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STUDIES ON THE FLUORODERIVATIVES OF LAYER SILICATES

II. THE EFFECT OF FLUORIDE SOLUTIONS ON THE STRUCTURAL AND SURFACE PROPERTIES OF MONTMORILLONITE

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Abstract. The nature of structural changes of montmorillonite effected by ammonium fluoride solutions have been investigated and the degradation processes of that mineral analysed. The effect of activation conditions on some physico-chemical properties of the reaction products have been determined basing on X-ray, IR spectroscopic and electron microscope investigations, as well as on measurements of argon, n-hexane and methyl alcohol vapour sorption.

INTRODUCTION

Recently, there has been lively interest in the properties and methods of preparation of fluoroderivatives of layer silicates. Several authors have studied the problems related to that subject, e.g. ionic substitution OH^-/F^- (Romo, Roy 1957; Fijał, Ziętkiewicz 1969; Hübner 1969), synthesis and evaluation of physico-chemical properties of fluoroderivatives thus obtained (Granquist, Pollak 1960; Granquist, Kennedy 1967; Barrer, Jones 1970, 1971a, b), structural changes of layer silicates effected by fluorine compounds (Fijał, Tokarz 1975).

The present studies aim to define the changes in the physico-chemical properties of montmorillonite, produced by reaction with ammonium fluoride solutions. The nature of structural changes of that mineral and chan-

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ges in its surface and sorption properties during fluorination have been investigated, and the effect of fluoride solution concentrations and activation time analysed.

EXPERIMENTAL

The sample of montmorillonite from Chmielnik and the products of its activation with NH_4F solutions were subjected to X-ray, infrared spectroscopic, electron microscope and sorption analyses. The effect of activation time and NH_4F solution concentration on the nature of structural changes of montmorillonite was determined.

The analysed samples were designated as follows:

M-0 — non-treated ammonium montmorillonite
M-1 — sample activated with 1.5 n NH_4F for 1 hour at 60°C
M-2 — sample activated with 1.5 n NH_4F for 3 hours at 60°C
M-3 — sample activated with 1.5 n NH_4F for 5 hours at 60°C
M-4 — sample activated with 1.5 n NH_4F for 15 hours at 60°C
M-5 — sample activated with 1.5 n NH_4F for 3 months at 25°C
M-6 — sample activated with 3.0 n NH_4F for 3 hours at 60°C
M-7 — sample activated with 3.0 n NH_4F for 5 hours at 60°C
M-8 — sample activated with 3.0 n NH_4F for 15 hours at 60°C

X-ray analyses were carried out in TUR M-61 diffractometer. Infrared absorption spectra were recorded on UR-10 (Zeiss) spectrophotometer. Electron microscope investigations were performed by means of a Tesla transmission microscope, using an accelerating voltage of 100 kV. The surface and sorption properties were defined on the basis of sorption of argon, methyl alcohol and *n*-hexane vapours.

X-RAY INVESTIGATIONS

X-ray investigations were carried out on non-treated sample and on the products of its reaction with NH_4F solutions.

X-ray diffraction pattern of sample *M-1* (Fig. 1) shows the reflections of montmorillonite (d_{hkl} = 12.5, 4.51, 2.58, 2.21 Å) and NH_4MgAlF_6 (d_{hkl} = = 5.81, 3.03, 2.90, 2.31, 2.05, 1.91 Å). The diffusion of *001* reflection suggests a decrease in the number of montmorillonite crystallites, whereas its lower intensity compared with non-treated sample indicates that the crystal lattice of montmorillonite has become defect. A weak reflection d_{hkl} = 3.34 Å is due to the presence of trace amount of quartz.

X-ray diffraction patterns of sample *M-2*, *M-3* and *M-4* (Fig. 1) show reflections of the same components as have been noted on the X-ray pattern of sample *M-1*. However, further decrease in the intensity of *001* reflection of montmorillonite and its diffusion may be observed while the intensity of reflections produced by NH_4MgAlF_6 increases. This variability becomes conspicuous if the intensity of reflections 5.85 Å (NH_4MgAlF_6, Campbell *et al.* 1972) and 4.50 Å (montmorillonite) is compared on the X-ray diffraction patterns of all samples.

Investigations were also carried out on sample activated with NH_4F solution for 3 months at 25°C. Its X-ray diffraction pattern (Fig. 1) reveals

a substantial increase in the amount of NH_4MgAlF_6, resulting from prolonged fluorination.

X-ray examinations of samples activated with 3 n NH_4F solution have shown that the process of montmorillonite destruction is much faster than in samples treated with fluoride solutions of lower concentration.

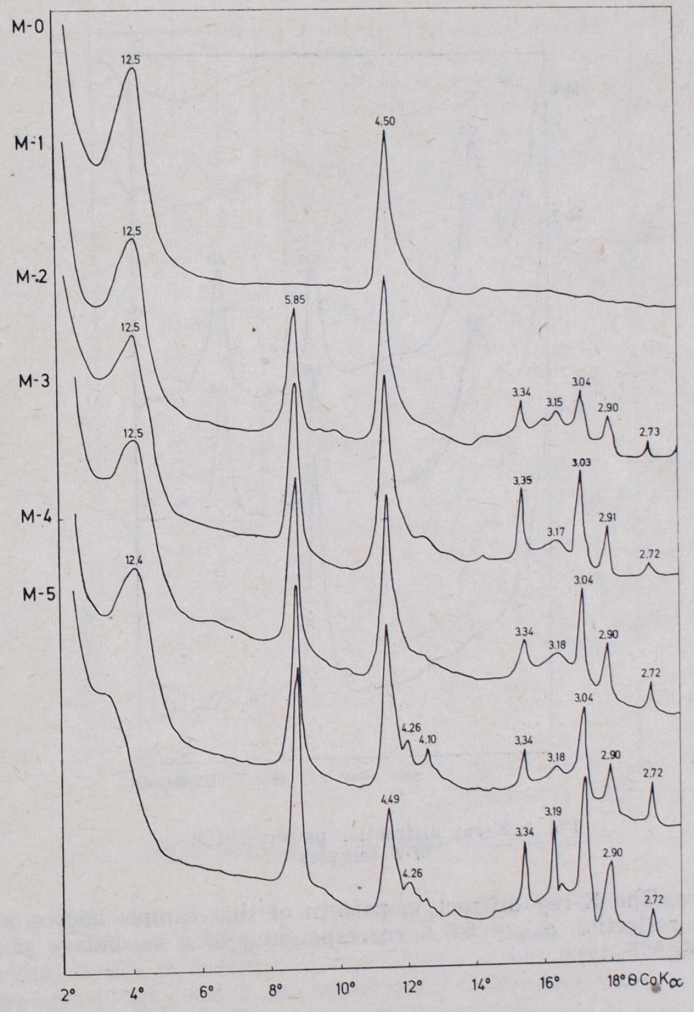

Fig. 1. X-ray diffraction patterns of *M-0*—*M-5* samples

On the X-ray diffraction pattern of sample activated for 3 hours (Fig. 2, sample *M-6*), a pronounced decrease in the intensity of *001* reflection of montmorillonite (d_{001} = 12.5 Å) may be noticed, which evidences that the crystal lattice of that mineral has become defect. A reflection about 5.8 Å

due to the presence of a secondary phase of the NH_4MgAlF_6 type is also visible. After 5-hour activation, the structural changes in montmorillonite become more profound, which is indicated by further diffusion and weakening of *001* reflection and higher intensity of the reflection produced by NH_4MgAlF_6 (5.8 Å; Fig. 2, sample *M-7*). Prolonged activation (15 hours; Fig. 2, sample *M-8*) results in complete disappearance of montmorillonite

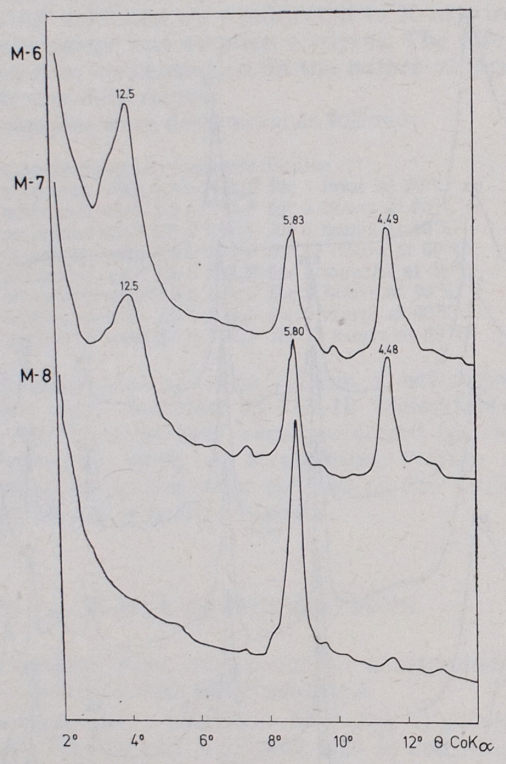

Fig. 2. X-ray diffraction patterns of *M-6*—*M-8* samples

reflections. The X-ray diffraction pattern of that sample shows only an intensive reflection $d_{hkl} = 5.8$ Å corresponding to a secondary phase of the NH_4MgAlF_6 type.

INFRARED SPECTROSCOPIC INVESTIGATIONS

The process of degradation and partial decomposition of the structure of montmorillonite is documented by IR absorption spectra of sample *M-0* to *M-8*. The spectra of samples *M-0* to *M-4* (Fig. 3) evidence the structural changes occurring in montmorillonite as activation with 1.5 n NH_4F solu-

tion is prolonged. Differences between the spectra in the area of ν_3 vibrations of SiO_4^{4-} tetrahedra in the range of 1000 — 1200 cm^{-1} have been noted. During fluorination the octahedral layer is the first to decompose, which results in a higher intensity of the band 1080 cm^{-1}. Simultaneously, the intensity of Al—O band at 520 cm^{-1} decreases, and so does the intensity of bands arising from valence and deformation vibrations of OH

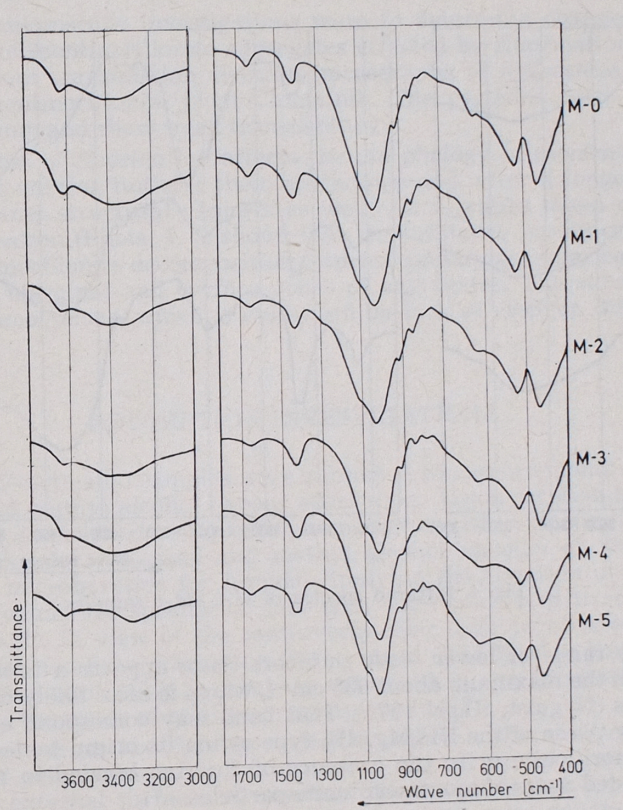

Fig. 3. Infrared spectra of *M-0*—*M-5* samples

groups at 3630 and 920 cm^{-1}, respectively. Moreover, the band 520 cm^{-1}, produced by Al—F bonds forming in the process of F^- incorporation in the crystal lattice of montmorillonite, shows an increase in intensity. The appearance of that band is due additionally to the formation of secondary phases resulting from the breakdown of montmorillonite.

At high concentrations of ammonium fluoride solutions (3 n), the course of the fluorination process is different than in the case when lower concentrations are used. The structural changes occurring in montmorillonite under those conditions are evidenced by the infrared spectra shown in Figure 4. They may be readily observed on the spectrum of sample activated with 3 n NH_4F solution for 3 hours (Fig. 4, sample *M-6*). Variations in

the contour of ν_3 bands of SiO_4^{4-} tetrahedra (diffusion towards higher wave numbers), as well as the appearance of the band about 1170 cm^{-1} and the maximum 800 cm^{-1} are indicative of changes in the ordering of the lattice within the tetrahedral layers. Those changes result in three--dimensional condensation of SiO_4^{4-} tetrahedra in the degraded zones of montmorillonite aggregates, from which octahedral cations (Al^{3+} and Mg^{2+}) have been partly leached.

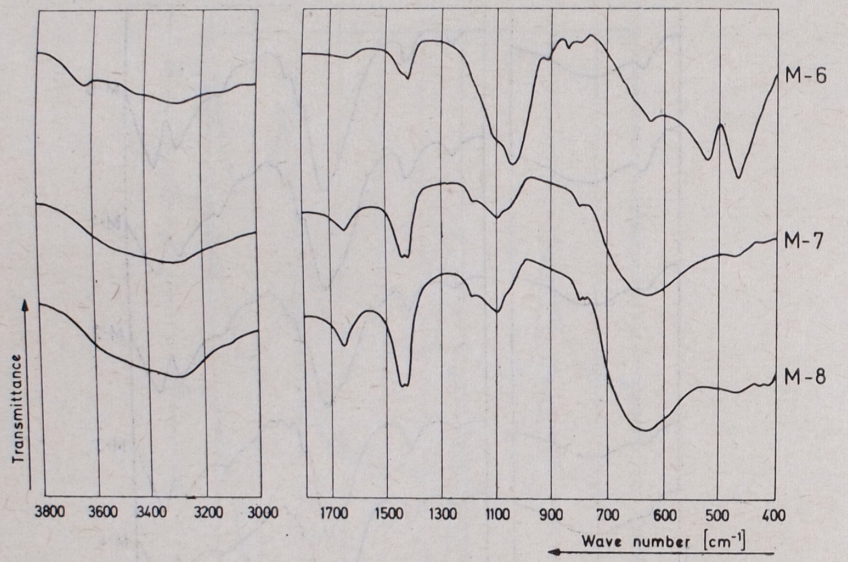

Fig. 4. Infrared spectra of *M-6*—*M-8* samples

In the range of lower wave numbers there appears a broad, diffused band with the maximum about 635 cm^{-1}, which is most likely due to Al—F vibrations (Nyguist, Kagel 1971). That band may correspond either to the secondary phase of the NH_4MgAlF_6 type owing its origin to decomposition of montmorillonite or to the presence of fluorine bonded to Al^{3+} ions in the degraded zones of montmorillonite particles.

Further activation of montmorillonite (5 hours) results in practically complete decomposition of its structure (Fig. 4, sample *M-7*). Weak bands in the range of Si—O vibrations (1000 — 1200 cm^{-1} and 400 — 500 cm^{-1}) correspond to residual montmorillonite as well as to quartz, whose presence in the sample is revealed only after nearly complete breakdown of montmorillonite.

Similar to the above spectrum is that of the sample activated for 15 hours (Fig. 4, sample *M-8*). The basal absorption bands (630, 1410, 1440, 3100 and 3300 cm^{-1}) are due to the presence of secondary ammonium fluoroaluminate. The other bands correspond to a small admixture of quartz which, under the experimental conditions, has not been completely decomposed yet.

From the above investigations it appears that fluorination with 1.5 n NH_4F solution leads to partial breakdown (degradation) of the structure

of montmorillonite. Under those conditions, the process of OH/F substitution occurs simultaneously. Higher NH_4F concentrations bring about primarily the decomposition of montmorillonite.

ELECTRON MICROSCOPE INVESTIGATIONS

Electron microscope investigations were to determine changes in the morphology of montmorillonite aggregates effected by fluorination. Phots. 1 and 2 present transmission electron micrographs of aggregates characteristic of montmorillonite from Chmielnik. The particles have angular, rugged contours and show weak transparency.

The process of fluorination affects the morphology of montmorillonite aggregates, involving initially their breakdown and, after a longer period of time, distinct structural changes as well. Micrographs taken after 15--hous fluorination (Phots. 3, 4) shows that the substance produced as a result of montmorillonite decomposition forms secondary granular concentrations in the marginal and surface zones of aggregates. The substance in question is amorphous, which is evidenced by lack of electron diffraction.

ADSORPTION INVESTIGATIONS

The NH_4F-activated samples were subjected to measurements of argon, *n*-hexane and methyl alcohol vapour adsorption. Argon sorption isotherms at 77K were determined using sorption manostats, whereas sorption equilibrium curves for *n*-hexane and methyl alcohol vapours at 298K were obtained in microburettes for liquids. Applying the equation of the BET theory, the values for specific surface area were calculated from the isotherms (Tab. 1). In view of the controversy over their physical sense, the values determined from adsorption isotherms of CH_3OH were treated only as a parameter permitting to compare variations in the sorption capacity of samples in the range of relative pressures up to 0.3.

As appears from the data provided by other authors, adsorption of molecules of polar substances, i.e. of methyl alcohol as well, proceeds not only on the external surfaces of montmorillonite aggregates but also, and above all, in the interlayer and pore spaces to which gives rise the textural orientation of montmorillonite particles and domains that make up the aggregates.

The primary factor controlling the amount of sorbed vapours of polar substances is the interlayer cations. From the studies carried out by Żyła (1972) it is evident that sorption of polar substance vapours depends on the valency of a cation, and in the case of equivalent cations, on the size of their ionic radii. There is also a possibility for methyl alcohol molecules to be linked by a hydrogen bond. *N*-hexane and argon molecules may be bound by dispersive forces.

The adsorptive properties of activated samples were compared with those of ammonium montmorillonite. A survey of the specific surface areas (Tab. 1) reveals a systematic decrease in the sorption capacity (CH_3OH) with the activation time (sample *M-0* to *M-5*). This fact is highly suggestive

of a decrease in the number of sorption polar centres during the reaction of NH_4F with montmorillonite. This is due to partial degradation of the octahedral layer of montmorillonite, which, in turn, results in that the number of exchange cations is reduced. The substitution of OH groups by fluorine ions should enhance methyl alcohol adsorption since F^- has greater electronegativity compared with OH^-; yet, a decrease in the exchange capacity is the dominant process.

The surface area values determined from sorption isotherms of argon and *n*-hexane vapours increase with activation time due to the structure of montmorillonite becoming accessible to molecules of those adsorbates.

It is interesting to note that the surface area values determined from the methyl alcohol and argon sorption isotherms for samples activated for 8 and 15 hours are similar. This fact strengthens the evidence that montmorillonite undergoes degradation under the influence of NH_4F.

Figure 5 presents curves of pore volume distribution against Kelvin radius, plotted from argon desorption isotherms (Brunauer *et al.* 1938).

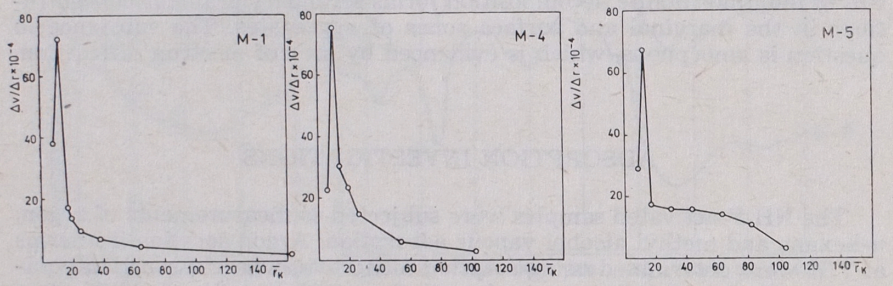

Fig. 5. Pore volume distribution curves against Kelvin radius, plotted from argon desorption isoterms for *M-1*, *M-4* and *M-5* samples

Pore volume distributions for samples activated with 1.5 n NH_4F do not show any visible changes in the initial phase of activation (up to 8 hours). Additional porosity has been noted in sample *M-4*. It is, however, prolonged activation (sample *M-5*) that produces more profound changes in the pore structure and is responsible for additional porosity in the range of transitional pores (from 25 to 90 Å r_k).

The presence of an intensive peak at the r_k value of about 12 Å (corresponding to about 15 Å of the effective radius r_e) is due, in the authors' opinion, to the fact that the degradation products retain layered structure even after a longer period of activation with 1.5 n NH_4F (Fijał, Kłapyta *et al.* 1975).

DISCUSSION

The mechanism of reaction between fluoride solutions and montmorillonite is controlled by the reaction conditions. The concentration of fluoride solutions is of prime importance in that process. Low concentrations (up to 1 n) cause mainly the OH^-/F^- substitution to take place,

whereas higher concentrations result in the first place in the destruction of the crystal lattice. Depending on the conditions, one or the other type of reaction prevails, but, as a rule, the reactions proceed simultaneously.

The OH/F substitution is effected by diffusion of F^- ions into the crystal lattice of montmorillonite. Depending on the reaction conditions and the degree of dispersion of the sample, either substitution in the surface zone of aggregates or the replacement of OH groups inside the montmorillonite particles is involved.

The processes of degradation or decomposition of the montmorillonite structure initiated by intensive fluorination (at higher concentrations) are associated with the breaking of the continuity of the lattice and result in the distruption of Si-O-Si and Si-O-Al oxygen bridges. Initially, the degradation processes are confined only to the surface zones of montmorillonite aggregates and particles, involving partial breakdown of the crystal lattice and its amorphization. This is evidenced by the results of X-ray and electron microscope investigations since the external zones of montmorillonite aggregates with rugged and defect contours fail to give electron diffraction. The superficial destruction of the lattice is attended by incorporation of fluorine in the sites of O^{2-} ions. Further activation of montmorillonite involves the decomposition of its structure due to the removal of cations from the tetrahedral (Si^{4+}) and octahedral layers (Al^{3+}, Mg^{2+}, Fe^{3+}), notably from the defect zones. Complex ions, AlF_6^{3-}, SiF_6^{2-}, MgF_6^{4-}, go then into solution, forming subsequently secondary phases of the NH_4MgAlF_6 type that have been identified by X-ray method.

Prolonged fluorination of montmorillonite with solutions of high concentration may result in complete breakdown of its structure and the replacement of that mineral by secondary fluorosilicates and fluoroaluminates.

The process of fluorination has been also reflected in the results of adsorption investigations. The systematic decrease in the values of specific surface areas determined from sorption of methyl alcohol vapours is highly suggestive of a decrease in the number of polar centres (drop in the number of cations on the exchange positions) during activation with 1.5 n NH_4F solution. Partial destruction of the lattice and loosening of the structure of montmorillonite aggregates, effected by 1.5 n NH_4F, are reflected in the higher values of surface areas determined from sorption of vapours of nonpolar substances (argon, *n*-hexane). Samples activated with 3 n NH_4F solution have very low surface area values due to far-advanced degradation of the structure of montmorillonite.

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Z BADAŃ NAD FLUOROPOCHODNYMI KRZEMIANÓW PAKIETOWYCH

II. WPŁYW ROZTWORÓW FLUORKÓW NA STRUKTURALNE I POWIERZCHNIOWE WŁASNOŚCI MONTMORILLONITU

Streszczenie

Przebadano naturę przeobrażeń strukturalnych montmorillonitu pod działaniem roztworów fluorku amonowego. Analizie poddano przebieg procesów degradacji tego minerału, określono wpływ warunków aktywacji na niektóre fizykochemiczne własności produktów reakcji w oparciu o pomiary sorpcji par argonu, n-heksanu i alkoholu metylowego. Analizowano wyniki badań rentgenowskich i spektroskopowych w podczerwieni oraz elektronograficznych.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy rentgenowskie próbek *M-0* do *M-5*
Fig. 2. Dyfraktogramy rentgenowskie próbek *M-6* do *M-8*
Fig. 3. Spektrogramy w podczerwieni próbek *M-0* do *M-5*
Fig. 4. Spektrogramy w podczerwieni próbek *M-6* do *M-8*
Fig. 5. Krzywe rozkładu objętości porów w funkcji promienia kelwinowskiego wyznaczone z izoterm desorpcji argonu dla próbek *M-1*, *M-4* i *M-5*

OPIS FOTOGRAFII

Fot. 1. Obraz elektronowy agregatów montmorillonitu z Chmielnika. Pow. × 45 000
Fot. 2. Obraz elektronowy agregatów montmorillonitu z Chmielnika. Pow. × 20 000
Fot. 3. Obraz elektronowy produktów fluorowania montmorillonitu (próbka *M-4*). Pow. × 30 000
Fot. 4. Obraz elektronowy produktów fluorowania montmorillonitu (próbka *M-4*). Pow. × 40 000

Ежи ФИЯЛ, Зенон КЛАПЫТА, Януш ЗЕНТКЕВИЧ, Мечыслав ЖИЛА

ИССЛЕДОВАНИЕ ФТОРСОДЕРЖАЩИХ СЛОИСТЫХ СИЛИКАТОВ

Ч. II. ВЛИЯНИЕ РАСТВОРОВ ФТОРИДОВ НА СТРУКТУРНЫЕ И ПОВЕРХНОСТНЫЕ СВОЙСТВА МОНТМОРИЛЛОНИТА

Резюме

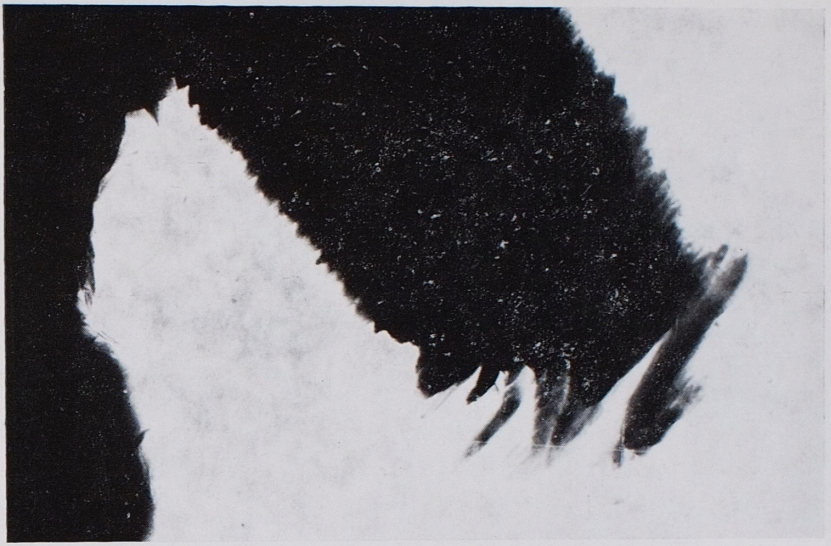
Изучено природу структурных изменений монтмориллонита под воздействием растворов фторида аммония. Подвергнуто анализу ход процессов деградации этого минерала, на основании сорбции паров аргона, n-гексана и метилового алкоголя, определено влияние условий активации на некоторые физико-химические свойства продуктов реакции. Проанализировано результаты рентгеновских, электронографических, а также инфракрасно-спектроскопических исследований.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы образцов *M-0* до *M-5*
Фиг. 2. Дифрактограммы образцов *M-6* до *M-8*
Фиг. 3. ИК-спектры образцов *M-0* до *M-5*
Фиг. 4. ИК-спектры образцов *M-6* до *M-8*
Фиг. 5. Кривые распределения объема пор в функции Кельвина, построенные по изотермах десорбции аргона для образцов *M-1*, *M-4* и *M-5*

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

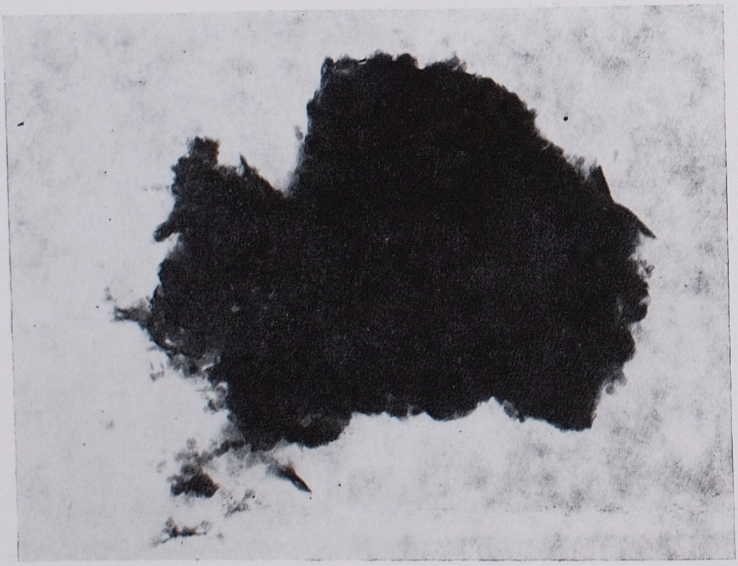
Фот. 1. Электронное изображение агрегатов монтмориллонита из Хмельника, × 45 000
Фот. 2. Электронное изображение агрегатов монтмориллонита из Хмельника, × 20 000
Фот. 3. Электронное изображение продуктов фторирования монтмориллонита (образец *M-4*), × 30 000
Фот. 4. Электронное изображение продуктов фторирования монтмориллонита (образец *M-4*), × 40 000



Phot. 1. Electron micrograph of untreated montmorillonite from Chmielnik. × 45 000

Phot. 2. Electron micrograph of untreated montmorillonite from Chmielnik. × 20 000

Phot. 3. Electron micrograph of fluorinated montmorillonite (*M-4* sample). × 30 000



Phot. 4. Electron micrograph of fluorinated montmorillonite (*M-4* sample). × 40 000