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ON THE MECHANISM OF ACID ACTIVATION OF MONTMORILLONITE
II. CHANGES IN THE MORPHOLOGY AND POROSITY IN THE LIGHT OF ELECTRON MICROSCOPIC AND ADSORPTION INVESTIGATIONS

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Abstract. In an earlier publication (Fijał *et al.* 1975) the authors discussed the mechanism of acid activation of Ca-montmorillonite derived from the Chmielnik deposit. Changes in the structure and sorption properties as a function of the activation time have been investigated. The object of the present paper was to determine the effect of activation on: 1) the morphology of montmorillonite aggregates as shown by electron microscopic examinations, 2) the porous structure of these aggregates (changes in the pore volume distribution as a function of their effective radii) as shown by sorption investigations.

EXPERIMENTAL PROCEDURE

The analyses were carried out on samples of natural Ca-montmorillo-nite and those activated with hydrochloric acid for 1, 3, 4, 5 and 10 hours. Argon adsorption and desorption isotherms were obtained at 77°K using sorption manostats (Ciembroniewicz, Lasoń 1972). Electron microscopic investigations involving morphological micrographs and diffraction measurements were performed using a Tesla microscope (CSSR) with an accelerating voltage of 100 kV. Powder suspension technique was applied, the magnifications ranging from 10.000 to 80.000×.

Sorption analyses served as a basis for determining the porous structure of the adsorbents; it was defined by the pore volume distribution as a function of the pore radii, i.e. $\Delta v/\Delta r$ vs. r_k. The distribution is determined from Kelvin's equation from that part of the isotherm in which capillary condensation of vapours occurs:

$$\ln p_0/p = \frac{2\sigma M}{\delta r_k\, RT}$$

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where:

p_0 — saturated vapour tension over the flat surface of liquid at temperature T,

p — saturated vapour tension over the concave meniscus of liquid with the radius of curvature r_k at temperature T,

σ — surface tension of liquid at temperature T,

M — molecular weight in g,

δ — density of liquid at temperature T,

r_k — radius of curvature of the spherical meniscus in a capillary,

R — gas constant,

T — temperature in degrees Kelvin.

The equation was derived assuming that the equilibrium pressure p is a function of the capillary radius. Surface tension of the liquid and its density at a given temperature do not depend on the meniscus radius.

Kelvin's equation does not take into account the fact that upon evacuating liquid sorbate from the pores, there remains an adsorption layer in the pores. Hence, the values of pore radii calculated from this equation are smaller than the effective ones by the thickness of that layer:

$$r_e = r_k + l$$

When Kelvin's equation was combined with the above relationship, and the fact that the adsorption layer thickness l is a function of the relative pressure was taken into account, new equations could be derived (Barret et al. 1951; Dubinin 1956; Cranston, Inkley 1957, and others). The distributions of pore volumes and surfaces as a function of their effective radii are determined on their basis.

In this paper, the procedure developed by Dubinin (1956) was adopted. Accordingly, the desorption part of the isotherm was divided into n sections assuming that each of them corresponds to a desorption stage that involves evacuation of liquid sorbate from the pores with the radii corresponding to the given p/p_0 range, and reduction of the thickness of the adsorption layers in the pores evacuated during the preceding stages. The volume of pores being evacuated in the n-th stage of desorption was calculated from the formula:

$$\Delta V_n^* = \left[\Delta V_n - \Delta l_n \sum_{i=1}^{i=n-1} \frac{2 \Delta V_i}{\bar{r}_{k,i}} \right] \left(\frac{\bar{r}_n}{\bar{r}_{k,n}} \right)^2$$

where:

V_n^* — volumes of pores being evacuated in the n-th stage,

l_n — decrease in the mean thickness of the adsorption layer in the n-th stage,

V_i — amount of sorbate that desorbed in the i-th stage (cm³ of liquid sorbate/gram of sorbent),

$\bar{r}_{k,i}$ — mean Kelvin radius of pores evacuated in the i-th stage of desorption,

$\bar{r}_n$ and $\bar{r}_{k,n}$ — respectively, mean effective and Kelvin radius of pores being evacuated in the n-th stage,

i — stages of desorption from 1-th to $n-1$-th.

Electron microscopic investigations. Electromicrographs of powder preparations permitted to investigate the changes occurring in the morphology of montmorillonite aggregates during prolonged acid activation. Diffraction investigations have yielded supplementary data on the structural changes.

Electromicrographs of the initial sample of montmorillonite from Chmielnik (Phots 1, 2) present complexes of grains aggregates averaging some microns, with the morphology typical of this mineral. Their edges are sharp and rugged (Phot. 1). The aggregates are granular concentrations, non-transparent, as a rule, to an electron beam.

An analysis of the electromicrographs of acid-activated samples has shown that they positively differ from the initial sample in the structure of aggregates. After 3-hour activation certain loosening of the aggregate complexes may be observed (they become partly transparent to an electron beam). The edges of the montmorillonite aggregates lose their original angularity, becoming rounded and translucent (Phot. 3). Though morphological changes have been recorded, the diffraction patterns obtained for this sample confirm the presence of the montmorillonite phase alone.

Further activation (5 hours) advances the degradation of montmorillonite grains (Phots 4, 5). Not only do the aggregates become loosened and their edges rounded, but also larger areas transparent to an electron beam appear. Moreover, peculiar forms with granular structure may be observed on the aggregate edges.

After 10-hour activation, the granular forms occupy the greater part of the volume of aggregates (Phots 6, 7). The rise of such forms in the process of activation reflects the profound structural changes. Electron diffraction investigations performed for those transformed zones of aggregates have shown their complete amorphization. This is further evidence of structural changes of montmorillonite that result in the formation of an amorphous substance of the silica gel type, thus confirming the results of earlier studies (Fijał et al. 1975, part I).

Granular structure is peculiar to typical silica gels. Photograph 8 presents an electromicrograph taken from a sample of fine-grained silica gel "aerosil". The characteristic agglomerations of granular forms in the gel sample show a striking similarity to the afore-discussed electromicrographs of the montmorillonite sample activated for 10 hours (Phots 6, 7).

Adsorption investigations. Figure 1 shows isotherms of low-temperature argon sorption on the initial montmorillonite and on acid-activated samples. From the desorption part of the isotherms, pore volume distributions as a function of the mean effective radii were calculated. The distribution diagrams are presented in Figure 2.

The data yielded by the adsorption analyses imply that the following changes occur in the porous structure during activation of montmorillonite:

1. The initial montmorillonite with a surface area of 43.9 m²/g has the dominant pore radius about 15.0 Å.

2. In the sample activated for 1 hour no changes in the porous structure have been noted; yet, the volume of the dominant pores (15.0 Å) accessible to sorbate molecules increases. This is very likely due to a rear-
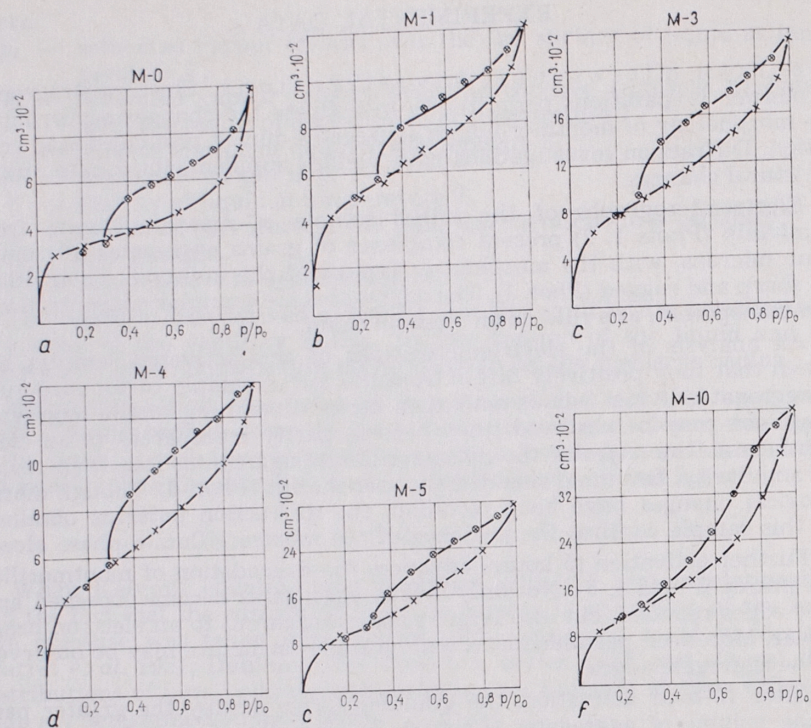
Fig. 1. Low temperature argon sorption isotherms on the investigated samples: M—0, M—1, M—3, M—4, M—5, M—10

rangement within the aggregates * and domains, which results in rendering more pores with a radius of 15 Å accessible to the sorbate.

3. A further increase in the volume of pores with an effective radius of about 15 Å accessible to sorbate molecules has been noted after 3-hour activation. This behaviour is due to the advanced degradation effected by the acid and its more intensive penetration into montmorillonite grains. These changes, particularly pronounced in the external zones of grains, have been also noticed on the electromicrographs.

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* When explaining the phenomena connected with the porosity of montmorillonite, the following terminology has been used:

— layer: the smallest structural unit consisting of 3 sheets (2 tetrahedral, 1 octahedral),

— particle: a combination of layers bounded by morphological surfaces,

— domain: a combination of particles displaying characteristic textural ordering (a type of oriented particle intergrowths),

— aggregate (grain): a combination of domains that can be separated from the surroundings.

The textural orientation of particles within domains may result in the formation of a porous structure in the inter-particle spaces, the mode of orientation modifying the character of this structure.
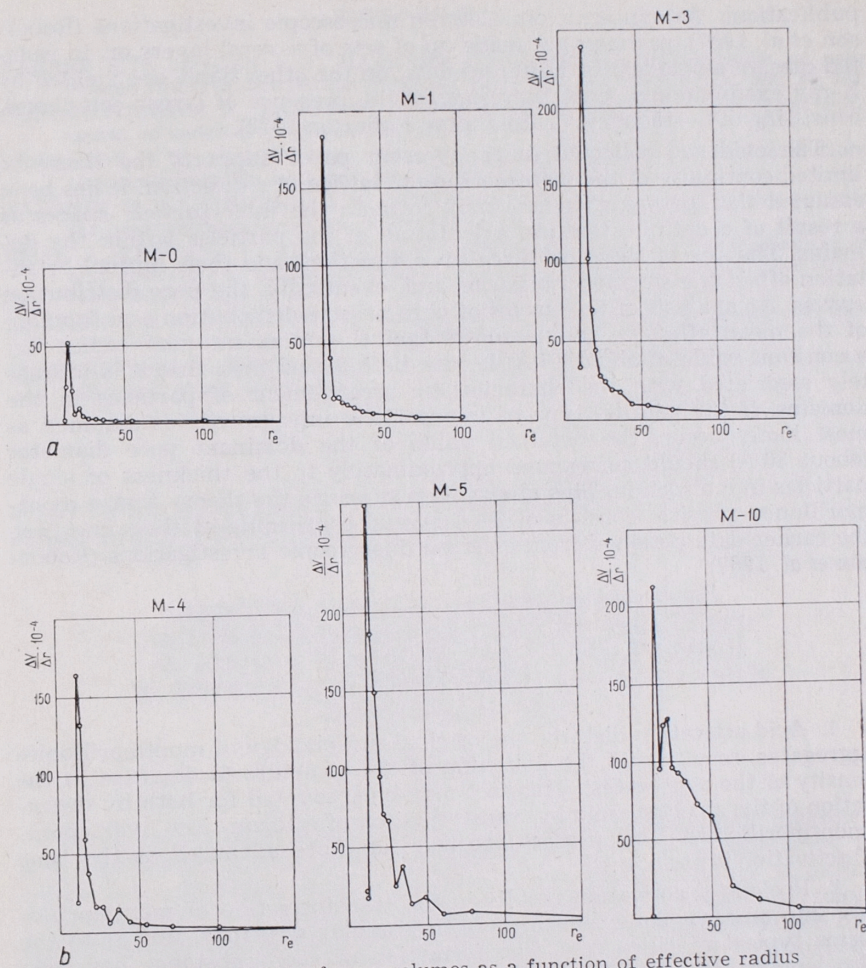
Fig. 2. Distributions of pore volumes as a function of effective radius

4. In the more degraded montmorillonite sample (5 hours), additional pores with higher values of the effective radii have been recorded.

5. Additional porosity becomes pronounced after 10-hour activation of a montmorillonite sample. There is a broad band in the range from 15 to 50 Å on the pore distribution curve, but simultaneously an extreme of 15 Å that is characteristic of the montmorillonite structure is preserved.

Equally characteristic is a change in the shape of isotherms and the conspicuous contraction of the hysteresis loop. The authors believe that the above facts may be accounted for by the presence of newly-formed substance of the gel type with globular structure.

The problem of textural orientation of montmorillonite particles and their size in c direction, which is tantamount to the determination of the number of layers that make up a particle, has been discussed in several

publications. As appears from electron microscopic investigations (Roberson et al. 1967), particles are made up of sets of several layers or, in isolated case, of single layers. Different data, on the other hand, are yielded by X-ray examinations, since they suggest the presence of larger complexes, consisting of 8—15 layers (Tettenhorst, Roberson 1973).

The evidence collected in the present paper supports the thesis of limited continuity of the montmorillonite lattice in c direction. It has been assumed that porous structure may form in the inter-particle spaces as a result of a definite textural orientation of the particles within the domains. The size of these particles (in c direction) and their mutual orientation affect the sorption isotherms and, eventually, the pore distribution curves. An analysis of the curves of pore volume distribution as a function of the mean effective radius shows that the dominant pore radius has a constant value of about 15 Å. It may be inferred then that it is intimately associated with the characteristic arrangement of particles in the domains. If the parallel type of interparticle intergrowths is assumed as most likely occur, the obtained value of the dominant pore diameter (about 30 Å) should correspond approximately to the thickness of single particles in c direction. This observation supports the theory that a montmorillonite particle consists of 3—4 layers, confirming at the same time the earlier data obtained from electron microscopic investigations (Roberson et al. 1967).

DISCUSSION

1. Acid activation disturbs the original morphology of montmorillonite aggregates, resulting in the loosening of the structure (a decrease in the density of the aggregates). This fact may be accounted for both by degradation of the structure and by transformation of calcium- into hydronium- -montmorillonite. This process becomes far more advanced as the time of activation is prolonged.

2. Prolonged activation results in the transformation of montmorillonite into an amorphous substance with granular structure, similar to the forms typical of silica gels. The formation of such substance has been also demonstrated by infrared spectroscopy.

3. Changes in the morphology and internal structure of montmorillonite agregates have been confirmed by sorption investigations. The first stage of activation increases only the accessibility of the internal porous structure of montmorillonite by loosening the aggregates. This is evidenced by the stable position of the maximum of the dominant pore radius. The secondary porosity is due to gradual transformation of a part of montmorillonite into amorphous silica.

4. The authors suggest that the studies of the porous structure of montmorillonite (based on sorption methods) can be used for explaining the problems connected with the internal ordering and the size of its morphological forms, i.e. sets of layers (particles) within montmorillonite aggregates.

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BADANIA NAD MECHANIZMEM PROCESU AKTYWACJI KWASOWEJ MONTMORILLONITU II. ZMIANY W MORFOLOGII I POROWATOŚCI W ŚWIETLE BADAŃ ELEKTRONOGRAFICZNYCH I ADSORPCYJNYCH

Streszczenie

Praca ta jest kontynuacją badań nad procesem aktywacji kwasowej montmorillonitu ze złoża Chmielnik (Fijał et al. 1975). Zasadniczym jej celem było określenie wpływu procesu aktywacji na zmiany struktury i własności sorpcyjnych montmorillonitu. Rejestrowano zmiany morfologii agregatów montmorillonitu na podstawie badań elektronograficznych oraz charakter przeobrażeń struktury porowatej tych agregatów na podstawie efektywnych przebiegu krzywych rozkładu objętości porów według ich efektywnych promieni, wyznaczonych z badań sorpcyjnych. Zbadano poszczególne etapy przeobrażania się montmorillonitu w substancję o strukturze zbliżonej do żelu krzemionkowego.

Autorzy sugerują możliwość wykorzystania badań struktury porowatej montmorillonitu (na podstawie metod sorpcyjnych) dla wyjaśnienia problemów wewnętrznego uporządkowania i wielkości jego podstawowych form morfologicznych, a więc zespołów pakietów (krystalitów) w obrębie agregatów montmorillonitu.

OBJAŚNIENIE FIGUR

Fig. 1. Izotermy niskotemperaturowej sorpcji argonu na badanych próbkach: M—0, M—1, M—3, M—4, M—5, M—10
Fig. 2. Rozkłady objętości porów w funkcji promienia efektywnego

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ИССЛЕДОВАНИЕ ПРОЦЕССА КИСЛОТНОЙ АКТИВАЦИИ МОНТМОРИЛЛОНИТА II. ИЗМЕНЕНИЯ ПОРИСТОСТИ И МОРФОЛОГИИ ПО ДАННЫМ ЭЛЕКТРОНОГРАФИЧЕСКИХ И СОРБЦИОННЫХ АНАЛИЗОВ

Резюме

Данная работа является продолжением исследования процесса кислотной активации монтмориллонита из месторождения Хмельник (Фиял и др. 1975). Основной целью работ было определение влияния процесса активации на изменения структуры и сорбционных свойств монтмориллонита. Отмечались изменения морфологии агрегатов монтмориллонита с помощью электронографических анализов и характер изменений структуры этих агрегатов по форме кривых распределения пор на основании их эффективных радиусов, определенных сорбционным методом. Исследовались отдельные этапы перехода монтмориллонита в вещество со структурой, напоминающей силикатный гель.

Авторы считают возможным использовать наблюдения над пористой структурой монтмориллонита с помощью сорбционных методов в изучении проблем внутреннего строения этого минерала и величины его основных морфологических форм, т.е. групп кристаллитов, слагающих агрегаты монтмориллонита.
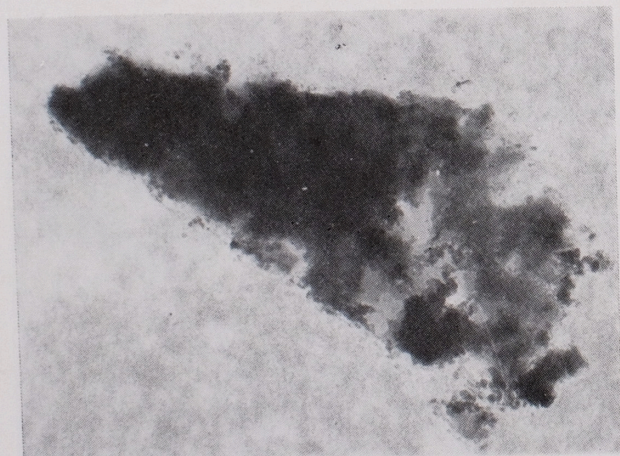
ОБЪЯСНЕНИЯ К ФИГУРАМ

Phot. 1. Electron micrograph of montmorillonite from Chmiel-
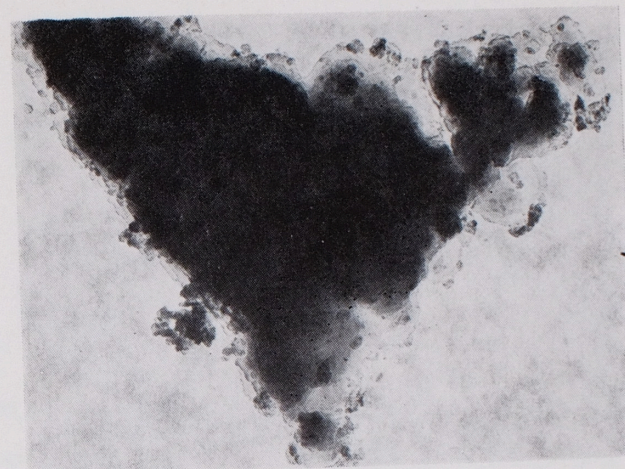nik. Magn. $\times$ 42.000

Phot. 2. Electron micrograph of montmorillonite from Chmiel-
nik show mainly thick, irregular, sharp-edged particles.
Magn. $\times$ 21.000
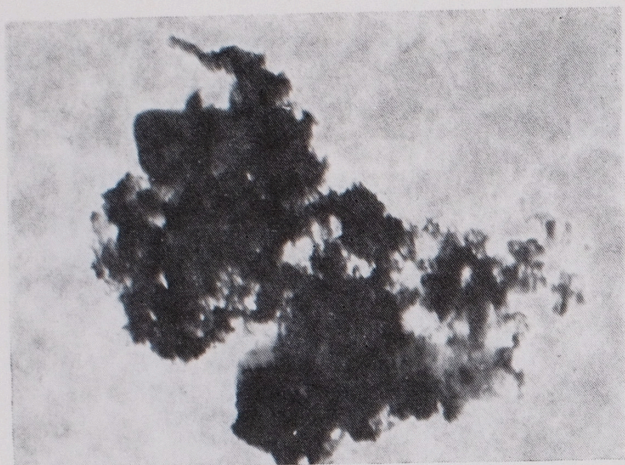
Phot. 3. Montmorillonite after 3-hour activation. Grains are rounded and becoming translucent. Magn. × 15.000
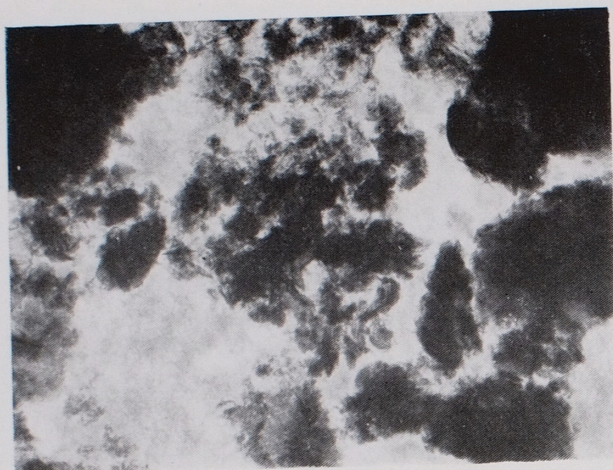

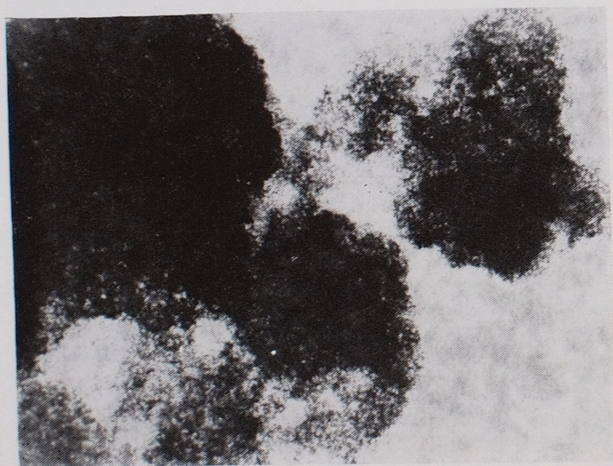Phot. 4. Montmorillonite after 5-hour acid activation. Grain with rounded borders. Magn. × 15.000

Phot. 5. Montmorillonite after 5-hour acid activation. The micrograph shows the degradation of grain. Magn. × 21.000
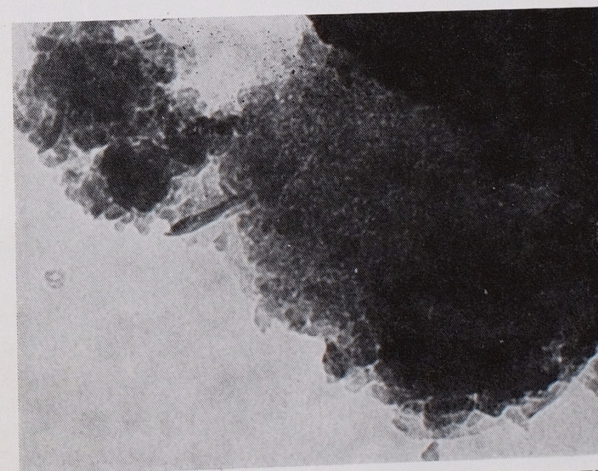
Phot. 6. Montmorillonite after 10-hour acid activation. The peculiar granular forms can be seen on the edges of grain. Magn. × 90.000

PLATE IV

Phot. 7. Montmorillonite after 10-hour acid activation. Aggregations of particles. Magn. $\times$ 30.000

Phot. 8. Electron micrograph of silica gel. Magn. $\times$ 21.000

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