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STUDIES ON THE FLUORODERIVATIVES OF SILICATE MINERALS WITH LAYERED STRUCTURE I. SOME ASPECTS OF THE REACTION OF KAOLINITE WITH FLUORIDE SOLUTIONS

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Abstract. The mechanism of the action of ammonium fluoride solutions on the crystal lattice of kaolinite has been investigated. Special attention has been paid to the process of kaolinite degradation in fluoride solutions and to the crystallochemical character of the resultant reaction products. A method of determining the degree of degradation of the surficial zones of the kaolinite crystallite aggregates involving measurements of the intensity ratio of the reflections *001* and *002* has been suggested.

INTRODUCTION

The paper presents the data yielded by a study of the degradation of kaolinite caused by the action of ammonium fluoride solutions. The effect of alkaline fluoride solutions on silicates with layered structure was investigated by several authors (Dickman, Bray 1941; Samson 1952; Romo, Roy 1957; Fijał, Ziętkiewicz 1968, 1969; Hübner 1969). Yet, their works dealt with the ionic substitution OH^-/F^- and the procedures adopted in the investigations of those phenomena rather than with the crystallochemical character of the degraded mineral substances obtained as products of the reaction with fluorides. These problems are the subject of the present paper.

It is well known that the reaction of fluoride solutions with clay and other minerals containing hydroxyl groups is attended by an increase in alkalinity of the solution due to the OH^- groups passing to the liquid phase. This process may be accounted for both by the substitution of OH^- by F^- and by the decomposition of the mineral structure. These pheno-

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mena are accompanied by degradation of minerals (amorphization), leaching of some ions from the crystal lattice, and by the rise of secondary phases formed from the products of mineral decomposition. Applying a combination of phase and chemical methods, it is possible to predict the probability of occurrence of each type of reaction or the simultaneity of their occurrence. Infrared absorption spectroscopy proved to be particularly useful for this purpose since it permits to follow the progress of the reaction of mineral phases with fluoride solutions and to evaluate quantitatively the substitution processes (Romo, Roy 1957; Fijał, Ziętkiewicz 1968, 1969).

EXPERIMENTAL PROCEDURE

The analyses were carried out on an almost monomineral kaolinite sample obtained by elutriation of kaolinite clay derived from the Jegłowa deposit. X-ray examinations have revealed only a slight admixture of illite and quartz.

This material was treated with NH_4F solutions under different conditions. The effect of the fluoride solution concentrations, the time of the process and of temperature on the course of reaction was determined. The following concentrations of NH_4F solution were used: 0.5, 1.0, 1.5, 2.0 and 3.0 n. The character of structural changes was recorded as the activation time was prolonged. The effect of temperature on the process of kaolinite decomposition was investigated at 20 and 50°C.

The progress of the reactions was followed using X-ray, infrared spectroscopic and electron microscope methods.

EXPERIMENTAL DATA

a) X-ray examinations

X-ray investigations were carried out on the TUR-M61 diffractometer. The character of the structural changes in kaolinite occurring in the course of reaction with ammonium fluoride was determined, and the secondary phases formed in this process were identified.

X-ray diffraction patterns of a non-treated sample and those fluorinated with 1.5 n NH_4F solution for 1, 3, 5 and 15 hours at 50°C (Fig. 1 *a*—*e*) were taken. To investigate the relative changes in the intensity of reflections coming from different lattice planes in the structure of kaolinite, samples were prepared so as to eliminate the effect of preferred orientation of kaolinite flakes on the intensity of *001* reflections. Accordingly, kaolinite samples with a 20% addition of powdered cork (fraction $< 230\ \mu$) were prepared.

As appears from the diffraction patterns, the intensity of kaolinite reflections gradually decreases as the reaction time is prolonged. This evidences on one hand that the degradation of the structure of kaolinite (its amorphization) is advancing and, on the other, that kaolinite becomes solubilized, which enables the formation of secondary phases. Changes in the intensity of the reflections *001*, *020* and *002* were observed. The in-

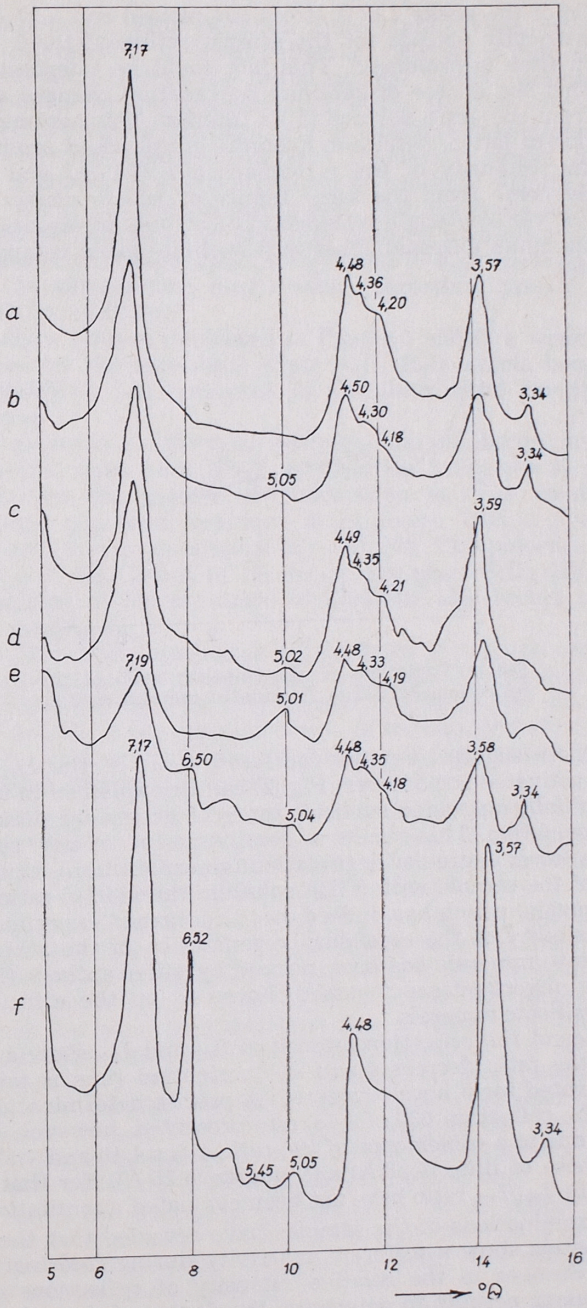

Fig. 1. X-ray diffraction patterns

a — initial kaolinite sample (from Jegłowa), *b*—*e* — kaolinite samples fluorinated with 1.5 n NH_4F solution at 50°C for 1, 3, 6 and 15 hour, respectively, *f* — kaolinite sample fluorinated with 1.5 n NH_4F solution for 3 months at 20°C

tensity ratio of the peaks 7.17 Å (from *001* planes) and 3.57 Å (*002*) decreases systematically (except for the sample activated for 5 hours) as the fluorination time is prolonged. This fact could be interpreted on an assumption that the degree of kaolinite degradation changes as the process advances from the grain surface to its interior. This assumed gradient of concentration of lattice defects in kaolinite grains could produce the differences in the intensity of the reflections *001* (7.17 Å) and *002* (3.57 Å), though they come from the same family of lattice planes. It has been assumed that the low-angle reflection *001* affords information on the ordering of the more external zones in a kaolinite grain compared with the reflection *002*.

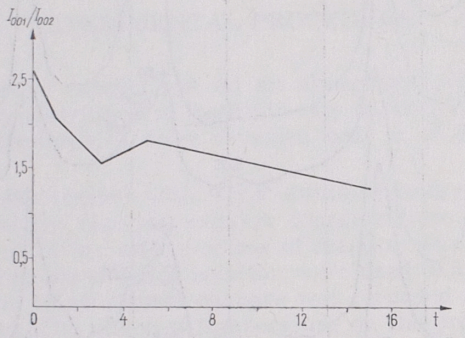

Fig. 2. Variations in the intensity ratio of the reflections *001/002* of fluorinated samples vs. time

The authors suggest that the increased value of the I_{001}/I_{002} ratio in the sample activated for 5 hours (Fig. 2) can be explained in the following way: the initially degraded surficial zones of grains are dissolved due to further fluorination. This results in local exposure of new surface layers that show a lower degree of degradation (amorphization). Upon prolonged treatment of the sample with NH_4F solution, the I_{001}/I_{002} ratio is expected to increase again, which has, indeed, been confirmed experimentally.

The possibility of the secondary regeneration of the surface zones of aluminosilicate minerals has been noticed by other authors (Ferrel, Grim 1967). Their investigations focussed, however, on the effect of alkaline medium on silicate minerals.

The ratios of the reflection intensities I_{001} and I_{002} show a similar tendency, i.e. the ratio decreases as the fluorination time is prolonged, the sample activated for 5 hours excepted. A precise determination of the intensity of the reflection *020* of kaolinite presented, however, considerable difficulties due to a coincidence of the reflections 4.48 and 4.17 Å of kaolinite with those of illite (4.50 Å) and quartz (4.25 Å). For that reason, variations in the I_{001}/I_{020} ratio have not been evaluated guantitatively.

X-ray examinations of the samples have revealed that the constituent silicate minerals show a different reactivity during fluorination. A comparison of changes in the relative intensity of reflections of kaolinite, illite and quartz permits to determine the degree of degradation of these minerals under the influence of NH_4F. The highest reactivity is shown by kaolinite, the reflections of which disappear systematically as the activation time is prolonged. Illite is much more stable; even after 15-hour activation the intensity of its basal reflection (9.95 Å) is only slightly lowered compared with that of the initial sample. Quartz practically does not decompose at the applied concentration of the fluoride solution (1.5 n). The pronounced decrease in the intensity of kaolinite reflections, with the intensity of illite and quartz reflections remaining almost unchanged, indicates that degradation of the structure of kaolinite results in the formation of an X-ray-amorphous substance. The reactions of dissolution of the degraded surface zones of kaolinite proceed parallel with this process. This makes the complex ions $[AlF_6]^{3-}$ and $[SiF_6]^{2-}$ pass to the liquid phase, which, in consequence, may produce secondary phases — fluoroaluminates and fluorosilicates.

The diffraction pattern presented in Figure 1 shows a weak reflection 6.50 Å produced by the secondary phase $AlF_3 \cdot H_2O$ which, because of its low water solubility, has remained in the fluorinated samples despite repeated washing.

Figure 1 *f* presents a diffraction pattern obtained during activation of a kaolinite sample with 1.5 n NH_4F solution for 3 months at 20°C. This pattern shows that the process of fluorination in these conditions also tends to produce degraded structure in kaolinite. This is evidenced by the intensity ratio of the reflections *001* and *002*. The presence of the reflections 6.50, 5.45 and 5.05 Å of the secondary phase $AlF_3 \cdot H_2O$ indicates that decomposition of the structure of kaolinite also occurs under low-temperature conditions.

It appears then that fluorination of kaolinite at a given concentration of fluoride solution in low-temperature conditions (20°C) and at an elevated temperature (50°C) gives very similar results despite essential differences in the length of the reaction times. It follows, therefore, that temperature has no vital effect on the mechanism of fluorination process but, on the other hand, affects appreciably the reaction rate.

b) Infrared spectroscopic investigations

Infrared spectroscopic investigations were carried out on the C. Zeiss UR-10 spectrophotometer using KBr disks. Spectra of oriented preparations obtained by sedimentation were also recorded.

Infrared spectroscopic analysis was to yield data on the character of chemical reactions of alkaline fluoride solutions with kaolinite. It is worth noting that spectroscopic analyses permit to view the fluorination process in a slightly different aspect than X-ray examinations. In the spectra of fluorinated samples there is a superposition of absorption bands coming both from crystalline and amorphous constituents of the sample, while X-ray investigations yield, naturally, no data on amorphous substance. Moreover, passing through the preparation that is transparent to it, an infrared radiation beam affords information both on the internal and external zones of kaolinite grains, whereas X-ray diffractometry yields more or less exact data on the more surficial zones of grains only.

Figure 3 shows the absorption spectra of the initial sample of kaolinite (*a*) and of those treated with 1.5 n NH_4F solution for 1, 3, 5 and 15 hours, respectively (*b*—*e*); it presents also the spectrum of a sample activated with 3n NH_4F solution for 3 hours (*f*).

Fluorination produces several changes in the absorption spectra of fluoride-treated samples. Yet, a similarity of the spectra of fluorinated samples (Fig. 3 *b*—*e*) and that of the initial samples (Fig. 3 *a*) implies that

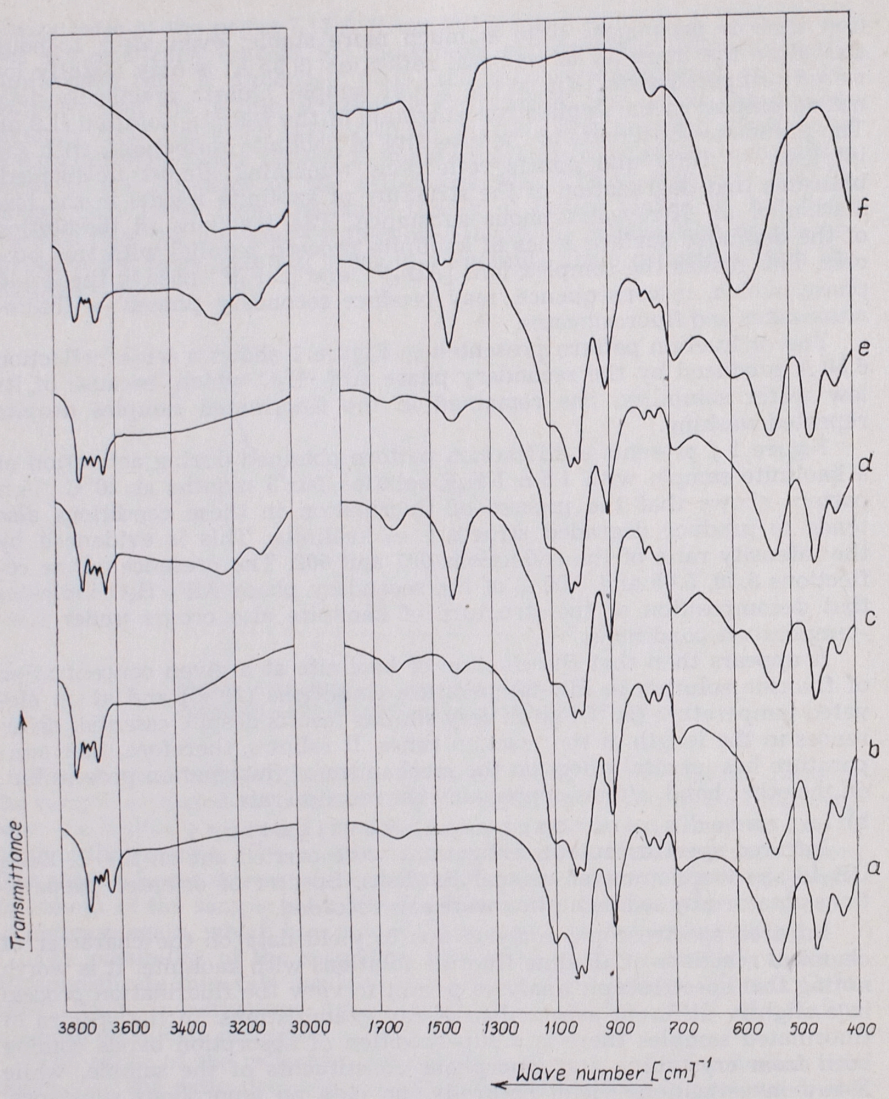

Fig. 3. Infrared absorption spectra

a — initial kaolinite sample (from Jegłowa), *b*—*e* — kaolinite samples fluorinated with 1.5 n NH_4F solution at 50°C for 1, 3, 5 and 15 hour, respectively, *f* — kaolinite sample fluorinated with 3 n NH_4F solution for 3 hour

the original character of the structure of kaolinite becomes only modified during that process. A decrease in the intensity of the valence ($\sim$3600 cm^{-1}) and deformation (920 cm^{-1}) bands of OH groups in the spectra of fluorinated samples is a characteristic indicator of the process of substitution and degradation of the structure of kaolinite. Measurements of the intensity of these bands as the activation time is prolonged make it possible to evaluate quantitatively the intensity of substitution and degradation processes in kaolinite.

Changes in ν_3 vibrations of the SiO_4 tetrahedra in the range of 1000—1200 cm^{-1} have also been recorded. The band 1120 cm^{-1} decreases almost systematically in intensity with time. Simultaneously, the ν_3 bands become slightly broadened towards higher wave numbers. On the slope of these bands at 1160—1300 cm^{-1}, a bending of the spectral line with the maximum about 1200 cm^{-1} appears, being particularly conspicuous in the spectrum of the sample fluorinated for 15 hours (Fig. 3 *e*). In the spectra of fluorinated samples the band 535 cm^{-1} produced by Al—O vibrations lowers its intensity, and so does the band 755 cm^{-1} produced by Si-O-Al vibrations, though its intensity is also affected by coincidence with the broad Al—F band.

All the above changes should be attributed to the disarrangement of the structure of the octahedral and tetrahedral sheets of kaolinite during fluorination. They may be due to both the removal of Al^{3+} ions from the octahedral sites and the breaking of Si-O-Al oxygen bridges binding the octahedral sheet with the tetrahedral one in the layers.

Apart from the above changes in the absorption bands corresponding to kaolinite, additional bands have been noted in the spectrum. These are: a broad band with the maximum at 605 cm^{-1}, which coincides with the kaolinite maxima in the range of 500—750 cm^{-1}, and intensive (particularly in spectra *d* and *e*) bands produced by valence and deformation vibrations of NH_4^+ ions (3130, 3240 and 1435 cm^{-1}). It should be assumed that the appearance of these bands is due to an admixture of insoluble ammonium fluoroaluminate of the $(NH_4)_3AlF_6$ type in the samples since the band 605 cm^{-1} is most likely produced by vibrations of the Al-F bonds. X-ray examinations failed however to reveal the presence of any phase containing NH_4^+. The authors assume, therefore, that the bands in question are primarily due to the presence of amorphous ammonium fluoroaluminate in the fluorinated samples. Independently of this, the Al-F bonds form very likely as a result of ionic substitution and degradation of kaolinite. Substitution processes cause the OH^- group bonded with Al^{3+} to be replaced by F^- ion, whereas degradation brings about the breaking of Si-O-Al oxygen bridges. The breaking of this bond by F^- ions may be attended by the formation of the unstable transitional system $Si\text{-}O^{(-)}$, which is an active electrodonor centre with an excess of negative charge. The unsaturated oxygen bond could react with the alkaline NH_4^+ cation supplied by the fluoride solution to form $Si\text{-}O\text{-}NH_4$ bond, the presence of which should be expected in the surficial degraded zones of kaolinite flakes.

The spectrum of kaolinite treated with 3 n NH_4F solution for 3 hours (Fig. 3 *f*) is different from the spectra of kaolinite and its fluoroderivatives shown in Figure 3 *a*—*e*. The analysis of this spectrum attests to the complete transformation of the structure of kaolinite (disappearance of all the basal absorption bands of this mineral) with the simultaneous formation of secondary phases, i.e. ammonium fluoroaluminates and fluorosilicates. In the range of 400—800 cm^{-1}, bands produced by Al-F (580 cm^{-1}) and Si-F (740, 480 cm^{-1}) vibrations may be observed. In the range of higher wave numbers, absorption maxima due to deformation

vibrations N—H of NH_4^+ (1400—1500, 3100—3400 cm^{-1}) have been recorded. On the basis of comparative data (Nyquist, Kagel 1971) ammonium cryolite $(NH_4)_3AlF_6$ and bararite $(NH_4)_2SiF_6$ have been identified.

Some additional data on the mechanism of kaolinite fluorination are yielded by an analysis of the spectra of oriented preparations in the range of valence vibrations of the OH^- groups. Publications dealing with the investigations of oriented nontreated samples (Serratosa, Bradley 1958; Serratosa, Hidalgo, Vinas 1962; Wolff 1963) and fluorinated ones (Hübner 1969) consider the possibility of determining on that basis the orientation of dipoles of the OH^- groups in the crystal lattices of layered silicates. The intensity of absorption bands corresponding to valence vibrations of the OH^- groups is, as is well known, a function of the angle between the bond direction and the vibration plane of the electric vector of the incident infrared radiation.

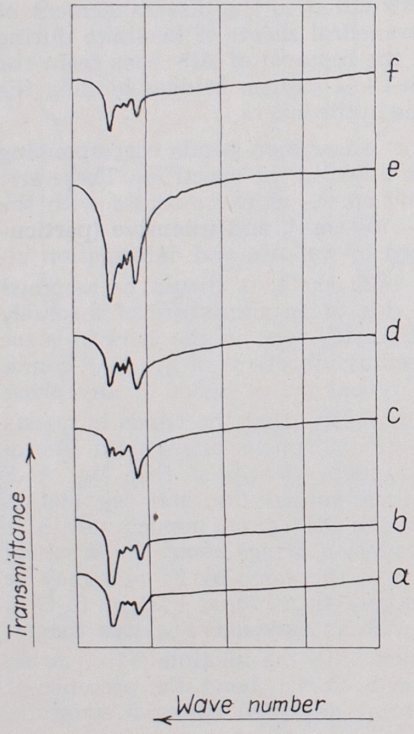

Fig. 4. A comparison of absorption bands of hydroxyl groups of non-treated and fluorinated kaolinite samples

a — of non-treated (sample oriented at an angle of 0°), *b* — of non-treated (sample oriented at an angle of 45°), *c* — of fluorinated (sample oriented at an angle of 0°), *d* — of fluorinated (sample oriented at an angle of 45°), *e* — of non-treated (non-oriented sample), *f* — of fluorinated (non-oriented sample)

In the absorption spectrum of kaolinite, some types of hydroxyl groups may be distinguished. These are:

1) grups inclined at a small angle to the flake surfaces, almost unbounded (free of hydrogen bonds), with the absorption maximum about 3700 cm^{-1},

2) groups deflected towards vacancies in octahedral sites with the maximum 3625 cm^{-1},

3) groups involved in the interlayer hydrogen bonds with the maxima 3655 and 3675 cm^{-1}.

The maximum 3700 cm^{-1} shows distinct absorption anisotropy. Figure 4 presents the spectra of non-treated kaolinite samples oriented at an angle of 0° (curve 4 *a*) and 45° (curve 4 *b*) with respect to the incident infrared radiation beam (the surface of kaolinite flakes is perpendicular to that beam). In the first case the intensity of the band 3700 cm^{-1} nearly equals that of the band 3625 cm^{-1}, whereas in the second case it is evidently higher. This indicates that the orientation of these hydroxyl groups is close to the direction perpendicular to the surface of kaolinite flakes (planes *001*).

The spectra of the fluorinated oriented kaolinite samples (orientation 0° — curve 4 *c*, 45° — curve 4 *d*) show a similar variability as those discussed above. It is interesting to note, however, that at an orientation

of 0°, the intensity of the band 3700 cm^{-1} compared with that of the band 3625 cm^{-1} is much lower than on curve 4 *a*. This evidences that fluorination, involving incorporation of F^- ions into the crystal lattice of kaolinite, produces changes in the orientation of hydroxyls due to disturbance of the crystal field forces of this mineral. An analysis of the spectra 4 *c* and 4 *d* shows that the OH dipoles in partly fluorinated kaolinite assume an orientation almost perpendicular to the direction of *001* planes.

For comparison's sake, the spectra of random non-treated (Fig. 4 *e*) and fluorinated (Fig. 4 *f*) kaolinite samples, obtained using KBr disks, are presented. It is evident from the spectra that, though fluorination lowers the intensity of the bands of hydroxyl groups (their number in the structure of kaolinite decreases due to, e.g. substitution), the intensity ratio of the two bands (3625 and 3700 cm^{-1}) remains unchanged.

c) Electron microscope investigations

The investigations were carried out by means of Tesla electron microscope, using an accelerating voltage of 100.000 V and a range of magnifications from 10.000 to 30.000×. Electron micrographs were made using powder and replica * techniques. The observations were to determine the effect of fluorination on the morphology of kaolinite grains. Electron diffraction patterns served as a basis for the identification of crystalline phases and the investigation of the process of amorphization of kaolinite.

The investigations were performed on non-treated kaolinite samples and those fluorinated for 5 and 15 hours with 1.5 n NH_4F and for 8 hours with 2 n NH_4F solution.

Electron micrographs of the initial kaolinite sample (Phots 1, 2) show the morphology of kaolinite flakes and polycrystalline aggregates. Single kaolinite grains have frequently a hexagonal habit (Phot. 1) and are usually sharp-edged.

5-hour fluorination (Phots 3, 4) produces profound changes in the morphology of grains, disarranging their structure. Photograph 3 shows the loosening of polycrystalline aggregates caused by fluorination. Most degraded are the marginal parts which, as shown by electron diffraction studies, became completely amorphized. On the edges of monocrystalline kaolinite flakes, characteristic etchings appear (Phot. 4). After 15-hour activation these transformations become intensified (Phots 5, 6). Photograph 5 shows the transformations occurring in a single kaolinite flake; the presented fluorination product does not cause electron diffraction since it is completely amorphous. The kaolinite crystal visible on Photograph 6 as a rod was also transformed this way. Electron microscope and, above all, diffraction investigations evidence directly the progress of amorphization processes resulting from zonal dissolution and removal of ions from the crystal lattice of kaolinite.

Some pertinent data on the mechanism of fluorination process are yielded by the study of electron micrographs made by replica technique. Photograph 7 shows the surface morphology of kaolinite crystallite aggregates that form complexes with parallel intergrowths according to the direction of *001* planes. Electron micrographs of fluorinated samples (Phot.

* Electron microscope investigations by means of replica technique were performed at the Greifswald University (GDR), Sektion Geologische Wissenschaften.

8) reveal that fluorination at a relatively high concentration of fluoride (2n NH_4F solution — 8 hours) results in local dissolution of the kaolinite grain surfaces (etching figures).

DISCUSSION

The reactions of kaolinite with ammonium fluoride solutions have been investigated. The effect of time, concentration and temperature on the structural transformations of this mineral has been analysed.

It has been found that the reactions: mineral phase — alkaline fluoride solution have a complex character. The process in question may involve stoichiometric substitution of OH^- by F^- ions but also degradation (amorphization) and decomposition of the mineral with the formation of new chemical compounds containing fluorine (fluorosilicates and fluoroaluminates). In either case the processes are accompanied by an increase in alkalinity of the solution due to the introduction of hydroxyl groups. It has been noticed that the reactions of ionic substitution and decomposition of the crystal lattice (degradation) of kaolinite proceed, as a rule, simultaneously, their intensity depending evidently on the reaction conditions.

It will be readily noticed that the prime factor affecting the mechanism of kaolinite fluorination is the concentration of fluoride solutions. When analysing (by infrared spectroscopy) the influence of the concentration of ammonium fluoride solutions (0.5, 1.0, 1.5, 2.0 and 3.0 n) on the fluorination process, it has been found that at low concentrations (up to 1.0 n) stoichiometric substitution of OH^- by F^- ions prevails. This reaction involves a decrease in the intensity of kaolinite absorption bands that correspond to hydroxyl groups. The other bands remain unchanged. During fluorination at low concentrations, only a trace amount of Al^{3+} ions are leached from the octahedral sheet of kaolinite. Fluorination at higher concentrations of fluoride solutions (above 1 n) results in degradation and then decomposition of the structure of kaolinite.

The two types of kaolinite fluorination reactions may be expressed in simplified form as follows:

— ionic substitution:

$$Al_4[(OH)_8 \mid Si_4O_{10}] + xNH_4F \rightarrow Al_4[(OH_{8-x}F_x) \mid Si_4O_{10}] + xNH_4OH$$

— degradation of the structure (decomposition):

$$Al_4[(OH)_8 \mid Si_4O_{10}] + nNH_4F \rightarrow Al_2[(OH,F)_2 \mid Si_4O_{10}] + 2(NH_4)_3[AlF_6] + mNH_4OH$$

The rise of ammonium cryolite $(NH_4)_3AlF_6$ is due to leaching of aluminium from the octahedral sheets, which seem to react more readily with F^- ions than the silicon-oxygen tetrahedral sheets. The reaction begins presumably with the replacement of OH^- groups by fluorine followed by substitution of O^{2-} ions, which involves the breaking of Al-O-Si oxygen bridges. The aluminium ion that has passed to the solution appears as the complex ion $[AlF_6]^{3-}$, which combines to form the relatively sparingly soluble ammonium cryolite.

X-ray investigations (a comparison of the intensity ratios I_{001}/I_{002} and I_{001}/I_{020}) make it possible to determine how far advanced the degradation processes are. It has been found that degradation of the structure of kaolinite in fluoride solutions concerns primarily the surface zones of grains, the concentration of defects due to fluorination decreasing in the deeper zones. Basing on the variations in the I_{001}/I_{002} ratio with time (Fig. 2), the present authors assume that, as a result of further fluorination, the initially degraded (amorphized) surface zone of grains is dissolved, thus rendering accessible the underlying layers. The process of dissolution (etching) of some areas on the surfaces of kaolinite grains has been investigated and confirmed by electron microscope studies using the replica technique.

It is assumed on the basis of infrared spectroscopic analyses that in the degraded fragments of the structure of kaolinite there rise electrodonor centres (due to the breaking of the Si-O-Al oxygen bridges), capable of binding NH_4^+ ions with the formation of a bond of the Si-O-NH_4 type.

Moreover, the effect of substitution and degradation in the structure of kaolinite on the orientation of hydroxyl groups coordinated by Al^{3+} ions has been investigated by means of infrared spectroscopy. A change in the spatial orientation of the OH^- dipoles, i.e. their deflection in the direction almost perpendicular to the surface of kaolinite flakes, has been noted.

REFERENCES

DICKMAN S. R., BRAY R. H., 1941: Replacement of adsorbed phosphate from kaolinite by fluoride. — *Soil. Sci.* 52.

FERREL R. E. Jr., GRIM R. E., 1967: The influence of alkaline solutions on the alteration of the clay minerals. — *Clays and Clay Min.* 15th. Nat. Conf.

FIJAŁ J., ZIĘTKIEWICZ J., 1968: O zastosowaniu substytucji grup OH do interpretacji niektórych pasm absorpcyjnych w podczerwieni na przykładzie widma wibracyjnego diasporu. *Spraw. Pos. Kom. Nauk. O/PAN w Krakowie.*

FIJAŁ J., ZIĘTKIEWICZ J., 1969: Experimental study on the substitution of OH groups by F ions in minerals. — *Bull. Sér. Sci. Géol. Géogr.* 18, 1.

HÜBNER M., 1969: Untersuchung der F/OH Austauschadsorption an Mineralen der Illitgruppe. — *Freiberger Forschungshefte* C 244.

NYGUIST R. A., KAGEL R. O., 1971: Infrared spectra of inorganic compounds. Academic Press, New York—London.

ROMO L. A., ROY R., 1957: Studies of substitution of OH by F in various hydroxylic minerals. — *Amer. Miner.* 42.

SAMSON R. H., 1952: Fluoride absorption by clay minerals and hydrated alumina. — *Clay Min. Bull.* 8.

SERRATOSA J. M., BRADLEY W. F., 1958: Determination of the OH bond in layer silicates. *J. Phys. Chem.* 62, 1164.

SERRATOSA J. M., HIDALGO A., VINAS J. M., 1962: Orientation of OH bonds in kaolinite. *Nature* 195, 486.

WOLFF R. G., 1963: Structural aspects of kaolinite using infrared absorption. *Amer. Miner.* 48, 390—399.

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Z BADAŃ NAD FLUOROPOCHODNYMI MINERAŁÓW KRZEMIANOWYCH O STRUKTURZE PAKIETOWEJ I. NIEKTÓRE ASPEKTY ODDZIAŁYWANIA KAOLINITU Z ROZTWORAMI FLUORKÓW

Streszczenie

Określano charakter przeobrażeń strukturalnych kaolinitu pod wpływem roztworów fluorku amonowego. Szczególną uwagę zwrócono na przebieg procesów degradacji jakim ulega sieć krystaliczna tego minerału oraz na określenie krystalochemicznej natury powstających produktów reakcji. Stosowano metody rentgenowskie, spektroskopowe w podczerwieni i elektronograficzne. Stwierdzono wpływ stężeń roztworów fluorku na mechanizm procesu fluorowania kaolinitu. Przy wyższych stężeniach (powyżej 1 n) obok procesu substytucji grup OH^- przez jony F^-, przebiegają głównie reakcje degradacji struktury minerału prowadzące do strefowego rozpuszczania się ziarn kaolinitu. Zaproponowano metodykę określania stopnia degradacji powierzchniowych stref agregatów krystalitów kaolinitu poprzez pomiar stosunku intensywności refleksów *001* i *002*.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy rentgenowskie
a — wyjściowa próbka kaolinitu (z Jegłowej), *b*, *e* — próbki kaolinitu fluorowane 1,5 n roztworem NH_4F w temperaturze 50° w czasie odpowiednio: 1, 3, 5 i 15 godz., *f* — próbka kaolinitu fluorowana przez okres 3 miesięcy 1,5 n roztworem NH_4F w temperaturze 20°C

Fig. 2. Zmienność stosunku intensywności refleksów *001/002* próbek fluorowanych, podana w funkcji czasu

Fig. 3. Widma absorpcyjne w podczerwieni
a — próbka wyjściowa kaolinitu (z Jegłowej), *b*, *e* — widma próbek fluorowanych 1,5 n roztworem NH_4F w temperaturze 50°C w czasie odpowiednio 1, 3, 5 i 15 godz., *f* — próbka kaolinitu fluorowana przez okres 3 godz. 3 n roztworem NH_4F

Fig. 4. Porównanie przebiegu pasm absorpcji grup hydroksylowych próbek naturalnych i fluorowanych kaolinitu
a — naturalnego (preparat zorientowany pod kątem 0°), *b* — naturalnego (preparat zorientowany pod kątem 45°), *c* — fluorowanego (preparat zorientowany pod kątem 0°), *d* — fluorowanego (preparat zorientowany pod kątem 45°), *e* — naturalnego (preparat nieorientowany), *f* — fluorowanego (preparat nieorientowany)

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Obraz elektronowy heksagonalnej blaszki kaolinitu z Jegłowej przed fluorowaniem. Pow. × 23 000

Fot. 2. Obraz elektronowy polikrystalicznych agregatów kaolinitu z Jegłowej przed fluorowaniem. Pow. × 32 000

Fot. 3. Obraz elektronowy agregatu kaolinitu po 5-godzinnym fluorowaniu w 1,5 n roztworze NH_4F. Pow. × 15 000

Fot. 4. Obraz elektronowy blaszek kaolinitu po 5-godzinnym fluorowaniu 1,5 n roztworem NH_4F. Pow. × 10 000

Fot. 5. Obraz elektronowy monokrystalicznej blaszki kaolinitu po 15-godzinnym fluorowaniu w 1,5 n roztworze NH_4F. Pow. × 17 500

Fot. 6. Elektronogram pojedynczej wytrawionej blaszki kaolinitu (widocznej jako pręcik) po 15-godzinnym fluorowaniu w 1,5 n roztworze NH_4F. Pow. × 20 000

Fot. 7. Replika agregatów naturalnego kaolinitu z Jegłowej o równoległym typie zrostów. Pow. × 12 000

Fot. 8. Obraz elektronowy (wykonany techniką replik) agregatów kaolinitu fluorowanych przez 8 godzin w 2 n roztworze NH_4F. Pow. × 16 000

Ежи ФИЯЛ, Марек ТОКАЖ

ИССЛЕДОВАНИЕ ФТОРПРОИЗВОДНЫХ СИЛИКАТНЫХ МИНЕРАЛОВ С ПАКЕТОЧНОЙ СТРУКТУРОЙ I. НЕКОТОРЫЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ КАОЛИНИТА С РАСТВОРАМИ ФТОРИДОВ

Резюме

Исследовался характер структурных изменений каолинита под влиянием растворов фторида аммония. Детально анализировался процесс разрушения кристаллической решетки этого минерала и исследовалась кристаллохимическая природа образующихся продуктов реакции. Применялись рентгеновские, ИК-спектроскопические и электронографические методы анализа. Констатировано, что концентрация фтористых растворов влияет на механизм процесса фторирования каолинита. При высоких концентрациях (выше 1 n), кроме замены групп OH^- ионами F^- происходят в основном реакции разрушения структуры минерала, вызывающие зональное растворение частиц каолинита. Предлагается методика определения степени разрушения поверхностных зон кристаллитовых агрегатов каолинита путем замера отношения интенсивности рефлексов *001* и *002*.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновские дифрактограммы
a — исходный образец каолинита из залежи Еглова, *b*—*e* — образец каолинита после фторирования 1,5 n раствором NH_4F в температуре 50°, в течение (соответственно) 1, 3, 5 и 15 часов, *f* — образец каолинита после фторирования 1,5 n раствором NH_4F в температуре 20°C в течение 3 месяцев

Фиг. 2. Изменения отношений интенсивности рефлексов *001/002* фторированных образцов в зависимости от времени

Фиг. 3. ИК-спектры поглощения
a — исходный образец каолинита из залежи Еглова, *b*—*e* — образец каолинита после фторирования 1,5 n раствором NH_4F в температуре 50°C, в течение (соответственно) 1, 3, 5 и 15 часов, *f* — образец каолинита после фторирования 3 n раствором NH_4F в течение 3 часов

Фиг. 4. Сопоставление линий поглощения гидроксильных групп естественных и фторированных образцов каолинита
a — естественного (препарат ориентированный под углом 0°), *b* — естественного (препарат ориентированный под углом 45°), *c* — фторированного (препарат ориентированный под углом 0°), *d* — фторированного (препарат ориентированный под углом 45°), *f* — естественного (препарат неориентированный), *f* — фторированного (препарат неориентированный)

ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

Фото 1. Элекртонный вид гексагональной чешуйки каолинита из залежи Еглова, до фторирования. Увел. × 23 000

Фото 2. Электронный вид поликристаллических агрегатов каолинита из залежи Еглова, до фторирования. Увел. × 32 000

Фото 3. Электронный вид агрегата каолинита после 5 часов фторирования 1,5 n раствором NH_4F. Увел. × 15 000

Фото 4. Электронный вид чешуек каолинита после 5 часов фторирования 1,5 n раствором NH_4F. Увел. × 10 000

Фото 5. Электронный вид монокристаллической чешуйки каолинита после 15 часов фторирования 1,5 n раствором NH_4F. Увел. × 17 500

Фото 6. Электронограмма отдельной, вытравленной чешуйки каолинита (на изображении в виде шестика) после 15 часов фторирования 1,5 n раствором NH_4F. Увел. × 20 000

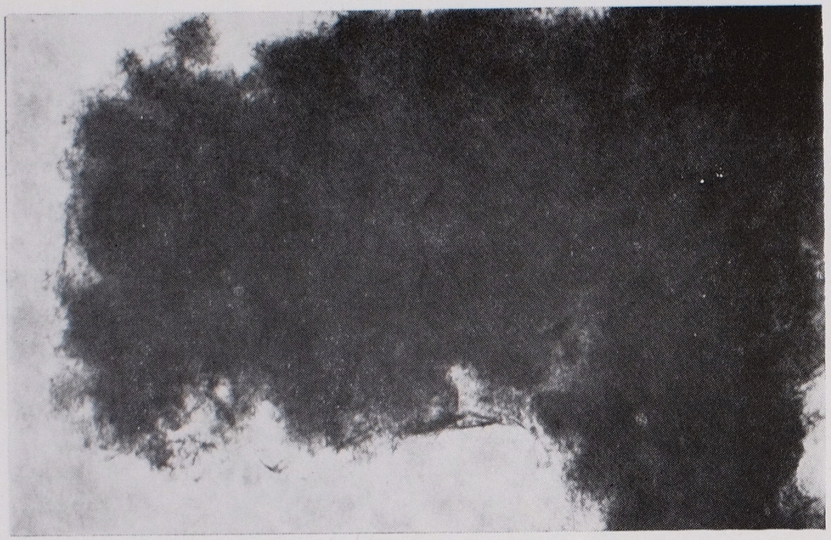
Фото 7. Реплика агрегатов природного каолинита из залежи Еглова, с параллельным типом срастаний. Увел. × 12 000

Фото 8. Электронный вид (полученный способом реплик) агрегатов каолинита, фторированных 8 часов в 2 n растворе NH_4F. Увел. × 16 000

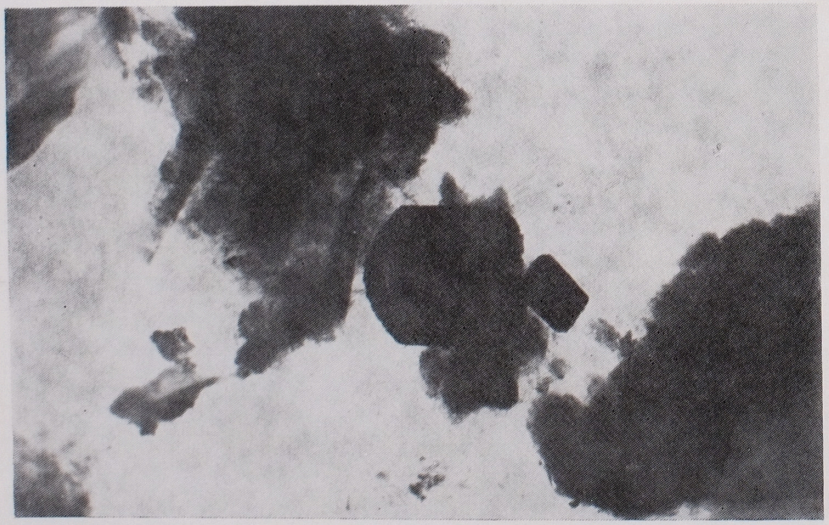
Phot. 1. Electron micrograph of a hexagonal kaolinite flake from Jegłowa before fluorination. Magn. × 23.000

Phot. 2. Electron micrograph of polycrystalline kaolinite aggregates from Jegłowa before fluorination. Magn. × 32.000

Jerzy FIJAŁ, Marek TOKARZ — Studies on the fluoroderivatives of silicate minerals with layered structure

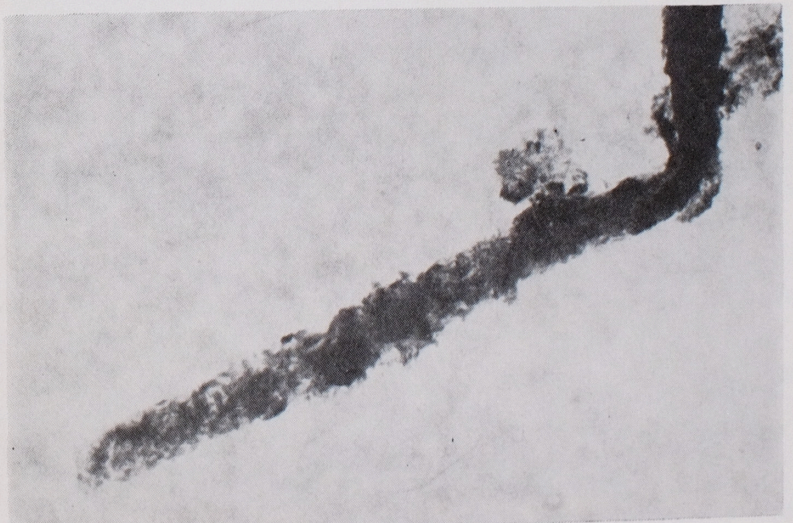


Phot. 3. Electron micrograph of kaolinite aggregate after 5-hour fluorination with 1.5 n NH_4F solution. Magn. × 15.000

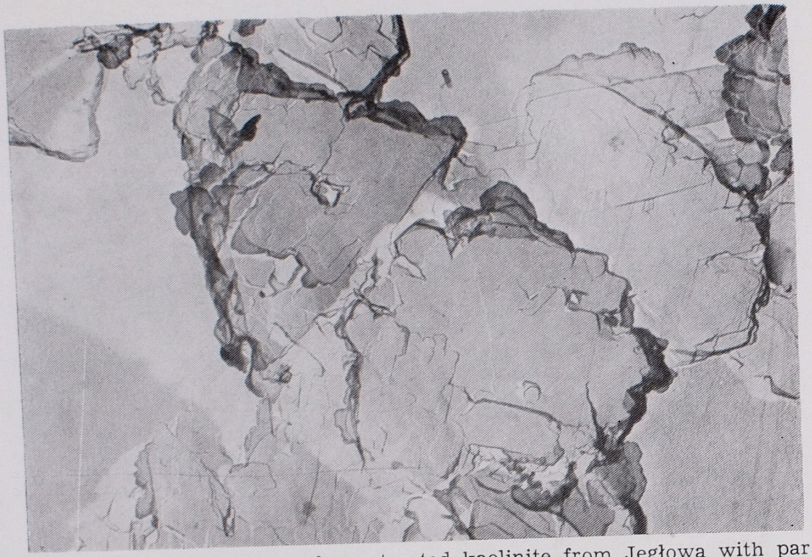


Phot. 4. Electron micrograph of kaolinite flakes after 5-hour fluorination with 1.5 n NH_4F solution. Magn. × 10.000

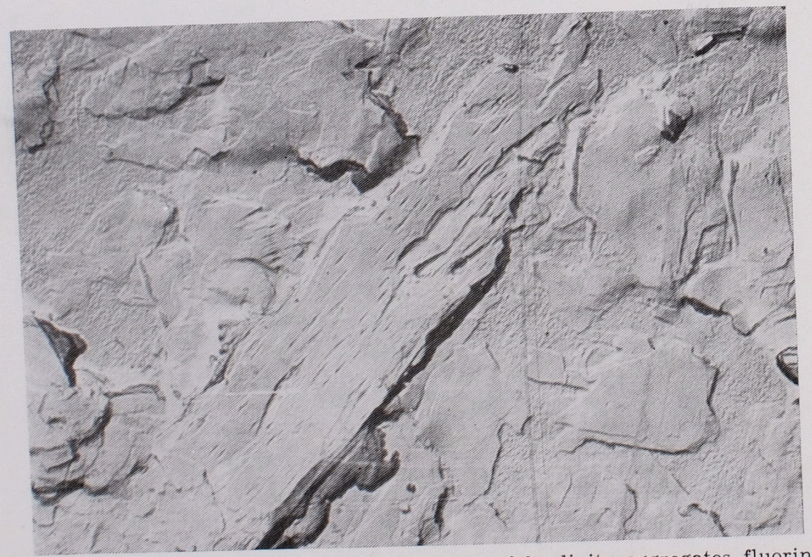
Phot. 5. Electron micrograph of a single kaolinite flake after 15-hour fluorination with 1.5 n NH_4F solution. Magn. × 17.000



Phot. 6. Electron micrograph of a single etched kaolinite flake (visible as a rod) after 15-hour fluorination with 1.5 n NH_4F solution. Magn. × 20.000



Phot. 7. Replica of aggregates of non-treated kaolinite from Jegłowa with parallel intergrowths. Magn. × 12.000



Phot. 8. Electron micrograph (replica technique) of kaolinite aggregates fluorinated with 2 n NH_4F solution for 8 hours. Magn. × 16.000