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CHARACTERIZATION AND ACID ACTIVATION OF PORTUGUESE SPECIAL CLAYS

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ABSTRACT

Portuguese smectites and palygorskites were treated with 1.0, 5.0, 7.0 and 9.0 N solutions of HCl for one hour under reflux. The solids obtained were characterised by their loss weight evaluation, X-ray diffraction, chemical analyses, surface area, texture and TEM. The results indicate that the mechanism of the activation shows a point of inflection at a certain acid concentration, which is of 7.0 N for palygorskite rich samples, and 5.0 N for smectite rich samples. We never assist to a complete destruction of the clay minerals structure. The properties of high acid attacked clays are very similar to those of the original material or the lower attacked one, what can be interpreted as «passivation» of the clay, resulting from the silica created in acid activation, that coats the silicate impeding further attacks.

Keywords: Acid activation; HCl; palygorskite; smectite; mineralogy; surface area.

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INTRODUCTION

Chemical and mineralogical characterization of sediments from Portuguese Tertiary basins (Dias, 1998) allowed the selection of some deposits rich in special clays, namely palygorskite and/or smectite. The most clayey deposits were also characterized in a textural and technological point of view (Prates & Dias, 1993-1997; Dias & Prates, 1995), with very compatible results within an industrial point of view, even with no commercial viability, as the samples with more interest belong to thinner deposits, lens or are in habitation areas.

Nevertheless considering the richness of some layers in special clays and its technological properties, like water and oil absorption, cation exchange capacity (CEC) and surface area (Dias, 1998), a more detailed study was done to them, which also included the evaluation of physico-chemical alterations that might occur to Portuguese smectites and palygorskites after treatment with progressive acid solutions.

Acid treatment of clay minerals, namely fibrous clays (Suárez 1992, Suárez *et al*, 1995, Vicente Rodriguez *et al*, 1994a and 1995a, Myriam *et al*, 1998), smectites (Vicente Rodriguez *et al*, 1994b, Prieto *et al*, 1999, Suárez Barrios *et al*, 2001) and kaolinite (Belver *et al*, 2002), is widely applied in order to optimize their physico-chemical behaviour, aiming better industrial properties. Xianzhen & Chuyi (1990) have done acid treatments with sepiolite, concluding that the silica obtained could be competetive in different industrial ways, with that obtained by precipitation. The acid treatment of clay minerals is usually referred to as «acid activation» because it increases the specific surface area and the number of active sites of the solids. This treatment modifies the surfaces of clays by disaggregations of particles, possible elimination of mineral impurities and removal of metal-exchange cations. The common commercial use of acid-treated bentonite is bleaching or decolourations of oils (Srasra *et al*, 1989) and in general in the fields of adsorption and catalysis (Fahn & Fenderl, 1983, Mokaya & Jones, 1995).

There are several studies showing that acid and thermal treatments of some clay minerals increase catalytic and adsorbent activities, however stronger treatments may introduce an opposite behaviour, decreasing this activity (Bonilla *et al*, 1981; Gonzalez *et al*, 1989; Pesquera *et al*, 1992; Dias, 1998).

All these kind of improvement in the technological capacities of special clays are obviously linked to their structure / morphology. Palygorskite is an aluminium-magnesium silicate and has a fibrous morphology, the resulting physico-chemical properties, namely sorptive and rheological properties, make it a potentially adsorbent and useful in many industrial fields (Alvarez, 1984). Smectite is a hydrated aluminium silicate with a lamellar morphology, and so, water and other polar molecules can easily penetrate into the smectite structure. As a consequence of these, smectites have huge plastic and colloidal properties with physical properties variations according with the nature of the exchangeable cations that neutralise the structure, and compositional variations that may occur in octahedral positions.

MATERIALS AND METHODOLOGY

Studies developed so far on Portuguese fibrous clays, show that almost in all the occurrences, palygorskite appears associated with smectite, and sometimes with illite (Carvalho, 1964, 1968; Cunha, 1992; Dias, 1993; Dias e Prates, 1994; Dias *et al*, 1997). Sepiolite associated with palygorskite was also reported in the Lower Jurassic and Lower Tertiary of Aveiro basin (Rocha & Gomes, 1992), being palygorskite mainly associated with silicifications and sepiolite with carbonates.

In this study five samples were chosen, four belonging to the Portuguese Tertiary Tagus basin, in Rio Maior and Castelo Branco regions, with different proportions of palygorskite, smectite and illite. The other one results from the eruptive rocks alteration, near Benavila (Alentejo, Portugal), and in its clay fraction is a pure smectite (Tables 1 and 2).

Table 1. Total mineralogy (%)

Sample	Phyllosilicates	Goethite	Quartz	Feldspars	Calcite	Dolomite
A	64	4	25	6		traces
B	39		traces		58	
C	38	traces	53	8	traces	
D	23		24	5	47	traces
E	70		traces	traces	25	

Table 2. Clay fraction (< 2 μm) mineralogy (%)

Sample	Palygorskite	Chlorite	Illite	Smectite	Kaolinite
A	100				
B	42		33	21	4
C	26	traces	26	43	traces
D	25		15	56	traces
E				100	

Only clay fraction (< 2 μm) was submitted to treatment with progressive acid solutions. This fraction was obtained by aqueous decantation and then air dried and pulverized in agate mortar. Six grams of pulverized clay were treated under mechanical stirring with 200 ml of 1.0, 5.0, 7.0 and 9.0 N solutions of HCl, for one hour under reflux, plus one more hour without heating, and fifteen minutes in ambient temperature water-bath. The solids obtained were washed until no chloride anions could be detected, dried at 60°C and pulverized.

The X-ray diffractograms were obtained on a Siemens D-500 diffractometer, using CuK_a radiation, monochromatized with a graphite filter.

Chemical analyses were carried out by atomic absorption, using a Varian equipment, model Spectra A-30.

The morphological analyses were obtained on Phillips and Jeol-Jem200ex transmission electron microscopes.

The specific surface area of the clay samples was determined by nitrogen adsorption-desorption isotherms at 77° K in a conventional precise high vacuum equipment, Micromeritics ASAP 2000. The samples were outgassed at 100°C for 8 hours, with a turbomolecular, at a pressure of 10^{-6} mm Hg. The BET method was used for the corresponding calculations, and also the porosity was studied through the t-curves.

RESULTS AND DISCUSSION

Loss weight evaluation

The loss weight obtained after treatment with progressive acid solutions varies from 25 % to 48 %, and it is higher from the natural sample to the treated one at 1.0 N and 5.0 N. Generally for 7.0 N and 9.0 N the loss weight proportion becomes stable or even slightly decreases, when compared with lower concentrations. It's also important to enhance that loss weight raise as smectite proportion in the clay sample increases and palygorskite decreases.

X-ray diffraction

Original samples show mainly quartz or calcite as mineralogical impurities, with traces of feldspars, goethite or dolomite (Table 1). Their clay fraction vary in special clays proportion, and discarding two monomineralic samples (sample A – palygorskite and sample E – smectite), the others show as accessory clay minerals illite and traces of kaolinite or chlorite (Table 2).

The X-ray diffractograms of natural and treated clay samples point to a decrease of the intensity of the main peak, from the natural to the 1.0 N and 5.0 N, however, to 7.0 N and to 9.0 N, that difference doesn't occur. So, the (001) reflection intensities decrease and become broader with the increasing of the acid concentration, indicating a growing delamellation of the original particles, and at higher concentration treatments, the X-ray diffractograms are similar to the natural ones. Figures 1 and 2 show respectively examples of the X-ray difractograms from palygorskite A and smectite E.

Considering XRD results, generally, the palygorskite rich samples present a greater resistance to the acid attack than smectite samples, although the formation of an amorphous silica phase can be deduced from the appearance of a broad band (between 2 θ = 16° - 30°, with a maximum near 21°). This amorphous silica is produced by the destruction of the silicates of the clay mineral structure (especially in the smectite rich samples – Fig. 2), and remains present due to its insolubility in acid solutions. The palygorskite dissolution doesn't seem to be related with a significant loose of the mineral crystallinity with the thickness at half height remaining almost constant, even the peak area variation points to an optimal concentration treatment at 5.0 N.

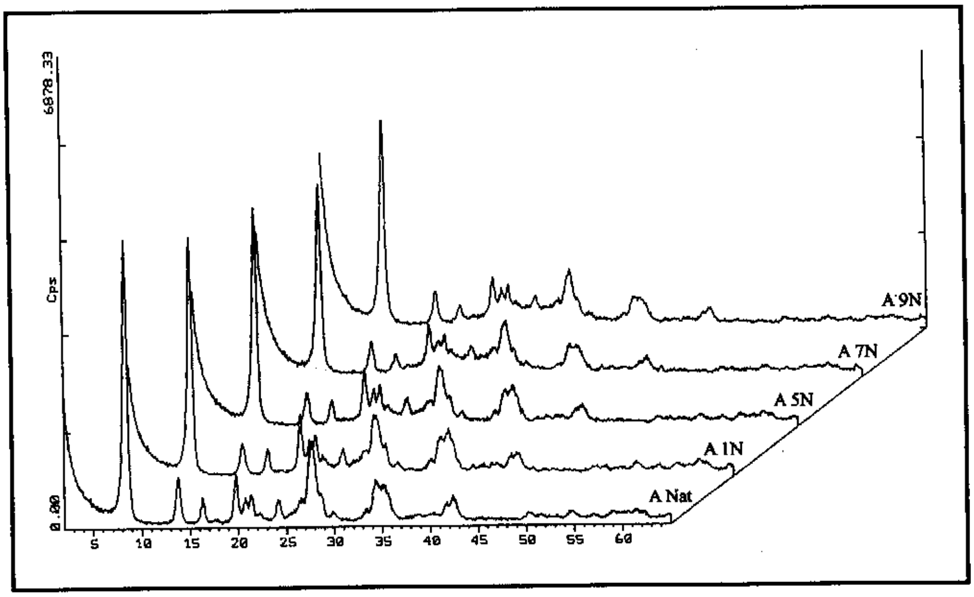

Fig. 1. XRD of natural palygorskite (A Nat) and samples treated with 1.0 N, 5.0 N, 7.0 N and 9.0 N.

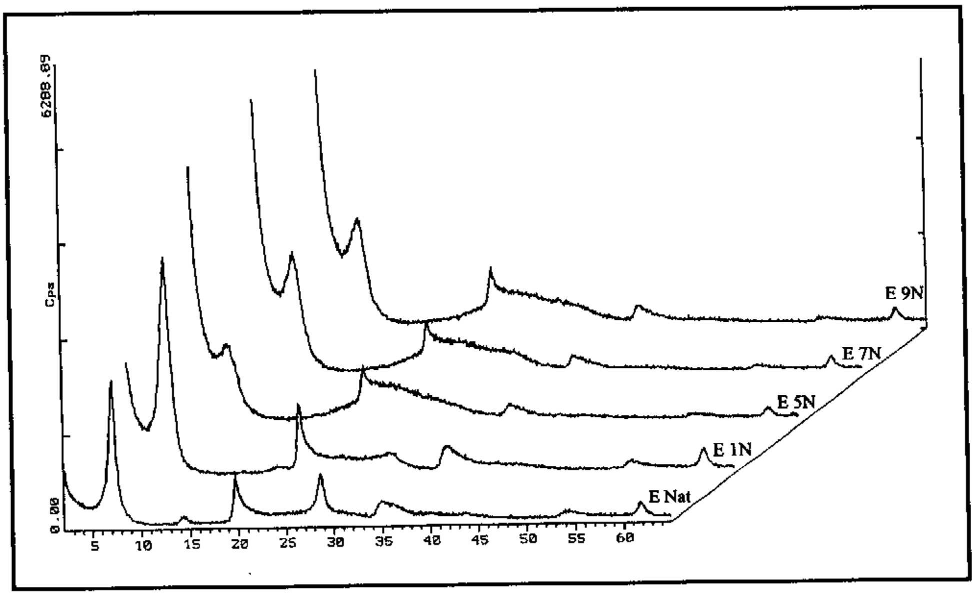

Fig. 2. XRD of natural smectite (E Nat) and samples treated with 1.0 N, 5.0 N, 7.0 N and 9.0 N.

The smectite, specially the E sample, shows greater crystallinity variations with the progressive HCl treatment with an important loose of the mineral crystallinity at 5.0 N, that recovers for higher concentrations to values similar to the natural ones. In the other samples (C and D) smectite collapse at 5.0 N. Smectite reflection intensities decrease and change positions (from 12.43 Å to 15.18 Å) as acid concentration increases up to 5.0 N (for higher concentrations presents a decrease tendency). Another phenomena observed in the smectite rich samples, is the growing delamellation of the original particles, with the (00l) reflection decreasing more than the (hk0) one (fig. 2).

Chemical composition

The chemical composition of palygorskite and smectite at natural and after progressive HCl treatments of the resulting solids is given in Table 3. After increasing concentrations, a SiO_2 content raise occur, that can be of 88 % after 5.0 N treatment for smectites, and of 84 % after 7.0 N for palygorkskites. For further attacks the SiO_2 content becomes stable, or show a slightly decrease (Fig. 3). The Al_20_3, MgO and Fe_20_3 + FeO content decreases, specially the magnesium. In this oxide is very clear that after treatment with 7.0 N HCl, the values almost reproduce those of natural samples (Fig. 4). The Fe_20_3 + FeO content can decrease intensely, with 90 % for pure smectite (E sample) and 50 % for pure palygorskite (A sample), with the lowest values about 1% (for smectite).

The MnO and K_2O content remains almost constant, although it is possible to find a slightly increase in the MnO and a slightly decrease in the K_2O (after 1.0 N and 5.0 N). This can be explained by the fact that those elements are due to impurities, such as feldspars or micas, which are very insoluble in the acid solutions.

The content of Na_2O doesn't change in palygorskite, while in smectite decreases strongly, perhaps because its presence is due to an addition of deflocullant in the initial preparation of the smectites samples, and so is of easy removal.

The content of CaO decreases in the calcite rich samples after the first attack, as was expected.

The behaviour showed by the Al_20_3, MgO and Fe_20_3 + FeO content with progressive acid treatment is related to the progressive dissolution of the clay minerals (more effective in smectites in accord with Vicente Rodríguez *et al*, 1996). The octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solids, due to its insolubility. Pesquera *et al* (1992) suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerized by the effect of such high acid concentrations and is deposited on the undestroyed silicate fractions, protecting it from further attack. The authors interpret this fact as «passivation» of the rest of the clay. In the studied case that «passivation» might be the explanation for such a mineralogical and chemical behaviour after progressive intensifying acid attack.

Table 3. Chemical analyses of palygorskite and smectite after progressive acid treatments, expressed in oxide form (%)

	SiO_2	TiO_2	Al_2O_3	Fe Total	MnO	MgO	CaO	Na_2O	K_2O
A Nat	69,77	0,29	13,58	3,90	0,01	11,62	0,09	0,06	0,66
A 1N	83,56	0,37	8,27	3,65	0,06	3,21	0,10	0,15	0,63
A 5N	81,27	0,37	11,53	3,32	0,07	2,49	0,02	0,17	0,77
A 7N	83,72	0,37	10,92	2,51	0,04	1,72	0,022	0,20	0,51
A 9N	82,11	0,43	8,96	2,29	0,04	5,54	0,019	0,08	0,53
B Nat	67,65	0,62	16,73	5,24	0,04	7,06	0,83	0,07	1,76
B 1N	76,13	0,64	14,90	4,96	0,10	1,90	0,031	0,22	1,12
B 5N	81,65	0,54	11,82	3,34	0,04	1,78	0,01	0,19	0,63
B 7N	82,07	0,56	11,26	3,44	0,05	1,87	0,017	0,15	0,57
B 9N	79,46	0,76	9,19	3,26	0,04	6,59	0,014	0,10	0,61
C Nat	63,30	0,66	19,49	5,34	0,04	7,12	0,85	1,94	1,26
C 1N	74,28	0,52	16,79	5,06	0,08	1,55	0,03	0,25	1,44
C 5N	81,58	0,50	12,29	2,55	0,04	1,36	0,015	0,20	1,48
C 7N	80,63	0,60	13,47	2,50	0,04	1,31	0,017	0,20	1,23
C 9N	79,82	0,56	10,75	2,35	0,04	5,19	0,013	0,12	1,17
D Nat	61,49	0,80	20,96	6,63	0,02	5,46	1,05	1,86	1,72
D 1N	69,40	0,64	18,42	4,89	0,07	4,60	0,04	0,27	1,67
D 5N	75,25	0,69	15,68	2,43	0,04	4,06	0,01	0,24	1,62
D 7N	80,20	0,95	11,52	1,92	0,02	3,77	0,01	0,12	1,48
D 9N	80,32	0,76	11,59	1,91	0,02	3,75	0,01	0,16	1,49
E Nat	61,86	0,33	17,11	8,86	0,03	6,12	1,31	4,13	0,26
E 1N	71,35	0,27	17,07	7,59	0,05	3,13	0,09	0,17	0,27
E 5N	87,67	0,21	9,25	1,28	0,02	1,03	0,04	0,25	0,26
E 7N	86,57	0,21	9,39	1,98	0,01	1,37	0,02	0,16	0,28
E 9N	86,68	0,23	9,35	2,19	0,01	1,15	0,018	0,09	0,27

Surface area and textural measurements

The nitrogen adsorption isotherms at 77 K of the different analysed solids are similar to type II (Sing *et al*, 1985; Paniego, 1989). With the increase of the acid concentrations the type and form of the isotherms remains the same of the natural samples. The results obtained are given in Table 4.

The value of surface area increases as treatment progresses, particularly in the palygorskite cases for concentrations of 5.0 N, and in smectite cases of 7.0 N, where in both cases a S_{BET} decrease occurs (Fig. 5).

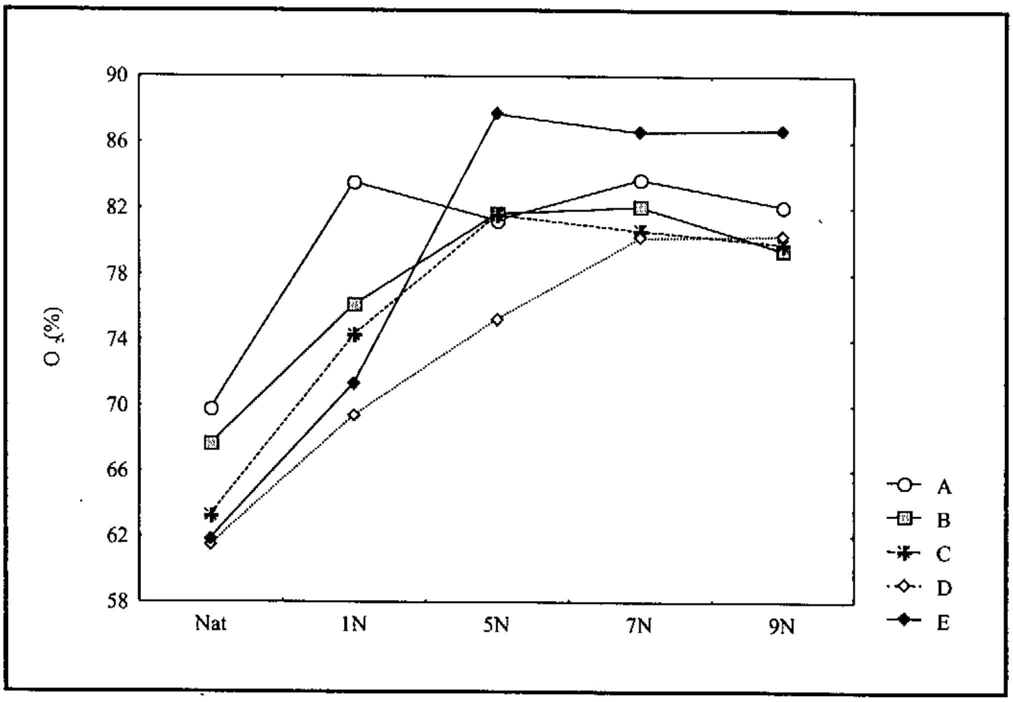

Fig. 3. SiO_2 content of natural and activated clay samples.

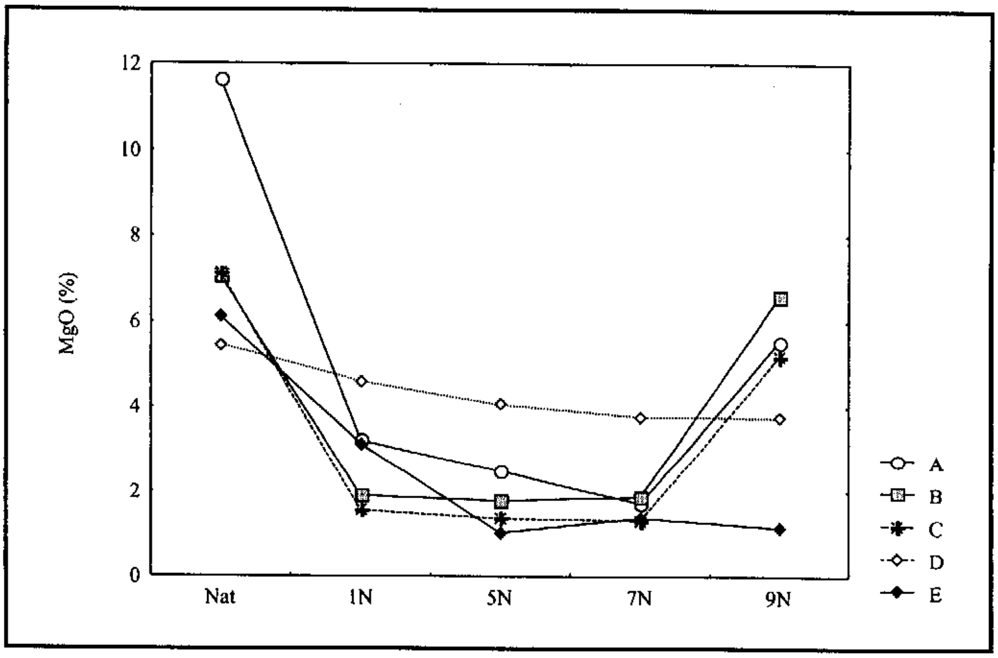

Fig. 4. MgO content of natural and activated clay samples.

The increase in the surface area from natural to activated samples is related to the elimination of the exchangeable cations, delamination of smectites and the generation of microporosity during all the process. The decrease observed for higher acid concentrations could be explained by the former mentioned process of «passivation».

Table 4. Parameters deduced from the *t*-curves and from the isotherms using the BET

Sample m^2/g	$S_{micropores}$ m^2/g	$S_{External}$ m^2/g	S_{BET}
A Nat	31	42	73
A 1 N	65	92	157
A 5 N	107	125	232
A 7 N	127	171	298
A 9 N	107	147	254
B Nat	29	39	68
B 1 N	70	136	206
B 5 N	30	125	155
B 7 N	37	127	164
B 9 N	38	130	168
C Nat	17	22	39
C 1 N	29	148	177
C 5 N	44	145	189
C 7 N	43	160	203
C 9 N	38	153	191
D Nat	9	16	25
D 1 N	55	160	215
D 5 N	46	192	238
D 7 N	38	171	209
D 9 N	30	162	192
E Nat	1	6	7
E 1 N	32	147	179
E 5 N	7	301	308
E 7 N	37	255	292
E 9 N	34	251	285

The raise of the surface area could be explicated by the increase generation of silica (as chemical data confirm), which also might explain the subsequent S_{BET} decrease. Thus, the free silica created during the process passivates the non-attacked clay minerals (namely smectite) by occlusion of the unaltered interlamellar spaces, protecting the clay sample from further attack. Also the enlargement of the relative proportions of insoluble impurities, like micas, which present a small surface area, contribute to the observed decrease.

It is important to enhance that the passivation phenomena is usually linked to textural changes (Mendioroz *et al*, 1987), with an increase of the mesoporosity,

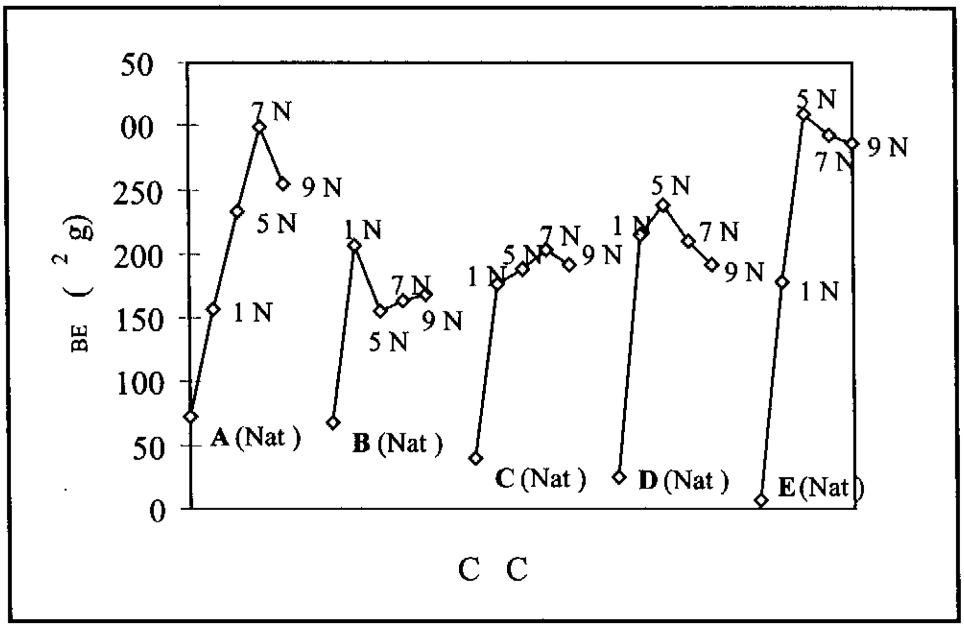

Fig. 5. S_{BET} of the natural and activated clay samples.

instead of microporosity from the resulting solids. Nevertheless, in the studied cases, even the increase of the surface area is preferably connected with the external surface, it is also related with the creation of microporosity. Also the decrease of the S_{BET} is accompanied by a microporosity reduction (Table 4) in accord with Suarez *et al* (2001).

The more observed increase from the natural sample to the 1.0 N, and from this one to the 5.0 N, could then be explained by the «cleaning process» which the sample had suffered, as well as, by the partial dissolution of the mineral, the successive decrease of the particle size and the delamination process (during the process samples become more disaggregated conducting to a greater individualization of the particles and later increase of surface area). This surface increase by creation of external surface is particularly important in sample E, which changes from 7 m^2g^{-1} to 308 m^2g^{-1} with the 5.0 N treatment. The raise of the micropores surface, what indicates a new pore system with less dimensioned pores, confirms this particle size decrease.

The surface decrease observed for higher acid concentrations, like 9N (even never achieving lower values than the observed for the natural sample), can also be explained by the partial destruction of the structural channel of the palygorskite rich samples. The attack at more aggressive conditions leads to a reordering of the Si amorphous previously generated, keeping the fibrous morphology (like observed in the TEM), but with reduced size particles, due to the attack and occurred dissolution (partial), conducting to a S_{BET} decrease (also the access to the inner particles diminished as seen in the surface micropores reduction).

In the palygorskite samples the microporosity assumes more importance relatively to the total area, what can be related to the structural specificity of this mineral, which fibre aggregates display can lead to an increase of the microporosity.

Electron microscopy

The natural samples and the different solids obtained after progressive acid treatment were studied by TEM in order to evaluate morphological changes. A decrease of the particle size was observed. However, as was observed in the results of the other analyses, we never assist to a complete destruction of the palygorskite or smectite, although the attack was more effective in smectite, and we really assist to an increasing of the silica. So, this silica obtained after acid treatment maintains the fibrous morphology of the natural palygorskite, and the usual shape and morphology of the smectites. It's also interesting to observe, that some fibres change dimensions, decreasing their length. And it's also possible to identify the presence of amorphous silica. The «textural continuity» due to the uncomplete destruction of the minerals, and also to the maintenance of the morphology by the silica obtained (confirmed by the chemical analyses and the XRD), was already observed by Gonzalez *et al* (1984), Suarez *et al* (1995) and Myriam *et al* (1998) and for fibrous clay minerals.

CONCLUSION

The progressive acid treatment of palygorskite and smectite clay samples from 1N to 9N didn't conduct to a complete destruction of their structure, especially in the palygorskites. However, a progressive removal of the octahedral cations occurs and the formation of silica from its tetrahedral sheet by the acid attack of palygorskites and smectites. In smectites the signs of delamellation and progressive destruction of the octahedral sheet are obvious, and the destruction of the octahedral sheet and tetrahedral sheet have been also observed.

All the results of the techniques used show that in the activation of the clay minerals by HCl there is a point of inflection in the tendency at a certain acid concentration, that is 7.0 N for palygorskite rich samples, and 5.0 N for smectite rich samples (especially for the pure ones). This behaviour at higher concentrations could be in part explained by the results of Pesquera *et al* (1992) for smectite and Gonzalez *et al* (1989) for palygorskite. The clay minerals react in a different way (like at lower concentration, or even natural sample) due to the silica produced during the reaction that undergoes polymerization under such high acid concentrations and coats the silicate, preventing further attack. This fact has been interpreted as «passivation» of the clay.

It's also important to notice that the silica obtained after the most effective attacks maintains the initial morphology of the clay mineral, suggesting a «textural continuity» respecting to the natural sample.

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