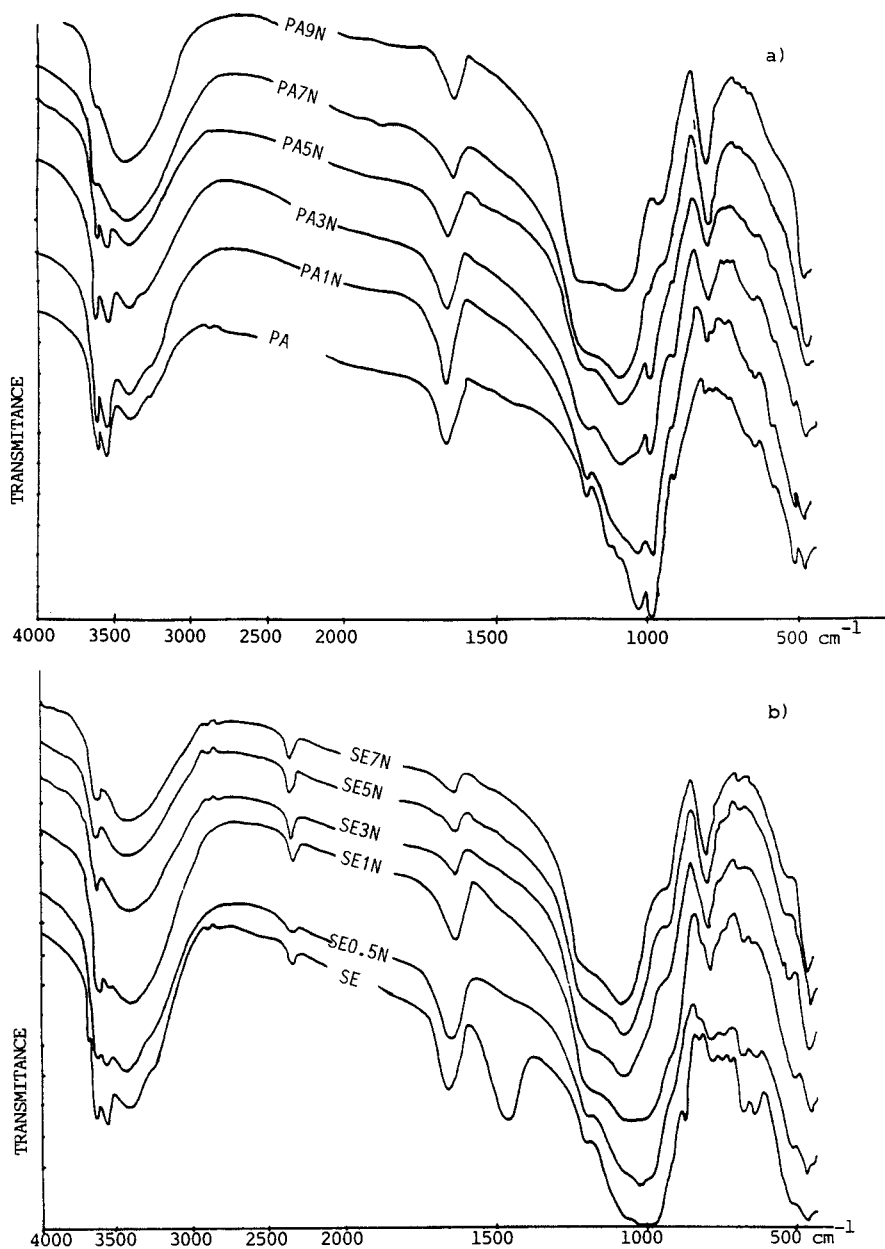


Figure 2. FTIR spectra of natural and acid-treated samples: a) PA series and b) SE series.

tack, 50% of Al_2O_3 and 60% of K_2O remained, due to the persistence of micas and feldspars as insoluble impurities. Mg and Fe were rapidly dissolved, and 95% of Mg and 85% of Fe were removed when a 3-N HCl solution was employed. The insoluble silica was accumulated in the solid obtained. Insoluble impurities (illite, quartz and feldspars) were more abundant in the SE7N sample; 5.34% of Al_2O_3 and 1.72% of K_2O remained even when the sepiolite was destroyed by complete dissolution of this octahedral layer. With this same concentration, Corma et al. (1986) removed 54%

of the Mg because the temperature used in the treatment of sepiolite was lower.

IR Spectroscopy

Study of the acid-treated solids by FTIR spectroscopy confirmed the dissolution of the octahedral layer and the generation of free silica when the sepiolite and palygorskite structures were destroyed by acid treatment (Figure 2).

In the high-wavenumber region, the bands assigned in the natural samples to (Me-Me)-OH (3700–3500

cm^{-1}) and to adsorbed water molecules ($3500\text{--}3200\text{ cm}^{-1}$) decreased with the intensity of acid attack. These bands appeared at 3688, 3620, 3565 and 3407 cm^{-1} in the SE sample and at 3616, 3549 and 3397 cm^{-1} in the PA sample. In the PA9N sample, this effect disappeared and only a broad band centered at 3420 cm^{-1} , originated by adsorbed water molecules, was observed. By contrast, in the most intensely treated sepiolite, 2 bands were observed: the same at 3420 cm^{-1} and another at 3628 cm^{-1} due to (Al-Al)-OH vibrations in the micas with remains as impurities.

A band at 1660 cm^{-1} appeared in 2 series of samples and decreased with the treatment. This band was due to the bending vibration mode of water. Between 1200 and 400 cm^{-1} , many bands characteristic of sepiolite and palygorskite were observed in the natural samples. These bands, corresponding to Si-O and Metal-O stretching vibration bonds, disappeared due to dissolution of the octahedral layer as acid treatment progressed. In the more strongly treated samples, bands characteristic of free silica at 1200, 1090, 790 and 470 cm^{-1} were observed. These results are in agreement with Mendelovici (1973), who also studied a palygorskite from Georgia by acid treatment with 5 N HCl. In the SE sample, the band at 1450 cm^{-1} was due to dolomite impurities.

Electron Microscopy

Study of the morphology of palygorskite and sepiolite and measurement of the size of their fibers were carried out with electron microscopy. In the natural samples, most fibers became grouped to form bundles and parallel aggregates. The size of the fiber aggregates ranged from $2\text{--}3.7\text{ }\mu\text{m}$ for palygorskite to about $0.5\text{ }\mu\text{m}$ for sepiolite. No isolated fibers were observed.

No significant morphological differences were observed in activated samples (Figure 3), even in the most activated samples, 96% of whose content was silica. The silica obtained after acid treatment maintained the fibrous morphology of natural silicates, which proves that the attack was produced throughout the structural microchannels and not by "out to in" dissolution of the particles, in accord with the continuous reaction model proposed by Abdul-Latif and Weaver (1969). Proton diffusion to the pores of sepiolite and palygorskite is possible. A persistence of the morphology of the silica obtained by acid treatment of fibrous silicates was found by Suárez et al. (1995) for palygorskite and González et al. (1984) and Vicente et al. (1994) for sepiolite.

Nitrogen Adsorption

The nitrogen adsorption-desorption isotherms at 77 K for the different natural and activated solids are similar to the type II isotherms of the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al. 1985). No significant differences were ob-

served in the nitrogen adsorption-desorption isotherms of the treated samples with respect to those of the natural samples. The fact that the shape of the isotherms does not vary implies that the adsorption process has not varied and that there will only be quantitative differences in porosity. However, there have been no great differences in the type of porosity, in accord with the results obtained by electron microscopy.

The specific surface areas of these solids were calculated with the Brunauer-Emmett-Teller (BET) method and the results are given in Table 2. In both series, acid treatment initially produced an increase in the specific surface area, S_{BET} (Table 2), the maximum being found in the PA5N and the SE1N samples. The value of the surface area increased from $208\text{ m}^2\text{ g}^{-1}$ for the PA sample of $265\text{ m}^2\text{ g}^{-1}$ for PA5N and from $213\text{ m}^2\text{ g}^{-1}$ for the SE sample to $340\text{ m}^2\text{ g}^{-1}$ for SE1N. More intense conditions of attack produced a decrease to $230\text{ m}^2\text{ g}^{-1}$ for PA9N and $153\text{ m}^2\text{ g}^{-1}$ for SE7N. Several authors have also found a decrease in the BET surface area under more intense conditions of attack with respect to the maximum reached (Corma et al. 1986; González et al. 1989; Vicente et al. 1994; Suárez et al. 1995).

The porosity of the solids was studied by numerical analyses of their nitrogen adsorption-desorption isotherms. A computer program (Rives 1991) was used to analyze these isotherms. Microporosity ($<10\text{ }\text{Å}$ of diameter) is studied by the t -plot and mesoporosity ($10\text{--}300\text{ }\text{Å}$ of diameter) is studied by the Pierce method (Pierce 1953). In the t -plots of the natural samples, no important degree in microporosity is seen (extrapolation of the corresponding t -plot was very close to zero). An increase in microporosity (Table 2) due to partial dissolution of the octahedral layer was seen in the less intensely treated samples. Mesopores of between 30 and $50\text{ }\text{Å}$ appeared and increased in number with the increase in the concentration of acid (3 N HCl). This slight modification of the micro- and mesoporosities together with particle disaggregation, surface cleaning and free silica generation contribute to the increase in surface area. In the more intensely treated samples, a decrease in microporosity due to destruction of the microchannels in the crystalline structure was observed.

CONCLUSIONS

A progressive destruction of the structures of palygorskite and sepiolite is seen parallel to the increase in acid concentration. This decay in the structures of the fibrous clays is due to the dissolution of the octahedral layer. Amorphous silica coming from the tetrahedral layer of fibrous silicates is generated. All the techniques used show that the more intense the acid attack, the more affected the structure of the palygorskite and sepiolite. Mild acid attack is sufficient to remove most of the octahedral cations in the sepiolite,

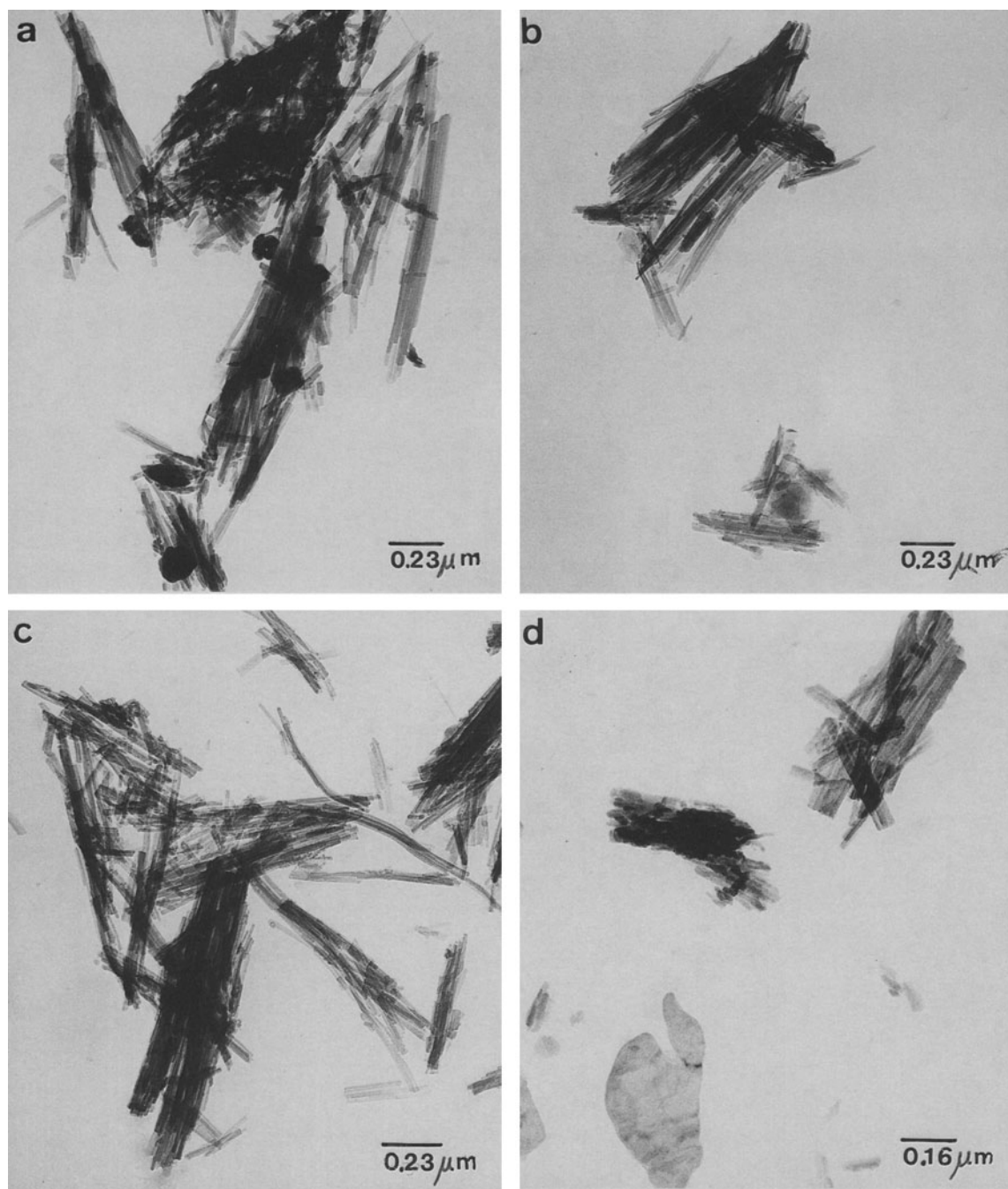


Figure 3. Microphotographs of samples: a) SE, b) PA, c) SE7N and d) PA9N.

but not in the palygorskite: after treatment with 9 and 3 N HCl, palygorskite and sepiolite, respectively, were completely destroyed.

Sepiolite is more easily destroyed than palygorskite because of its magnesian composition and the layer size of its structural microchannels. In spite of the partial dissolution of the samples, the fibrous morphology is

preserved; acid penetrates into the channels all over the surface.

An important increase in the surface area of the solids obtained is observed. The slight modification in the micro- and mesoporosities together with particle disaggregation, surface cleaning and free silica generation contribute to the increase in surface area. This

Table 2. Parameters deduced from isotherms of nitrogen adsorption-desorption of natural and treated samples. S_{BET} = specific surface area (m^2/g), S_{sp} = micropore surface area (m^2/g).

Sample	S_{BET} m^2/g	S_{sp} m^2/g
PA	208	42
PA1N	261	20
PA3N	264	80
PA5N	265	23
PA7N	263	—
PA9N	230	—
SE	213	33
SE0.5N	294	60
SE1N	340	72
SE3N	293	—
SE5N	150	—
SE7N	153	—

increase is 27% for palygorskite and 60% for sepiolite. The greatest surface area is observed when the octahedral layer is partially destroyed and microporosity is generated. The most intense attacks completely dissolve the fibrous clays and generate amorphous silica, whose specific surface area is larger than that of the natural samples.

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