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Texture Evolution of an Acid Activated Interstratified Illite-Smectite

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The change of the pore structure and the adsorption properties of an interstratified illite-smectite of Tunisia after treatment with 3 M HCl at 0.5, 2, 4, 7 and during 20 h were investigated. The pore size distribution, specific surface areas according to BET method, V_a–t plot, Dubinin-Radushkevich equation and f-plot were determined by the nitrogen adsorption. The results show that with the increase of the time treatment, the total pore volume increased, while the maximum value of the specific surface area was attained by the sample treated at 4 h. The difference between the pore structure and the adsorption properties were caused by the structural change and the decomposition of the samples.

INTRODUCTION

The activation of clays is frequently carried out in order to obtain full use of industrial products. Acid treated clays were used as catalysts[1]. The adsorptive capacity of acid activated clays is utilised by the industry to illuminate undesired accompanying materials from liquid, solvent and melt[2, 3].

The behaviour of acid activated clay as an adsorbent is governed mainly by the magnitude of its surface area and degree of surface activity. For many applications, detailed knowledge of its surface texture and porosity is necessary since this determines the sorption response to molecules of different sizes and shapes.

A study of textural changes, BET surface, pore volume distribution, t-plot, f-plot and the Dubinin-Radushkevich equation was done before and after acid activation. X-ray patterns and elemental analysis of the samples helped to elucidate the obtained results.

EXPERIMENTAL

A clay material from South Tunisia has been used as the raw material. It is an interstratified Illite-Smectite containing *ca.* 20% (quartz, calcite and kaolinite) as impurities. The smectite fraction of the interstratified phase is always larger than 50%. It is essentially sodic[4].

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The sample studied has the following formula:

$$Na_{0.60}K_{0.23}Ca_{0.08}[Si_{7.47}Al_{0.53}]^{IV}[Al_{2.75}Fe_{0.80}Mg_{0.51}]^{VI}O_{20}(OH)_4$$

The overall CEC of the purified interstratified illite-smectite mineral is about 71 meq/100 g of calcined material.

Acid activation: 10 g of purified clay were treated with 100 mL of 3 M HCl solution during 0.5, 2, 4, 7 and 20 h. After these treatments, the resulting samples were washed until no chloride anions could be detected. They were then dried up at 60°C. The product is denoted H_0 before activation and $H_{0.5}$, H_2, H_4, H_7 and H_{20} where 0.5, 2, 4, 7 and 20 refer to times in hours treatment.

Mineralogical and chemical analysis: X-ray patterns were obtained from the original raw material and treated samples using a Philips PW 1900 with Cu-K_α radiation.

Conventional analytical methods[5] were used to evaluate aluminium, iron, calcium and magnesium. The potassium and sodium were determined by flame photometer. The silica was determined quantitatively by the reduced silicomolybdic complex formed at 810 nm.

Adsorption measurements: The specific surface areas of samples were determined by the corresponding nitrogen adsorption isotherms at 77 K obtained from Carlo Erba Sorptomatic 1800 after degassing out the samples at 120°C for 12 h. The BET method was used for the corresponding calculation.

The distribution of the pore size applicable to the mesopore range was obtained by the method of Pierce[6]. V_a–t plots[7], f-plots[8] and Dubinin-Radushkevich equation[9].

RESULTS AND DISCUSSION

Chemical and structural changes: Table-1 shows the proportion of tetrahedral and octahedral cations before and after activation, expressed in percentage in oxide form. The percentage of octahedral cations Al, Fe and Mg decreases with time treatment indicating the destruction of the octahedral sheets. The percentage of silica generated by the destruction of the tetrahedral sheet, which is evaluated by the extraction with sodium carbonate[10], increases with time treatment.

The X-ray diffractograms of the purified sample and of the series treated with 3 M HCl are presented in Fig. 1. When the time of the treatment increases, the crystallinity of the sample decreases. The (hk_0) reflection intensities clearly decrease without changing the position. The (001) reflection, corresponding to the basal spacing, decreases rapidly with changing position (12 to 14.5 Å), indicating the tranformation of *Na saturated clay* to *Al (or Fe) exchanged clay*, and becomes broader as the time of activation increases, indicating a growing delamellation of the original particles.

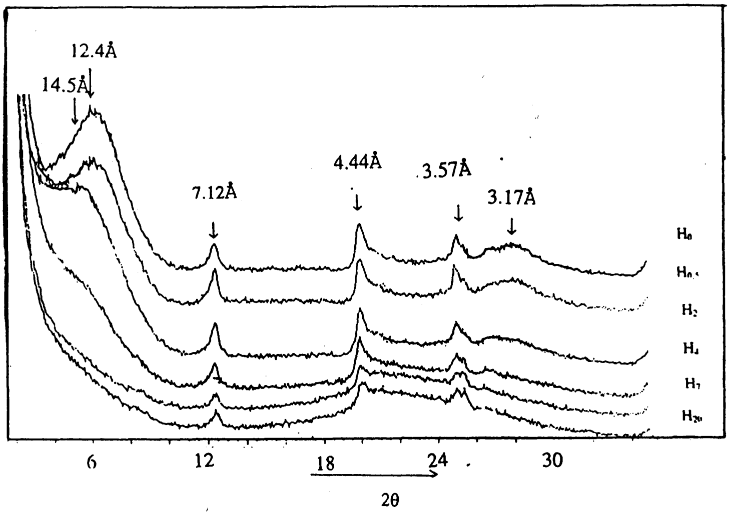

Fig. 1. X-ray diffraction pattern of the untreated and acid activated samples

TABLE-1
Si, Al, Fe AND Mg CONTENT (wt %) OF CALCINED NON-ACTIVATED AND ACTIVATED SAMPLES

Percentage of cations per g of calcined clay	H_0	H_2	H_4	H_7	H_{20}
SiO_2	61.00	70.00	78.00	86.00	90.00
Al_2O_3	22.80	16.80	12.25	8.80	7.30
Fe_2O_3	8.62	4.24	2.96	1.26	0.65
MgO	2.82	0.98	0.28	0.20	0.14
SiO_2^a	–	10.00	14.00	30.00	34.00

[a] Silica generated by acid treatment which remained in the solid phase and was then extracted with Na_2CO_3

Textural change

Nitrogen adsorption-desorption isotherms: The physical changes in the structures may be examined quantitatively by determination of the nitrogen adsorption-desorption isotherms from which the surface area and the pore volume are calculated (Table-2). the complete isotherms for the nitrogen adsorption-desorption at 77 K of activated and non-activated clay are shown in Fig. 2. A change from H_3 to H_2 type hysteresis[11] seems to be produced by acid at a different time treatment. Before the acid activation, the clay presents H_3 type hysteresis, characteristic of slit shaped pores[12]. This type of hysteresis is maintained for the sample treated at 4 h. For 7 and 20 h of treatment, the patterns present hysteresis more like H_2 indicating the presence of ink bottle pores[12].

TABLE-2
TEXTURAL PARAMETERS FOR NATURAL AND ACID TREATED CLAY

	H_0	$H_{0.5}$	H_2	H_4	H_7	H_{20}
A_{BET} (m^2/g)	49	146	242	266	233	220
V_p (cm^3/g)	0.1116	0.1956	0.3434	0.4637	0.4517	0.7061
A_t (m^2/g)	27	142	241	267	239	219
A_{ext_t} (m^2/g)	–	31	85	143	139	–
$A_{\mu p_t}$ (m^2/g)	–	111	156	124	100	–
$V_{\mu p_t}$ (cm^3/g)	0.013	0.077	0.1216	0.1240	0.1000	–
$V_{\mu p_{BR}}$ (cm^3/g)	0.025	0.073	0.1082	0.1186	0.1080	–

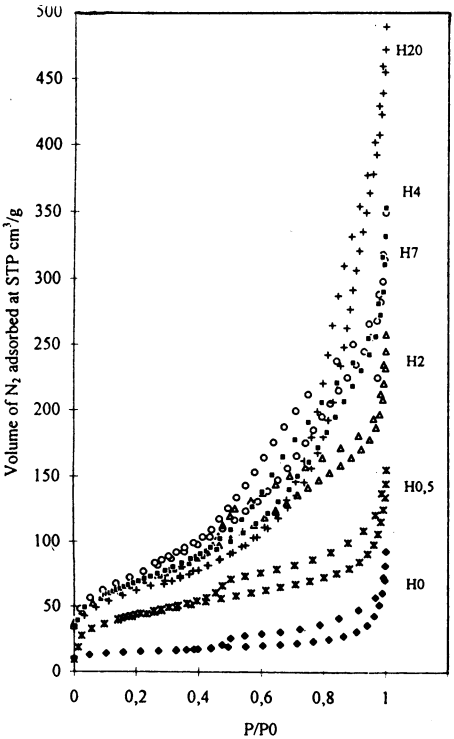

Fig. 2. Nitrogen adsorption-desorption of natural and acid activated sample.

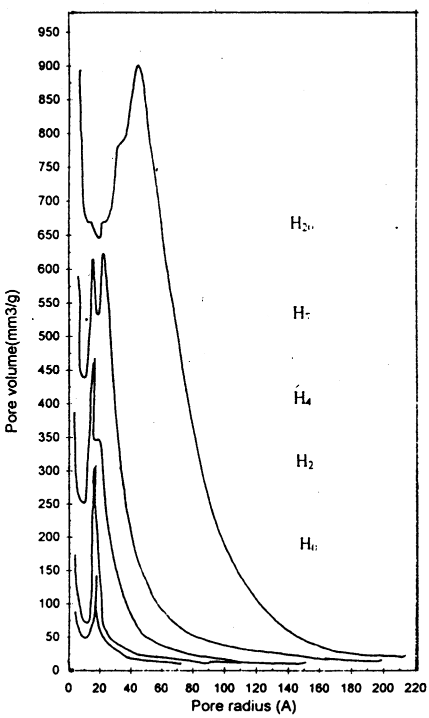

Fig. 3. Pore volume distribution curves of the natural and acid activated samples.

Pore size distribution: The changes occurring in the surface area and the pore type are best illustrated in the pore distribution plot (Fig. 3). The plot generated shows that in the natural sample, the surface of the clay has comparatively small pores of less than 20 Å diameter. These pores correspond to the two-dimensional sheets occurring between clay layers. Following the acid activation, the average of the diameter of pores has increased and the available surface is in pores having the diameter between 20 and 60 Å. These are pores which have begun to take on the three dimensional appearances.

f-plot isotherms: The f-plot is a method for comparing the shape of the isotherm of a given sample to a reference sample (in this case, the natural sample) and for obtaining information about variation in the porosity. The f-plot compares the quantities adsorbed by a given sample to the reference at constant intervals of P/P_0. The f-plot for the acid treated samples given in Fig. 4 shows that the acid treatment samples had greater adsorption capacities than untreated clay. The f-plots of $H_{0.5}$ and H_2 samples are almost parallel to the *x*-axis which is the consequence of these samples having the same morphology as that of a natural sample. The maxima of the f-plot of H_4, H_7 and H_{20} samples at higher relative pressures seem to indicate an increase in the mesoporosity of acid activated solids. At higher relative pressures, these mesopores are filled and the value of f decreases.

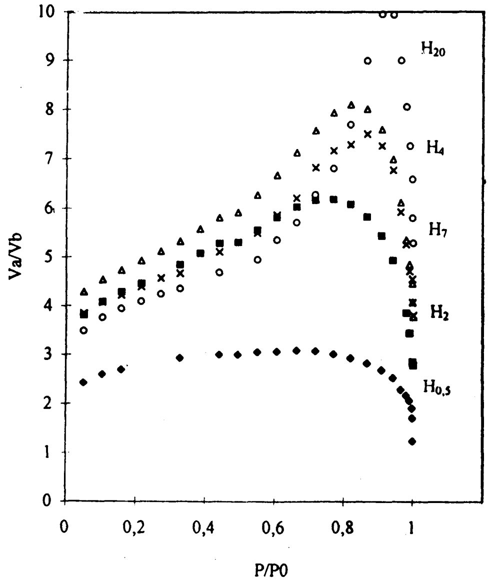

Fig. 4. f-plot of the ratio of N_2 adsorbed by acid activated samples to N_2 adsorbed by natural clay.

t-plot isotherms: V_a–t plots of natural and acid activated samples are given in Fig. 5. For the natural sample the curve is steel linear. The extrapolation to the adsorption axis gives a positive intercept which is equivalent to the micropore volume when converted to a liquid volume (by use of density of the liquid adsorptive). For acid activated samples the form of the curve is different indicating that the microporosity is associated with an appreciable external surface, or with mesoporosity, or with both. The curves present two linear branches. The first will be a straight line passing through the origin and having a slope proportional to the specific surface A of the powder. The values of the external specific surface (A_{ext}) are calculated from the slope to the second branch for $H_{0.5}$,.H_2, H_4 and H_7 samples. The microporous surface ($A_{\mu p}$) is obtained by the difference between the specific (A) and the external specific surface (A_{ext}) given in Table-2 for $H_{0.5}$, H_2, H_4 and H_7. The micropore volumes are deduced by the calculation: $(V_{\mu p})_t$ (cm^3/g) = t (nm) 10^{-3} $A_{\mu p}$ (m^2/g); t is the break point of each curve. At higher thickness of adsorbed layer, the V_a–t-plot of H_{20} sample shows increasing slope. The adsorbed volume is greater for the same t value of the adsorbed volume by the no porous solid. This indicate the capillary condensation in the mesopore.

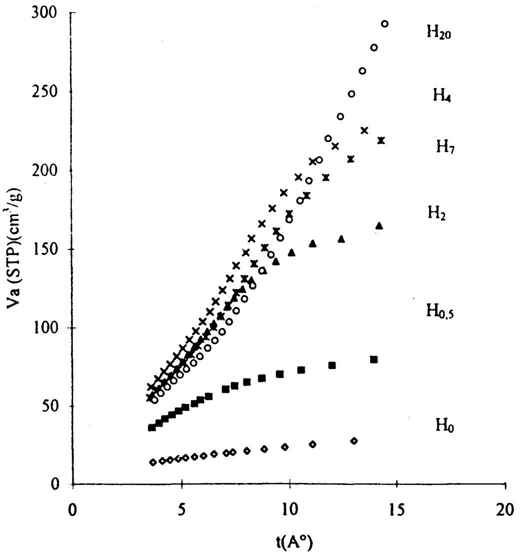

Fig. 5. V_a–t plot of the natural and acid activated samples.

Dubinin-Radushkevich (DR) plot: A positive deviation at higher t values in the V_a–t plots indicates the existence of the mesopores. Taking this into account, DR plots are established in Fig. 6 from which the micropore volume $(V_{\mu p})_{DR}$ are computed and these are given in Table-2. After the acid activation, the variation in micropore volumes is important. The maximum value of microporosity was attained by sample treated at 4 h. This result is in good agreement with that obtained by t-plot method.

Conclusion

The resulting solids consist of variable amounts of unaltered silicate and more or less silica-gel generated. The amounts of these two phases depend on the treatment time. Suitable conditions have been established for maximising the development of surface and porosity. Analyses of V_a–t plots, f-plots, Dubinin-Radushkevich and pore size distribution curves, show the evolution of the porosity of clay sample after acid activation. The microporosity is associated with an

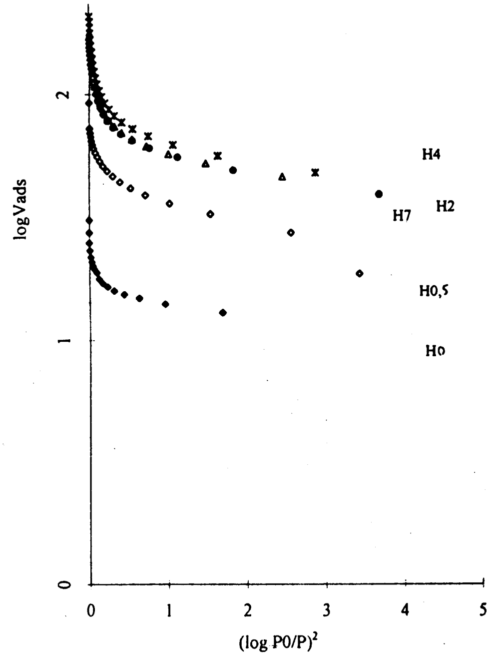

Fig. 6. Dubinin-Radushkevich plots of the natural and acid activated samples.

appreciable external surface and with mesoporosity. The specific surface area grows from 49 m^2/g from the natural sample to 220 m^2/g for 20 h treated sample, passing through a maximum of 266 m^2/g for the H_4 sample. The maxima of microporous volume (0.1240 by V_a–t plot and 0.1186 cm^3/g by DR method), and the external surface (143 m^2/g) are reached for the same sample.

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