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A MORPHOLOGICAL STUDY OF SELECTED SYNTHETIC CLAYS BY ELECTRON MICROSCOPY

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Abstract—The morphology of synthetic montmorillonite and hectorite was studied using electron microscopy and X-ray diffraction techniques. Interstratified montmorillonite-mica particles may be identified in these specimens by electron microscopy and electron diffraction techniques. Magnesium-substituted samples were found to exhibit an increasing amount of curling with increasing magnesium content except for the end-member magnesium clay. Synthetic hectorite clays do not necessarily have the same morphology as natural hectorite clays. A study was made also of the morphology of a series of samples obtained from a study of kinetics of crystallization. Boehmite and montmorillonite were the basic components of the system. It was found that the montmorillonite clay particles curled around the boehmite which had been adsorbed on the basal surfaces on the montmorillonite.

INTRODUCTION

RECENTLY, interest has arisin in synthetically producing certain clay minerals in order that specific properties and structures may be obtained. Different structures may be produced by varying the conditions of synthesis and the amount and kind of starting materials, leading to a variety of crystalline products with differing isomorphous substitutions within the structure.

Some of the early synthesis work on montmorillonite clay minerals was done by Noll (1936). The synthesis of magnesium-containing montmorillonite was studied and then the work was extended to the magnesium end-number of the series, hectorite, using high pressure techniques. Strese and Hoffman (1941) conducted extensive synthetic work in the same area and also included a study of the products obtained carrying out the synthesis at atmospheric pressure. More recently a study of hectorite synthesized at atmospheric pressure and reflux temperatue was published by Granquist (1960).

In this investigation X-ray diffraction and electron microscopy were used to study the morphology of a selected group of synthetic clays which are of interest as cracking catalysts. The synthetic clay materials were of two general species, montmorillonite and hectorite.

EXPERIMENTAL

Materials

The clay samples used in this study were provided by the Mellon Institute, Pittsburgh, Pennsylvania under a project sponsored by the Baroid Division of National Lead Company. The samples are designated in the following manner: Series I.—2H-2, 2H-3, 2H-4, 2H-5, 2H-6; Series II—1B-69B(3), 1B-69D(7), 1B-71A(1), 1B-71B(3), 1B-71C(5), 1B-71D(7), 1B-72B(3), 1B-72C(5), 1B-72D(7), MSL-147 and MH Bentonite. The numbers in parenthesis in the designation of Series II indicate the number of days required for the synthesis. No specific details can be given concerning the synthetic processes by which these samples were obtained other than the conditions of atmospheric pressure and reflux temperatures because patent litigation has not been completed at this time.

Methods of examination of materials

X-ray diffraction. A Philips Spectrogoniometer was employed using nickel-filtered Cu Kα radiation. The three phases of the X-ray diffraction included examination of powder samples, oriented samples, and glycolated-oriented samples.

Electron microscopy. A Hitachi HU-11a electron microscope was employed. An accelerating potential of 75 kV was used except where maximum penetration was required, when the potential was 100 kV, or when maximum contrast was desired. Approximately 0·01 per cent dispersions of the clay samples were prepared in water and ultrasonically dispersed, and small portions of these were allowed to dry on grids with collodion substrates.

RESULTS

Series I

Series I included samples 2H-2, 2H-3, 2H-4, 2H-5, and 2H-6. The general formula of these clay samples was $7\,SiO_2$: $(5-x)Al(OH)_3$:

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x $Mg(OH)_2$, where $x = 0,1,2,3$ and 4. This series was a mixed montmorillonite–hectorite group.

The group consisted of interstratified montmorillonite and mica, and differing in proportions of dioctahedral and trioctahedral montmorillonite. By x-ray diffraction, sample 2H-2 was shown to be dioctahedral interstratified mica-montmorillonite containing about two-thirds mica layers and one-third montmorillonite layers. Sample 2H-3 was predominantly montmorillonite with 10–20 per cent interlayered mica; most of the montmorillonite was dioctahedral, but some trioctahedral montmorillonite was present. Sample 2H-4 was predominently montmorillonite with 10–20 per cent interlayered mica; trioctahedral montmorillonite and dioctahedral montmorillonite were present in approximately equal amounts, as judged from the (060) diffraction line. The diffraction pattern of sample 2H-5 resembled chlorite; trioctahedral montmorillonite was much more abundant than dioctahedral. By X-ray diffraction, sample 2H-6 was an interstratified montmorillonite-mica in which the montmorillonite was trioctahedral.

Sample 2H-2, which contained no magnesium substitution, was shown by electron microscopy to consist in part of particles apparently similar to natural Wyoming sodium montmorillonite. These particles were very thin and appeared to be very irregular in shape with indistinct edges. The aggregates were for the most part dense and showed some curling along the edges. Figure 1 is a typical electron micrograph of sample 2H-2. The rectangular thin particles with sharp, regular edges found along side the denser curled aggregates were found in all specimens of sample 2H-2. In many photographs particles with these sharp edges mixed with particles with diffuse montmorillonite type edges appeared to be an indication of interstratification.

Selected-area electron diffraction was used to examine individual particles in sample 2H-2 to determine whether they were interstratified montmorillonite-mica. The electron-diffraction evidence agreed with the X-ray diffraction evidence and both indicated that interstratified montmorillonite-mica was present.

Figure 2 is a composite of electron micrographs of the samples of Series I. Figure 2A is sample 2H-2 where the amount of $x = Mg(OH)_2$ has $x = 0$; Fig. 2B is sample 2H-3, $x = 1$; Fig. 2C is sample 2H-4, $x = 2$; Fig. 2D is sample 2H-5, $x = 3$; and Fig. 2E is sample 2H-6, $x = 4$.

The particle size of magnesium-substituted sample 2H-3 was found to be sharply reduced compared to the size of the particles in sample 2H-2. The amount of particle curling increased considerably and was different from that normally found in natural Wyoming sodium montmorillonite. The particles seemed to be rolled up very tightly (Fig. 2B).

Sample 2H-4 displayed more curling and a sharp increase in aggregates of a type which could be easily penetrated by the electron beam and were web-like. Figure 2C illustrates the nature of these particles.

In sample 2H-5, where the amount of $Mg(OH)_2$ was greater than $Al(OH)_3$, curling was present to an even greater extent and aggregates were more abundant than in the other samples. Figure 2D shows the morphology of sample 2H-5.

The morphology of sample 2H-6 differed dramatically from the previous samples. The X-ray diffraction patterns indicated that this synthetic clay had the structure of hectorite. Its composition was $7\ SiO_2$: $Al(OH)_3$: $4\ Mg(OH)_2$. However, instead of long lath-like particles of natural hectorite, sample 2H-6 was made up of thin montmorillonite-like particles. Curling of particles was observed mainly on the edges which seemed to be very loosely rolled.

Several conclusions may be drawn about this particular synthetic clay series. First, there was a sharp decrease in particle size as soon as magnesium was substituted into the clay structure of $7\ SiO_2$: $(5-x)Al(OH)_3$: $x\ Mg(OH)_2$ where $x = 1$. Second, as the amount of magnesium present in the clay product increased, the amount of curling of the clay particles increased until a maximum was reached in sample 2H-5 where $x = 3$. As the amount of curling increased, the tendency for aggregation also increased. In sample 2H-6 where $x = 4$, very little curling was found of the type as that observed in samples 2H-3, 2H-4, and 2H-5. Upon long exposure to the heat of the electron beam the rolled-up particles seemed to loosen and partially unroll.

The catalytic activities of the synthetic clays of Series I were selective. Samples 2H-2, 2H-3, and 2H-6 were excellent cracking catalysts. Since catalytic activity is related to the surface area available, it would be predicted that samples 2H-4 and 2H-5 would not be good catalysts because of the predominance of curled particles. The curling of particles found in 2H-4 and 2H-5 and to some extent in 2H-3 may be attributed to the presence of some magnesium ions in exchange sites of the clay. If this supposition is correct the hydrated magnesium ions may interact with the clay surface to allow curling to take place. This general type of curling has been observed for mixtures of montmorillonite and hydrous oxides (McAtee, 1966, 1967). Upon long exposure to the electron beam the water is driven off and a loosening and unrolling of the particles occurs.

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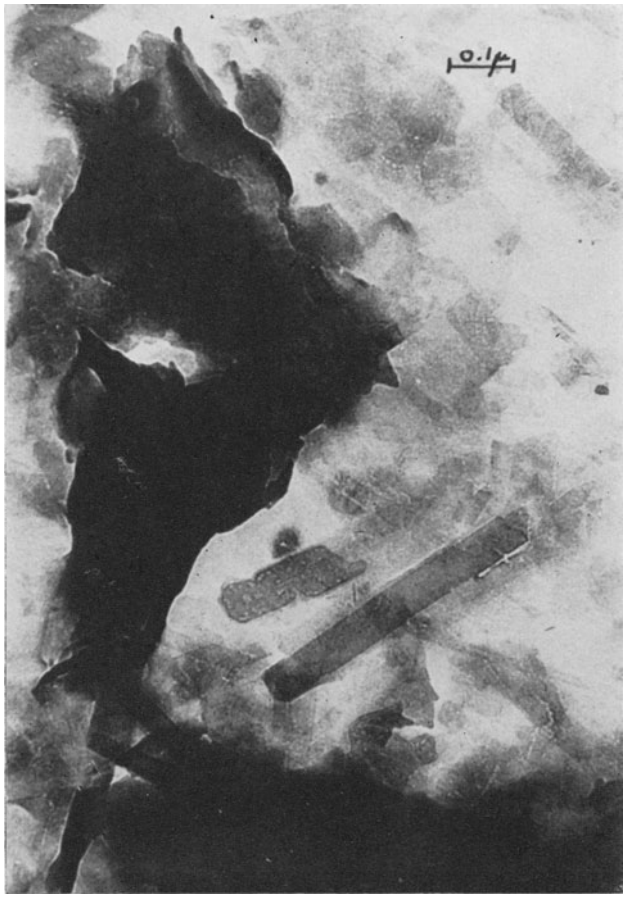


Fig. 1. Sample 2H-2, interstratified montmorillonite-mica, 53,500 ×.

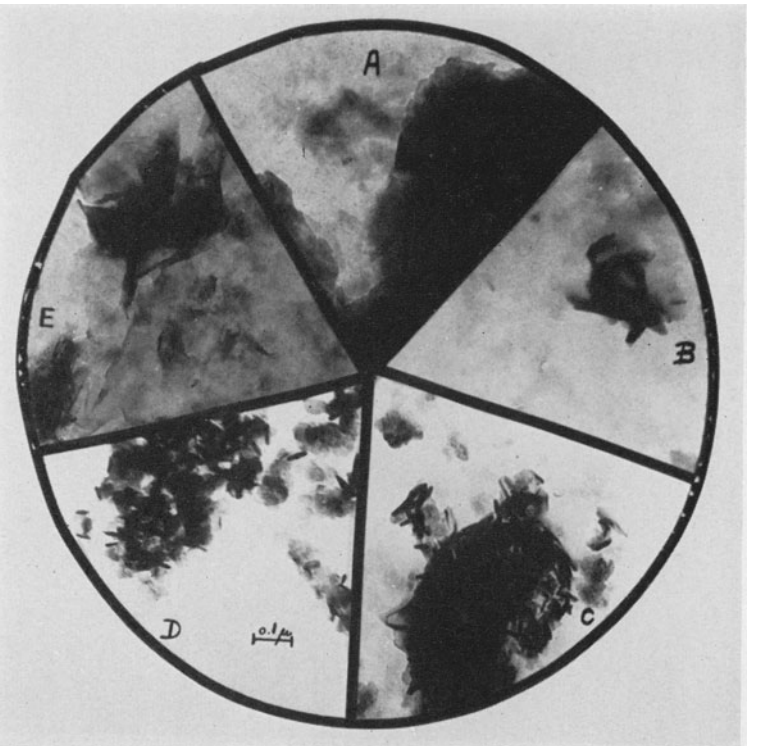


Fig. 2. Series I, $7SiO_2$: $(5 - X)$ Al $(OH)_3$: 4 $Mg(OH)_2$ where $X = 0, 1, 2, 3$ and 4 in A, B, C, D, and E, respectively 53,500 ×.

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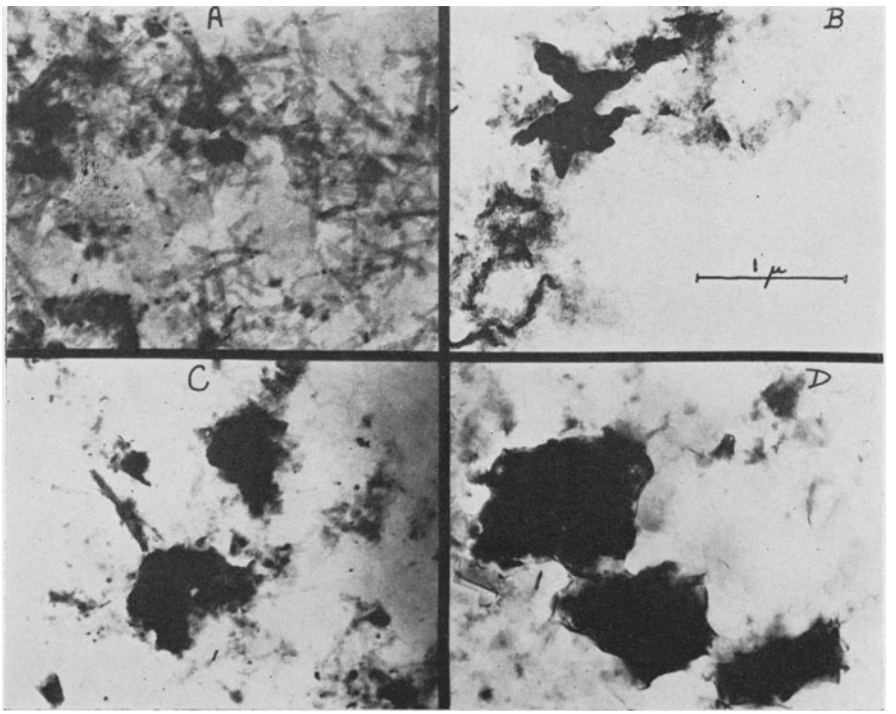


Fig. 3. Series II, Hectorites—A, natural hectorite; B, 1B-72D (7); C, MH Bentonite; D, 2H-6 of Series I. 24,000 ×.

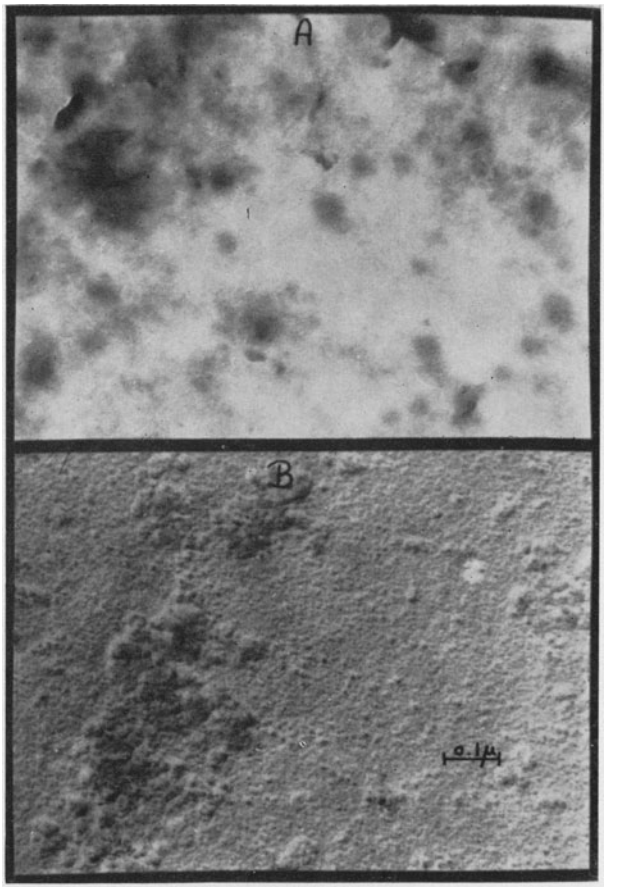


Fig. 4. MSL-147 synthetic hectorite—A, regular sample; B, shadowed with tungsten oxide at angle of 10°. 57,500 ×.

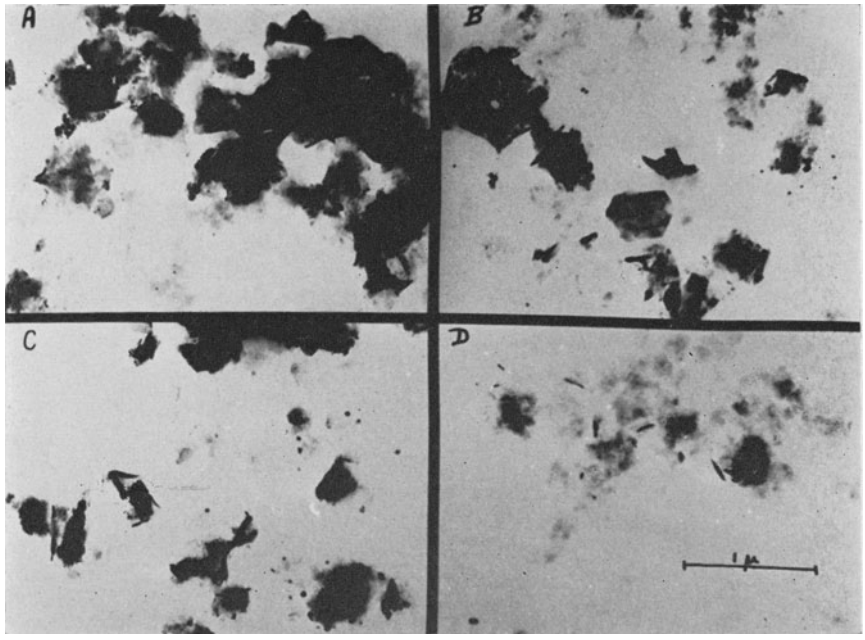


Fig. 5. Series III, A, RCB-1-23 @ 270° showing adsorbed boehmite on clay; B, RCB-1-23 @ 280°; C, RCB-1-23 @ 300°C (3); D, RCB-1-23 @ 300°C (5). 21,000 ×.

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Series II

The second series of samples studied were synthetic hectorite clays designated as follows: 1B-69B(3), 1B-69D(7), 1B-71A(1), 1B-71B(3), 1B-71C(5), 1B-71D(7), 1B-72A(1), 1B-72B(3), 1B-72C(5), and 1B-72D(7). These clays were prepared by Granquist (1960) and used in a comparative study with some hectorites synthesized by the Strese and Hoffman method (1941). The samples were prepared by basing the starting ratios of the constituents on the general formula of $[(Li_xMg_{6-x})Si_8O_{20}(F_g(OH)_{4-g})]^{x-} \cdot x\,Na^+$. The diagnostic criterion used to determine whether these samples were hectorite-type clays was (060) spacing greater than 1·5 Å. The ratio of $SiO_2/MgO/Li_2O/Na_2O$ for the 1B-69 series was 1·33/1·0/0/0·124, for the 1B-71 series 1·33/1·0/0·124/0 and for the 1B-72 series 1·33/1·0/0·248 (LiF)/0.

Another more recently synthesized hectorite sample designated MSL-147 was also studied. Finally samples of MH Bentonite, a natural clay, which X-ray diffraction indicated to be hectorite, were also studied and included.

Natural hectorite is made up of very thin low-contrast, lath-like particles, but the synthetic hectorite clays are sheet-like particles that resemble the morphology of montmorillonite.

Figure 3 shows some samples of Series II hectorites. Figure 3A is natural hectorite. If one compares Fig. 3A with Fig. 3B, sample 1B-72D (7), the difference in morphology may be seen. Other samples in Series II were similar to this specimen.

Two samples of MH Bentonite, a naturally occurring clay, shown to be trioctahedral magnesium montmorillonite by X-ray diffraction data were studied; however, its rheology was different from other natural hectorites. Figure 3C shows that MH Bentonite did not have the same morphology as natural hectorite, but was similar to natural montmorillonite. Some lath-like particles are present, but they are minor. Figure 3D shows sample 2H-6 of Series I. The size and shape of the particles of this sample were very similar to dioctahedral sodium montmorillonite.

Electron micorgraphs of MSL-147 synthetic hectorite are shown in Fig. 4A. This synthetic hectorite was made up of very small irregularly-shaped particles. Figure 4B is an electron micrograph of a MSL-147 sample shadowed at an angle of approx 10° with tungsten oxide.

Series III

Series III consisted of the following samples: RCB-1-23 @ 270°C, RCB-1-23 @ 280°C, RCB-1-23 @ 290°C, RCB-1-23 @ 300°C(0), RCB-1-23 @ 300°(3), and RCB-1-23 @ 300°C(5). The figure in parenthesis indicates the number of days of synthesis. These samples were obtained at various temperatures and times of reaction from pilot plant synthetic clays and had compositions which should lead to montmorillonites. The samples were studied to determine the best temperature for the reaction synthesis and also to ascertain if any advantage could be gained by extending the time the sample was held at the reaction temperature. By X-ray diffraction the two main components of these samples were found to be montmorillonite and boehmite in varying amounts.

The electron microscopy study of the samples showed that as the series progressed from RCB-1-23 @ 270°C to RCB-1-23 @ 300°C(5), the end-member of the series, the pronounced curling of the clay decreased. By X-ray diffraction, sample RCB-1-23 @ 270°C had the greatest concentration of boehmite of the six samples, while RCB-1-23 @ 300°C(5) exhibited the least curling and had a much lower concentration of boehmite.

The activity of the clay as a catalyst again was related to the amount of curling present. It is believed that the degree of curling is directly related to the amount of boehmite present in the sample. McAtee and Shaw (1965) showed that the mutual adsorption of hydrous chromium oxide and sodium montmorillonite caused curling of the montmorillonite clay. The amount of curling present was related to the proportion of chromium oxide in the sample mixture. McAtee and Wells (1967) showed that hydrous aluminum oxide and sodium montmorillonite behaved in a similar manner.

Figure 5 shows electron micrographs of Series III at a magnification of ×21,000. Figure 5A exhibits the adsorption of the boehmite on the synthetic sodium montmorillonite clay RCB-1-23 @ 270°C. Figure 5B shows sample RCB-1-23 @ 280°C. Again a large amount of curling was found to be present. Figure 5C, RCB-1-23 @ 300°C(3), showed that the curling present in the sample decreased appreciably and the aggregates were of RCB-1-23 @ 300°C(5). The clay in this sample exhibited very little if any more curling than was found in natural montmorillonite clay.

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Résumé – La morphologie de la montmorillonite et de l'hectorite synthétiques a été étudiée à l'aide de techniques de microscopie électronique et de diffraction à rayons X. Les techniques de microscopie et de diffraction électroniques permettent d'identifier dans ces échantillons des particules de montmorillonite et de mica interstratifiées. Des échantillons à substitution de magnésium avaient une tendance croissante à onduler à mesure que le contenu de magnésium augmentait, sauf pour l'argile de magnésium du dernier membre. Les argiles d'hectorite synthétique n'ont pas nécessairement la même morphologie que les argiles d'hectorite naturelle. On a également étudié la morphologie d'une série d'échantillons obtenus à la suite d'une étude de la cinétique de la cristallisation. La boehmite et la montmorillonite formaient les constituants de base du système. Les particules d'argile de montmorillonite formaient des ondulations autour de la boehmite qui avait été absorbée sur les surfaces de base de la montmorillonite.

Kurzreferat – Die Morphologie von synthetischem Montmorillonit und Hektorit wurde unter Verwendung der Elektronenmikroskopie und Röntgenbeugungstechnik studiert. Montmorillonit-Glimmer Teilchen mit Zwischenschichtung konnten in diesen Proben durch Elektronenmikroskopie und Elektronenbeugungstechniken identifiziert werden. In Mg-substituierten Proben wurde festgestellt, dass mit steigendem Magnesiumgehalt eine zunehmende Neigung zur Krümmung auftritt. Eine Ausnahme bildet der Endglied-Magnesiumton. Synthetische Hektorittone haben nicht unbedingt die gleiche Morphologie wie natürliche Hektorittone, Ferner Wurde eine Studie der Morphologie einer Reihe von Proben durchgeführt, die in einer Untersuchung der Kristallisationskinetik erhalten wurden. Die Grundbestandteile des Systems waren Boehmit und Montmorillonit. Es wurde festgestellt, dass sich die Montmorillonitteilchen um den Boehmit legen, der an den Grundflächen des Montmorillonits absorbiert worden war.

Резюме—Морфология синтетического монтмориллонита и гекторита исследовалась, пользуясь электронной микроскопией и методами дифракции рентгеновских лучей. Переслаивающиеся частицы монтмориллонита—слюды могут быть отождествлены в этих образцах электронной микроскопией и методами дифракции электронов. Замененные магнием образцы показали повышенную степень закручивания, по мере увеличения содержания магния, за исключением концевого элемента—магниевой глины. Синтетические гекторитовые глины не обязательно имеют ту же морфологию, как естественные гекторитовые глины. Исследовали также морфологию серии образцов, полученных при изучении кинетики кристаллизации. Бемит и монтмориллонит были основными составными частями этой системы. Было доказано, что частицы монтмориллонитовой глины завились вокруг бемита, поглощенного на базалвных поверхностях монтмориллонита.

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